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Immobilization of heavy Pb(II) and Cd(II) ions from aqueous discharges

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Abstract

Jordanian sand deposits are naturally available in enormous amounts, located in Sweileh area, West Amman, which are mainly composed of low costs constituents from silica, Kaolin Clay, and metal oxides. A novel and simple methodology is presented for preparation, characterization, and behavior assessment of the potential nano-Kaolinite/ Silica oxides composites (nKSOC), for the immobilization of heavy Pb(II) and Cd(II) ions from aqueous solutions' discharges. In this study, the synthesis of nKSOC composites was conducted from the Jordanian sand deposits, mechanically reduced in size and then chemically acid-activated at room temperature, for the scope of wastewater purification through adsorption of heavy Pb(II) and Cd(II) ions from an aqueous medium. The synthesized nKSOC were subjected to analytical techniques; X-ray diffraction (XRD) and size reduction, to deduce their appropriate characterizations. Key parameters, considered for the enhancement of the adsorption technique, were pH, initial metal ions concentration, contact time, sorbent's dosage, and temperature. Experimental data were analyzed by Langmuir and Freundlich isotherm models, for the prediction of the adsorption behavior. Langmuir isotherms reproduce the experimental data with a maximum adsorption capacity of 172.4 $(mg/g_{adsorbent})$ and 158.7 $(mg/g_{adsorbent})$ for Pb(II) and Cd(II) ions, respectively, under unchangeable conditions of the constant temperature of 303K and slightly acidic pH in the range of 5.5 - 6. The adsorption of heavy metal ions was spontaneous and endothermic; (ΔH^o) (7.47 kJ/mol) and 7.87 (kJ/mol) for Pb(II) and Cd(II) ions, respectively, and with negative Gibbs free energy (ΔG^o), the adsorption process is performed under mild conditions. In virtue of these remarkable findings, nKSOC could be effectively used as a low-prized adsorbent to uptake heavy Pb(II) and Cd (II) metals from aqueous waste media.

Paper type: Research paper

Keywords: Sand deposits, nano-Kaolinite/Silica oxides composites, adsorption isotherms, heavy metals, thermodynamics.

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Introduction

Water is an essential element for the existence of human beings. Nowadays, a great challenge is the remediation of polluted aqueous effluents with contaminates resulting from domestic and agro-industrial activities. Water pollution has a major impact not only on health but also on the disturbing ecosystem and its sustainable growth. Heavy Lead (Pb(II)) and Cadmium (Cd(II)) metals belong to the most deleterious contaminants in industrial wastewaters produced from many vital applications, even in small concentrations (Al-Zboon *et al*. (2011); Mehdizadeh *et al*. (2014); Taamneh *et al*. (2017); Haouti *et al*. (2018)). Due to their radiation and corrosion resistance, high ductility, and malleability, Pb(II) and Cd(II) are introduced in extensive industries such as pharmaceuticals, glass industry and ceramics, paints, protective coatings and pigments, acid storage batteries, petroleum refinery and mining operations (Eaton (2005); Alasadi *et al*. (2019); Wang *et al*. (2020)).

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These metal ions are poisonous and non-biodegradable, thus, much focus has been adapted to develop cost-effective technologies, for remediation of such toxic heavy metal ions from aqueous media. One of the most practiced technologies is the adsorption technique, which has several advantages when compared to other physical and chemical purification methods, concerning energy, capital, and operating costs in addition to the relatively high removal efficiencies (Aguado *et al*. (2008); Addy *et al*. (2012); Ahmed *et al*. (2020)). Natural silica and modified composites adsorbents were proved to have superior capacity for immobilization of harmful heavy metal (HM) ions from aqueous industrial discharges, such studies are to be mentioned, utilizing ordinary sand, silt-clay and very fine sand, riverbed sands, modified natural silica, Manganese oxide-coated sand and surface modified sand with Manganese, silica/ Polyethyleneimine composite micro-particles, sands with bio-surfactant solution (Awan *et al*. (2003); Mustapha *et al*. (2017); Nasrabadi *et al*. (2017); Hadjar *et al*. (2004); Charbonnet *et al*. (2020); Chaudhry *et al*. (2016); Lee *et al*. (2010); Bucatariu *et al.* (2020); Haryanto and Chang (2014); Al-Rawajfeh *et al.* (2018), Al-Wahbi (2019)). Accordingly, these investigations have been performed with natural silica to remove HM ions from wastewater streams, especially for wastewater treatment in developing countries. These methods are characterized to be low-priced, and no need for any regeneration processes of the adsorbents. Meanwhile, humble removal efficiency for HM was obtained, so other investigations have been conducted with modified adsorbents to enhance the immobilization efficiency of HM from wastewaters. The modification processes were performed under complex procedure (both physical and chemical) to improve the surface chrematistics of the adsorbents, e.g., only Titania-coated silica and its modified composites by sodium alginate, Silica nano hollow sphere and silica gel, a porous silica surface modified with a new β-Ketoenolic host, modified Pisha sandstone with Natrium ion, Iron oxide rich sand, Silica nano-particles, and Silica/ graphite oxide composite, aqueous amine-functionalized mesoporous silica, silica sand with modifying its surface with Phosphorus(V) oxychloride ($POCl_3$), modified Silica gel with salicylaldoxime, Silica-mutated montmorillonite, altered silica with tetra Zirconium(IV) chloride ($ZnCl_4$) in Ethanol (Kołodyńska *et al*. (2018); Najafi *et al*. (2012); Tighadouini *et al*. (2019); Wang *et al*. (2020); Haouti *et al*. (2018); Sheet *et al*. (2014); Aguado *et al*. (2008); Prado *et al*. (2005); Sarkar *et al*. (1969); Addy *et al*. (2012); Khalil *et al*. (2001). It was worthy to mention that the existence of an organo-chelating ligand in clay composite has remarkably enhanced the capability for HM immobilization from sludges of wastewaters. Whereas natural adsorbents, with significant removal ability for HM ions with low concentrations, were used such as Glauconite or so-called greensand (Iron Potassium Phyllosilicate mineral), which is characterized with green color and is very crumbly and has very low weathering resistance (Selim *et al*. (2018)). Also, natural dolomite was used including Ca-Mg oxides as an active site for HM ions' removal from wastewaters (Sdiri (2018)). Despite the recorded findings of these studies, two major obstacles are highlighted with these techniques: humble removal efficiencies of HM ions from aqueous solution, due to limited adsorption capacity in case of high concentrations of HM ions. To overcome an obstacle, organo-clay composites were modified, to develop efficient active sites on sorbent surfaces, and hence, enhance the uptake of HM ions from aqueous wastewaters. Another obstacle is that the modification of the sorbent surface is principally a complex stage, accomplished with high expenses and long periods for the synthesis of the sorbent, its regeneration, and consequently the disposal of the spent sorbents.

