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Thermodynamic study of lead ion removal by adsorption onto nanographene sheets

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ABSTRACT

A batch adsorption study was applied to investigate the adsorption of Pb^{2+} ions from aqueous solution by nanographene (nG).The adsorption percentage of Pb^{2+}ions onto nG samples at different initial pH, contact time (t_c), adsorbent dosage (m_{nG}) and temperature (T) were investigated. The results showed that nG is an excellent adsorbent for Pb^{2+}ions removal from aqueous solutions with an adsorption percentage of up to 79.8% at initial Pb^{2+}concentration of 20ppm and temperature of 298K.The experimental data could be well described by the Freundlich and Langmuire isotherm model; thermodynamic parameters of adsorption process (ΔG^0, ΔH^0, ΔS^o) were also evaluated. The overall adsorption process was exothermic and spontaneous in nature .The results indicate that Pb^{2+}ions adsorption onto nG may be chemisorption.

Keywords: Nanographene; Pb^{2+}ions; Adsorption; Isotherm; Thermodynamics

INTRODUCTION

Lead and its compounds are toxic and present in wastewater, effluents and soils [1]. Lead is used in some batteries, metal plating, photographic materials, explosive manufacturing and in some other application [2]. The presence of lead compounds in water may damage the kidney, nervous system, Liver, blood composition, reproductive system and brain due to its accumulation in the human body [3].

Treatment processes for metal ions removal from wastewater include precipitation, reverse osmosis, Reduction, filtration, membrane processing, ion exchange, coagulation and adsorption process [4]. Adsorption technique has been developed as an efficient method for treating various wastewaters, in which activated carbons from natural resources have been used as efficient and economical adsorbents for removing heavy metal pollutants [5]. Similarly, nG, consisting of bidimensional (2D) hexagonal lattices of sp^2 carbon atoms covalently bonded, has been theorized to have a huge specific surface area (over $260 m^2 g^{-1}$) [6,7]. nG as a newly emerging has unique physical, chemical, electrical and mechanical

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properties [8]. Recently graphene has been used as adsorbent to remove methyl orange, naphtalen, fluoride ion and Hg^{2+}ion from aqueous solutions [9, 10]. To our knowledge, no investigation has been carried on using graphene as an adsorbent to remove Pb^{2+} from aqueous solutions. The aim of this study is to investigate the adsorption behavior of Pb^{2+}ions onto nG as an adsorbent.

The effects of some parameters such as pH, adsorbent dosage, temperature and contact time on the adsorption efficiency were investigated to increase our understanding of the Pb^{2+}ions adsorption properties onto nG. Adsorption isotherm and thermodynamic studies were carried out to explain the adsorption mechanism of Pb^{2+}ions adsorption onto nG.

EXPERIMENTAL

Apparatus and materials

An AA 680 model atomic absorption spectrometer (Shimadzu Co.) was used for measuring the concentration of Pb^{2+}ion in studied solutions, a 820A model pH meter (Metrohm Co.) was used to measure pH of solutions and a thermostatic orbit incubator shaker neolab model (India) was used to measure contact time in solution. All chemical materials used in this study were of analytical grade. nG was prepared from TECNAN, Spain with purity 99.8%. Lead nitrate, was purchased from Merck company.

Batch adsorption experiments

Batch adsorption experiments were carried out to determine the Pb^{2+} ions adsorption isotherm onto nG and its thermodynamic properties. Pb^{2+} ions stock solution (100ppm) was prepared by dissolving the appropriate quantity of Pb $(NO_3)_2$ salt in deionized water.

Adsorption isotherms were obtained by using initial Pb^{2+}ion concentration ,C_o, and its equilibrium concentration, C_e, at 298K.The effect of pH on the Pb^{2+} ions adsorption onto nG was conducted in a pH range of 2-9.The pH of solutions was adjusted by 0.1 M HCl or 0.1M NaOH solutions. For every experiment, 100ml of the solution with Pb^{2+} concentration of 20ppm was mixed with 0.10 g of graphene in a 250ml glass conical flask. The flask was shaken in a thermostatic orbit shaker at 220rpm for 50min. The mixed was filtered through a 0.45 μm membrane filter. The filtrate was measured by atomic absorption then, the adsorption percentage (%A) was determined as:

$$\%A = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

where C_o and C_e are the initial and final concentration of Pb^{2+} ion in solution (mg L^{-1}), respectively. The amount (mg g^{-1}) of Pb^{2+} adsorbed at equilibrium was calculated using the following equation:

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (2)$$

where m is the mass of nG (g) and V is the volume of the solution (L).

To evaluate the thermodynamic properties of the adsorption process, 0.10 g of nG was added into the 100ml solution with pH of 7.0 and initial Pb^{2+} concentration ranging from 2 to 20ppm in every experiment. Each solution was shaken continuously for 50min at 298K.

RESULTS AND DISCUSSTON

Adsorption study

The effect of contact time

The effect of contact time, t_c , on the adsorption percentage of Pb^{2+} ion onto nG are shown in table 1 and ploted in fig. 1. A rather fast up take occurs during the first 30 min of the adsorption process. It becomes slower as the adsorbed amount of Pb^{2+} ion reaches its equilibrium value. It

can be seen that the adsorption process is rapid due to the availability of very active sites on the adsorbent surface at initial stage. This may be due to the special one-atom layered structure of nG [13]. The optimum contact time was obtained as 50 min.

Table 1. The effect of contact time, t_c, on the adsorption percentage (%A) of Pb^{2+}ions (C_o=20 ppm, m_{nG}=0.07g, T=298K, pH=6)

t_c/min	%A
10	52.60
15	56.61
20	65.38
30	74.80
40	78.84
50	79.80
60	79.60