On the other hand, mixed sand deposits mixed with other adsorbents enhance heavy metals uptake from aqueous media. Chawakitchareon and Veesommaia (2013) have utilized a benevolent geopolymer mortar prepared of Silica compounds, and pure Alumina from material residue to reduce HM ions' content. The analysis of HM’s content in extract solution has revealed that Pb(II), as well Cu(II), and Zn(II) had values less than 0.1 ($mg/l_{leachate}$). Close findings for Pb(II) ion removal from aqueous wastewater discharges were obtained in the study of Khaleque *et al*. (2011), where Amorphous zeolite was used. No attempts have been made to study the adsorption of mostly harmful Pb(II) and Cd(II) ions from aqueous media onto modified Sweileh sand deposits. The adsorption of the modified Sweileh sand has been studied to determine the tolerance of the system for the HM uptake. Moreover, the characteristics of the variable Sweileh sands have significantly different physicochemical properties, with fluctuated organic fractions in the sand composites. In the current investigations, the feasibility of the adsorptive characteristics of the modified sands, using nKSOC, has been investigated. The nKSOC were prepared by a simple chemical method from the natural Sweileh sand deposits, as an eco-friendly, low-prized, and practical sorbent for removal of Pb(II) and Cd(II) ions from aqueous solutions’ discharges.

1 Materials and Methods

1.1 Materials

Hypothetical sources for water contamination with the investigated heavy metal salts were obtained from analytical grade solutions of Lead nitrate ($Pb(NO_3)_2$) and Cadmium sulfate ($CdSO_4$) with different solutions, these HM solutions were acquired from Sigma-Aldrich Chemie GmbH located in Taufkirchen - Germany. Relevant chemicals such as Hydrochloric acid (HCL), Nitric acid (HNO_3), and Natrium hydroxide (NaOH) were ordered from local chemicals’ providers, which were used for the preparation of the modified nKSOC and pH value monitoring. Distilled and de-ionized water was implemented for washing and solution preparation.

1.2 Instrumentations

X-ray diffraction (XRD) analysis was performed using Malvern Panalytical diffractometer, where scanning was done according to 2° scanning range of 10–80°, continuously with 2°/minute as scan speeds, and the receiving slit width was 0.50mm. The concentrations of heavy Pb(II) and Cd(II) ions were determined by using a Sequential Plasma Emission Spectrometer (ICPS-7510, Shimadzu). PH measurements at different temperatures were reported by a Portable pH meter from Mettler Toledo, where pH values were adjusted by using two buffer solutions with either 0.01M HNO_3 and/ or 0.01M NaOH. Sieve opening of 325 US standard that been designated by a sieve size that corresponds to 44 (μm) as particle size.

1.3 Synthesis of nano-Kaolinite/SiO_2 composites

Sand samples were collected from Sweileh sand deposits from different locations in the western part of Amman-Jordan. Samples of sand were washed with distilled water to remove impurities of soil, plants residue, and other soluble metals and then were left to dry at a laboratory temperature of 303 K. A sample of 500g dried sand was sieved with 320 mesh to get a uniform size of sand particulates. Afterward, sand was treated with a (1:1) mass ratio of 10-20% diluted HCl concerning sample mass, under mechanical stirring for 4 hours at the foreseen laboratory temperature. When a yellowish-white emulsion started to appear, the sand sample was next treated with (1:1) mass ratio of 10-20% diluted NaOH to sample mass, with discontinuous agitation at laboratory temperature for additional 2 hours to ensure complete homogenization. Then the obtained emulsion was subjected to filtration on Whatman grade qualitative filter paper No. 1. The filter cake was washed out with de-ionized water and hot air-dried in an oven at 353K for 4 hours to obtain the fine powder, which is mainly formed of nKSOC.

1.4 Adsorption Isotherms

Adsorption equilibrium was obtained by shaking 5.0g of nKSOC in a series of 100ml flasks, containing 50 ml of initial concentration of Pb(II) and Cd(II) ions ranging from 10 to 120mg/L for 120 min. These ratios of adsorbent/ wastewater sample mass ratios were consistent with those of relevant studies (Amer *et al*. (2010), Alasadi *et al*. (2019)), to get a maximum adsorption capacity. The initial pH value of metal ion solutions was adjusted from 1 to 8.0, with either 0.0M HNO_3 or 0.01M NaOH at three temperatures: 293.15, 303.15, and 313.15K. Flasks were then agitated on a shaker at a constant shaking rate of 350 rpm for a time of 120min, to ensure equilibrium was established, Finally, the ion solutions were subjected to a filtration process, where the supernatant was analyzed for metal ions concentration by a Spectrometer (ICPS-7510). Each experiment was run several times and the mean values were recorded. The HM removal efficiency (R%) was determined according to the equation (1):

$$R\% = \left(\frac{C_o - C_e}{C_o}\right) \cdot 100\% \tag{1}$$

The number of metal ions adsorbed at equilibrium q_e, which represents metal ions uptake, was obtained (equation (2)):

$$q_e = \left(\frac{C_o - C_e}{m}\right) \cdot V \tag{2}$$

2 Results and Discussion

2.1 Characterization of nano-Kaolinite/SiO_2 composites

Figure1 shows the XRD for raw Sweileh sand and the modified nKSOC. Both are different from each other. This is an indication that the raw Sweileh silicate has been modified to the nKSOC during synthesis. Whereas X-ray fluorescence (XRF) analysis has shown that the raw sand sample is mainly composed of 78-80% SiO_2, 10-18% Kaolin clay, and about 2% soluble metal oxides. After chemical modification of the raw sand sample, XRF analysis has shown that the composition of the modified Kaloinite/ Silica composite is mainly 9.6 -12.5% Kaolin clay and 84 - 88% Silica, which is different from the composition of the raw sand sample. Again, it is evidence that the chemical modification process has resulted in changing the sand structure into a modified one of mainly nKSOC. According to Khaleque et al. (2020), the existence of soluble metal oxides in the raw sample would have an adverse effect on the modification process of the sorbent, since these soluble metal oxides provide extra nucleation sites for the precipitation of dissolved species. As a result, the microstructural porosity increases, and the resulting structure of nKSOC to achieve a better adsorption behavior of the adsorbent regarding the heavy metal ions.

2.2 Initial pH effect

The variation of the heavy metal removal efficiency of Pb(II) and Cd(II) ions onto the nano- Kaolinite/SiO_2 adsorbent with respect to the initial pH value of the metal ions solution is presented in **Figure 2**. The variation of the initial pH was performed under the conditions of a constant temperature of 303.15K and an initial ion concentration of 40 mg/L of the individual heavy Pb(II) and Cd(II) ions. The uptake of Pb(II) and Cd(II) ions percentage increases sharply with increasing pH of metal ions studied in the range from 1.0 to 6.0, then it slightly decreases with reaching a pH reading of 8.0. Maximum uptake was obtained of 96% and 93% for Pb(II) and Cd(II) respectively in an almost slight acidic medium of pH range of 5.5–6.

This uptake behavior of the heavy metal ions from the aqueous solutions could be explained by; an excess of H^+ ion in the acidic solution being presented. Eventually, a competition is established between the positively H^+ and HM ions for the available adsorption sites on the negatively charged adsorbent surface. As the pH increases, the competition between the positively charged ions towards the negative surface sites will decrease, hence then HM ions are the preponderating species, which will attract to the surface of nKSOC through Coulomb interactions (Al-Zboon *et al*. (2011); Khaleque *et al*. (2020)). These findings are consistent with the studies of Ayari *et al*. (2007) and Xu *et al*. (2008), where the maximum adsorption capacity of heavy Pb(II) was obtained of solution pH in the range of 5.5–6.

2.3 Adsorbent dosage effect

Adsorption dosage is an important parameter for determining adsorptive capacity. The adsorption efficiency for heavy Pb(II), Cd(II) ions as a function of nKSOC's dosage was investigated (**Figure 3)**, under a constant temperature of 303.15K. The adsorption efficiency of metal ions varied the adsorbent dosage from 0.1 to 1.0 ($g_{adsorbent}$/ $L_{solution}$), has been enhanced with the adsorbent loading up to a value of 0.9 ($g_{adsorbent}$/ $L_{solution}$0, then it establishes a constant value. This could be attributed to the fact that increasing the adsorbent dosage provides more active surface sites for binding heavy metal ions. Subsequently, the availability of more active sites would enhance the uptake capacity of the HM ions from the aqueous waste discharges to nKSOC, due to a greater driving force by a higher ion concentration gradient.

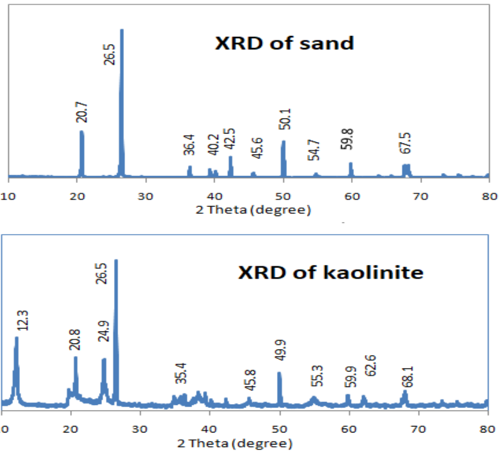

Fig. 1 XRD of samples for raw Sweileh sand and nKSOC.

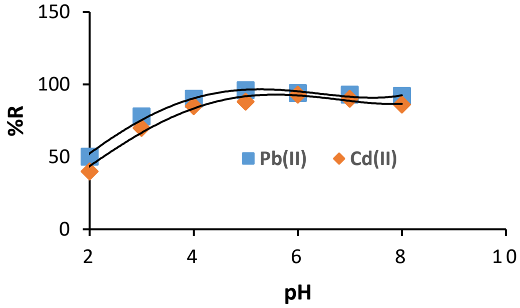

Fig. 2 Initial pH effect on the uptake of metal ions onto nKSOC adsorbent, at 303.15K; 40(mg/L) of metal ion concentration.

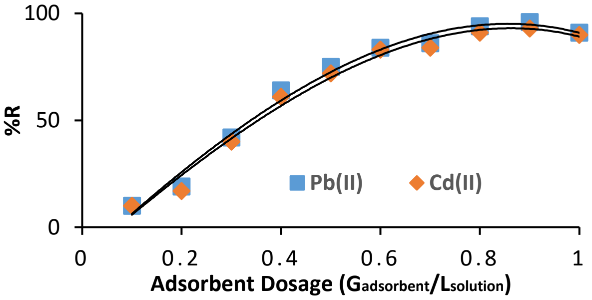

Fig. 3 Adsorption removal Pb(II) and Cd(II) ions onto nKSOC as a function of time, varied the adsorbent dosage from 0.1 to 1.0 ($g_{adsorbent}$/$L_{solution}$) with at pH 5.0-6.0 and 303.15K.

2.4 Contact time effect

The effects of contact time on the removal of heavy Pb(II) and Cd(II) ions by the adsorption process were studied, in the time range from 10 to 120 min at pH 5.0-6.0, and 303.15K with a fixed adsorbent dosage of 0.9 ($g_{adsorbent}$/ $L_{solution}$). The results of these findings are shown in **Figure 4**. It was observed that the immobilization of HM ions increases with the contact time until equilibrium is attained, between the amount of metal ion on nKSOC and the remaining metal in solution. The HM immobilization increases were attained to increase with contact time from 0 to 60 minutes, and thereafter it remains constant (plateau) to the end of the experiment. Significant removal of Pb(II) occurred within the first 60 min (96%) and a slight change concerning the removal was noticed after 1 hr. Similar findings were obtained in the studies of Mehdizadeh *et al*. (2014), and Taamneh *et al*. (2017), the equilibrium contact time for Cd(II) removal by Zeolite adsorbents after 60 min. It can be concluded that the removal of heavy Pb(II) and Cd(II) metal ions from aqueous media occurs sufficiently within 120 min shaking time to achieve the adsorption equilibrium. Therefore, this contact time interval was used in all subsequent experiments. At this equilibrium time interval, the uptake percentage of Pb(II) and Cd(II) from aqueous waste solutions were 96 and 93%, respectively.

2.5 Adsorption Isotherm study

Immobilization data for heavy metal ions removal onto SiO_2 compounds are most conveniently described by adsorption Isotherms (*Addy et al*. (2012); Awan *et al*. (2003); Hadjar *et al*. (2004), Haryanto and Chang (2014), Lee *et al*. (2010), Njafi *et al*. (2012), Sarkar *et al*. (1996), Sheet *et al*. (2014)). The experimental data for the removal of Pb(II) and Cd(II) ions onto nKSOC were processed, using the Langmuir and Freundlich Adsorption Isotherm models. Applying of Langmuir Isotherm (Langmuir (1918)) provides information on the adsorbent capacity by equation (3):

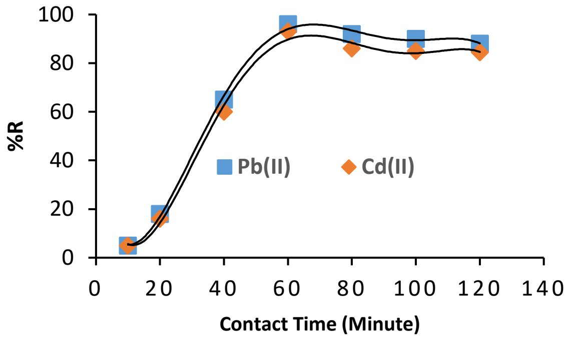

Fig. 4 Contact time effect on the removal of Pb(II) and Cd(II) ions onto nKSOC; fixed adsorbent dosage of 0.9 ($g_{adsorbent}/L_{solution}$) with at pH 5.0-6.0 and 303.15K

$$\frac{C_e}{q_e} = \frac{1}{q_m \cdot K_L} + \frac{1}{q_m} \cdot C_e \qquad (3)$$

By plotting the term (C_e/q_e) as a function of (C_e) for heavy Pb(II) and Cd(II) metal ions from aqueous media, a linear data fitting is obtained. The equilibrium capacity (q_m) is obtained from the calculation of the slope of the linear fitting. Whereas, from the relevant intercept with the ordinate line, the Langmuir constant is determined. The results of fitting Langmuir Isotherm for immobilization of heavy Pb(II) and Cd(II) ions are presented in **Figure 5**. An appropriate fitting of the experimental data with model expectations according to Langmuir Isotherm was achieved. The obtained values for the correlation factor (R^2) of Pb(II) and Cd(II) ions indicate that adsorption is properly fitted by the Langmuir model, the results are summarized in **Table 1**.

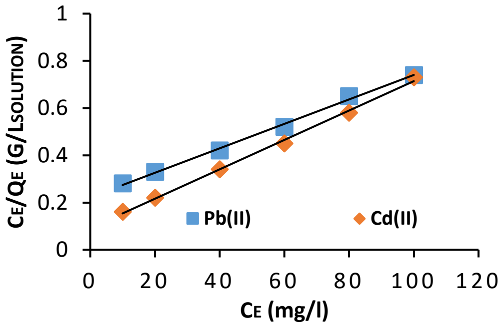

Fig. 5 Plotting C_e/q_e vs C_e according to Langmuir Isotherm; Eqn. (3).

Table 1 Relevant parameters for Langmuir and Freundlich Isotherms.

Metal ion	Langmuir			Freundlich		
	q_{max}	K_L	R^2	n	K_F	R^2
	($mg/g_{sorbent}$)	($L/g_{sorbent}$)	(-)	(-)	(-)	(-)
Pb(II)	172.41	1.3	0.99	1.87	11.49	0.98
Cd(II)	158.73	1.5	0.99	3.22	31.55	0.96

The nonlinear function that often occurs in the adsorption process follows the exponential form according to Freundlich and Hellen (1939). For data linearization, the natural logarithm of the exponential form is taken. Freundlich Isotherm equation is then expressed as a linear fitting according to equation (4):

$$ln q_e = ln K_F + \frac{1}{n} \cdot ln C_e \qquad (4)$$

Figure 6 illustrates the prediction of the Freundlich Isotherm model of the experimental adsorption data. Freundlich Isotherm model properly fits the adsorption data in the foreseen range of the investigated key parameters for remediation of heavy Pb(II) and CD(II) from aqueous solutions. By plotting the term (lnq_e) as a function of the (lnC_e), (K_F) is obtained from the intercept of the linearized Freundlich Isotherm' data with the ordinate line. Whereas the (n) parameter is attained from the slope of the linearized data plot. The (*n*) magnitude indicates the degree of non-linearity between the solution concentration and adsorption behavior in the following matter: the adsorption is linear when (*n*) equals unity. Meanwhile, the adsorption is a chemical process for (*n*) magnitudes smaller than unity, hence then HM ion exchange with other metal ions onto the adsorbent surface is foreseen. For the case, that (n) is greater than unity, then adsorption is a physical process, where Coulomb interactions are dominating the bonding between the positively charged ions and the negative active surface sites.

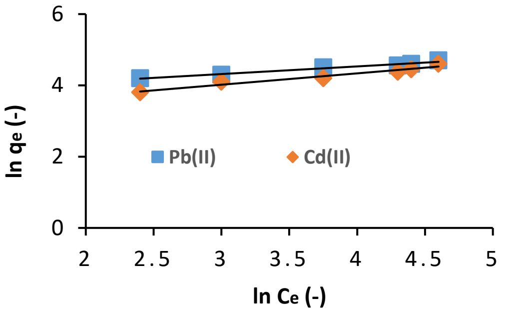

Fig. 6 Plotting lnq_e vs lnC_e according to Freundlich Isotherm; Eqn. (4).

Referring to Table 1, (*n*) is larger than unity, thus the heavy Pb(II) and Cd(II) metal ions have an affinity to be attached to nKSOC. Based on (R^2) figures for both Langmuir and Freundlich Isotherms, the adsorption experimental data are well re-produced to a great extent. under unchangeable adsorption conditions of the constant temperature of 303K and pH in the range of 5.5–6 for the removal of heavy Pb(II) and Cd(II) metal ions onto nKSOC. It is noticed that higher Isotherms constant values for (K_L) and (K_F) in the case of Cd(II) adsorption were obtained than those for Pb(II) adsorption in the range of the investigated experimental conditions. This finding can be attributed due to the higher solubility of Cd(II) salts in comparison to Pb(II) salts in the investigated temperature range, as presented in **Figure 7** for the HM's reported solubility data by Sigma-Aldrich Chemie GmbH. At the same concentration of both heavy metal salts, then more free Cd(II) ions are available in the solution with respect to Pb(II). Accordingly, the reported figures for HM solubility show that the solubility of Cd(II) ion solution is not changing remarkably, while the trend for Pb(II) ion's solution increases with temperature. As a consequence, this HM solubility behavior ensures that no remarkable change is foreseen even for other temperature ranges, and so the findings are still valid of higher Isotherms constant values for (K_L) and (K_F) in case of Cd(II) adsorption were obtained than those for Pb(II) adsorption.

2.5 Thermodynamic parameters

The thermodynamic parameters of free Gibbs–Helmholtz energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) were calculated from the following equations (Alasadi *et al*. (2019); Chaudhry *et al*. (2016)) equations (5 to 8) :

$$\Delta G^o = R \cdot T \cdot \ln K_D \tag{5}$$

$$where \quad K_D = \frac{C_a}{C_e} \tag{6}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{7}$$

$$lnK_D = \frac{\Delta H^o}{R} \cdot \frac{1}{T} + \frac{\Delta S^o}{R} \tag{8}$$

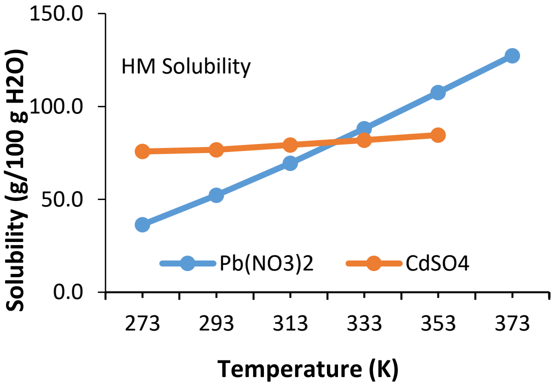

Fig. 7 HM solubility data, Sigma-Aldrich Chemie GmbH.

The change in (ΔG^o) is related to the (ΔH^o) and (ΔS^o) at constant temperature by Eq. (7), substitute for (ΔG^o) in Eq. (5), and re-arrange after taking the natural logarithm for both equation sides. Thus, a linearized plot is obtained, where (lnK_D) is varied with the inverse absolute temperature Eq. (8). The values of (ΔH^o) and (ΔS^o) were calculated from the plot slope and its intercept with the ordinate. The thermodynamics of Pb(II) and Cd(II) adsorption onto nKSOC were investigated at different pH values and different temperatures in the concentrations range 10–120 ($mg/L_{solution}$). Uptake capacity (q_e) is calculated according to Eq.(2), then Eq.(7) was used to determine energy parameters. The calculated values of thermodynamic parameters (ΔG^o), (ΔH^o) and ΔS^o for the adsorption of heavy Pb(II) and Cd(II) metal ions onto nKSOC with pH in the range of 5.5–6 and alteration of the adsorption temperature are listed in **Table 2**.

Table 2. Thermodynamic parameters of removal of Pb(II) and Cd(II) ions.

Metal ion	pH (-)	T (K)	K_D (-)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (J/mol.K)
Pb(II)	5.5	293	0.452	-1.1	7.47	29.25
	5.5	303	0.552	-1.39		
	5.5	313	0.648	-1.69		
Cd(II)	5.5	293	0.340	-1.42	7.87	31.7
	5.5	303	0.449	-1.73		
	5.5	313	0.547	-2.05		

The positive values of (ΔH^o) and (Δ*S*^{o}), and the decrease in the value of (Δ*G*^{o}**)** with increasing temperature, reveal that the adsorption process is endothermic, and more favorable at higher temperatures (Ahmed *et al*. (2020); Eaton (2005); Chawakitchareon and Veesommaia (2013); Sheet *et al*. (2014)). Negative values of (ΔG^o) emphasize the spontaneous nature of the adsorption process. This could be attributed to the activation of more sites on the adsorbent surface. The endothermic adsorption process could be attributed because the HM ions are well soluble (Alasadi *et al*. (2019); Chaudhry *et al*. (2016); Khaleque *et al*. (2020)). The HM ions require energy to be absorbed on the absorbent surface. The amount of this energy must reimburse the dehydration energy of the HM ions to be attached to the adsorbent surface. For physical adsorption, (Δ*G*^{o}) is within the range of -20 to 0 (kJ/ mol) (Addy *et al*. (2012); Aguado *et al*. (2009). While for chemical adsorption, (Δ*G*^{o}) varies within the limits of -80 to -400 (kJ/mol) (Ahmed *et al*. (2020); Bucatariu *et al*. (2020), Chaudhry *et al*. (2016); Gupta and Bhattacharyya (2009)). The (Δ*G*^{o}) for adsorption of heavy Pb(II) and Cd(II) metal ions onto nKSOC was obtained in the range of -1.1 to -1.69 (kJ/mol) and -1.41 to -2.05 (kJ/mol), respectively, for the investigated temperature domain. In this context, it could be confirmed that the adsorption process of these HM was predominantly physical adsorption. On the other hand, positive values of (ΔS^o) as 29.3 and 31.7 (J/ mol.K) for the adsorption of heavy Pb(II) and Cd(II) metal ions, respectively, onto nKSOC ensures that there is increased randomness at the adsorbent surface and aqueous solution interface during the adsorption of Pb(II) and Cd(II) ions onto nKSOC. The positive value of (ΔH^o) indicates that the entropy of the system increases after the adsorption process which also supports the explanation of the endothermicity process of the adsorption. When adsorption on nKSOC occurs, the hydrated water molecules are separated from the metal ion before they attach to nKSOC's surface or penetrate its matrix, this will increase the disorder of the heterogeneous system and thus increase its entropy.

2.6 Adsorption temperature effect

The temperature effect on the adsorption process of Pb(II) and Cd(II) is presented in **Figure 8**. It can be observed that the adsorption of Pb(II) and Cd(II) ions onto nKSOC increases with the increase of temperature. Temperature increasing in the range of 293–313K has enhanced the removal of Pb(II) ions from 143 to 172.4 (mg/$g_{adsorbent}$), whilst the removal efficiency for Cd (II) ions has been increased from 131 to 158.7 (mg/$g_{adsorbent}$). This finding is consistent with those of many studies (Hadjar *et al*. (2018); Khalil *et al*. (2001), Prado *et al*. (2005); Selim *et al*. (2018); Tighadouini *et al*. (2019)) who have stated that the adsorption process is better achieved on elevated temperatures. Elevated temperature contributes to increasing the HM solubility, Fig. 7, and hence more free HM ions will be concentrated in the aqueous media. Due to the higher temperature, these ions will keep in random motion throughout the warm aqueous media, to reach more active sites on the adsorbent surface, eventually the adsorption capacity will be promoted.

2.7 Comparison with other studies

The current findings are found very meaningful, by considering their significant achievements, and by assessment of other studies with different approved adsorbents and their corresponding findings, the assessment is summarized in **Table 3**. In the study of Taamneh et al. (2017), where JZ was used for the removal of Cd(II) and Cu(II) from wastewaters. Their findings were approaching stable sorption after 60 minutes. The humble capability of JZ to eliminate Cd(II) was estimated, according to Langmuir isotherm empirical formula, to be 25.9 (mg/$g_{adsorbent}$), which in turn is lower than the current investigations for Cd(II) ions elimination. Whereas

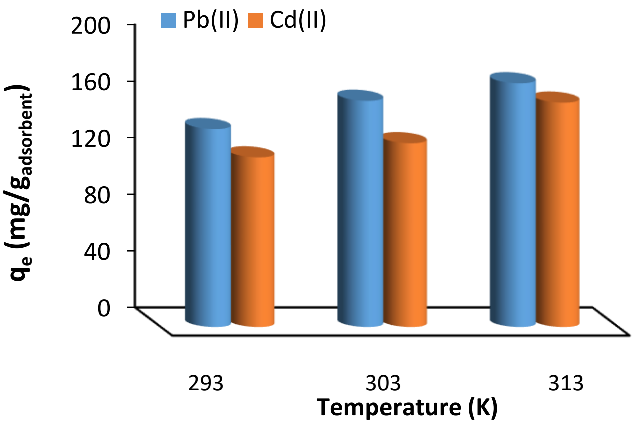

Fig. 8 Temperature effect on adsorption capacity of Pb(II) and Cd(II) metal ions onto nKSOC.

in the work of Aguado *et al*. (2008), mesoporous silica materials functionalized with multi-amine derivates have been investigated for selectively adsorption of aqueous Pb(II) and Cd(II) contaminants from wastewaters. Their findings deduced that such methods are restricted to only strong acidic conditions to prevent precipitation of insoluble species on the active sites of the sorbents, and hence, diminish the capability of HM adsorption, the stated adsorption for Pb(II) and Cd(II) was 284 and 50.6 (mg/g$_{adsorbent}$), respectively. Compared to current results findings, these adsorption capabilities were higher for Pb(II) but lower with respect to Cd(II) ions. In relevant investigations of Gupta and Bhattacharyya (2009), where Kaolinite and montmorillonite were activated through reaction with H_2SO_4 and further are used as clay adsorbents for the removal of Pb(II) and Cd(II). It was noticed that relatively longer equilibrium times were attained for Pb(II) and Cd(II) of 180 and 240 minutes, respectively. Accordingly, a feeble uptake capacity varied from 11.1-34.0 (mg/ g$_{adsorbent}$) and from 9.9-33.2 (mg/ g$_{adsorbent}$) for Pb(II) and Cd(II) ions, respectively. In comparison to current investigations, nKSOC had enhanced to a great extent the uptake of HM from wastewaters. Whilst, in recent research work of Wang *et al*. (2020) for removal of Cd(II) and Cu(II) from aqueous solution by PS and modified PS with Natrium ion, long reaction times in extent of 400 minutes were needed to establish the reasonable uptake of HM ions, the uptake figures for Cd(II) were stated as 5.5 and 6 (mg/g$_{adsorbent}$) for PS and Na-PS, respectively. Whereas organic-inorganic biohybrid composite adsorbent was synthesized in the study of Kołodyńska *et al*. (2018), based on only Titania-coated Silica (TS) and modified TS by Na-alginate for HM ions of Cu(II), Zn(II), Cd(II), and Pb(II) removal from stormwater. The HM uptake capabilities were lower than current investigations, especially for Cd(II), and Pb(II), and reported as 22.44, 19.95, 18.85, and 32.49 (mg/g$_{adsorbent}$) for Cu(II), Zn(II), Cd(II), and Pb(II), respectively. The reported figures for HM uptake could be attributed to the titania structure. However, when the suspension of nanosized TS is used for HM immobilization, aggregation of fine particles on active sites of silica, causing loss of their activity, and hence difficulty with the immobilizing of HM from wastewaters.

Table 3 Summary of current results & those of relevant studies on HM immobilization

Investigated HM	HM Uptake (mg/g$_{adsorben}$)	Adsorbent	Reference
Pb(II) & Cd(II)	172.4 & 158.7	nKSOC	Current study
Cd(II) & Cu(II)	25.9	jordanian zeolite (JZ)	Taamneh *et al.* (2017)
Pb(II), Cd(II)	284, 50.6	Mesoporous silica with multi-amine derivates	Aguado *et al*. (2008)
Pb(II), Cd(II)	11.1-34.0, 9.9-33.2	Kaolinite & montmorillonite	Gupta and Bhattacharyya (2009)
Cd(II)	5.5and 6	Pisha Sandstone (PS) and modified PS with Na^+	Wang *et al*. (2020)
Cu(II), Zn(II), Cd(II), Pb(II)	22.44, 19.95, 18.85, 32.49	Titania-coated Silica (TS) and modified TS by Na-alginate	Kołodyńska et al. (2018)

Conclusions

A promising adsorption process was successfully performed for the immobilization of Pb(II) and Cd(II) metal ions from aqueous media. The experimental investigations were conducted with implementing nano-Kaolinite/SiO_2 composites, under variation of batch adsorption parameters: solution pH, adsorbent dosage, initial metal concentration, and temperature. Those composites were modified from natural and low-cost Silica sand, which is available in enormous amounts in the western area in Amman. The maximum adsorption of Pb(II) and Cd(II) ions were obtained onto modified nKSOC at pH 5.0 - 6.0 and 303K; 172.41 and 158.73 (mg/g$_{adsorbent}$), respectively. The thermodynamic parameters for the HM adsorption process from aqueous discharges have exhibited an endothermic and spontaneous behavior of the adsorption process. Compared to other relevant findings in the literature, it could be revealed that the immobilization of Pb(II) and Cd(II) ions from aqueous discharges by the means of modified nKSOC is an effective process, to be applied in the treatment of contaminated aqueous effluents with heavy Pb(II) and Cd(II) metals ions, under a significant wide range of HM ions' concentrations and experimental conditions.

Nomenclature

C_0	=Initial concentration	[mg/L]
C_a	=Adsorbate concentration	[mg/$L_{solution}$]
C_e	=Equilibrium concentration	[mg/L]
ΔG°	=Free Gibbs–Helmholtz energy change	[kJ/mol]
ΔH°	=Enthalpy change	[kJ/mol]
K_D	=Distribution coefficient	[-]
K_F	=Freundlich constant	[-]
K_L	=Langmuir constant	[L/$g_{sorbent}$]
m	=Sorbent mass	[g]
n	=Deviation from linearity of media adsorption data	[-]
q_e	=Equilibrium adsorption capacity	[mg/$g_{sorbent}$]
q_{max}	=Maximum equilibrium capacity	[mg/$g_{sorbent}$]
R	=Universal gas constant 8.314	[J/mol.K]
$R\%$	=HM Removal Efficiency	[-]
R^2	=Correlation constant	[-]
ΔS°	=Entropy change]	[J/mol.K]
T	=Temperature	[K]
V	=Sample volume	[L]

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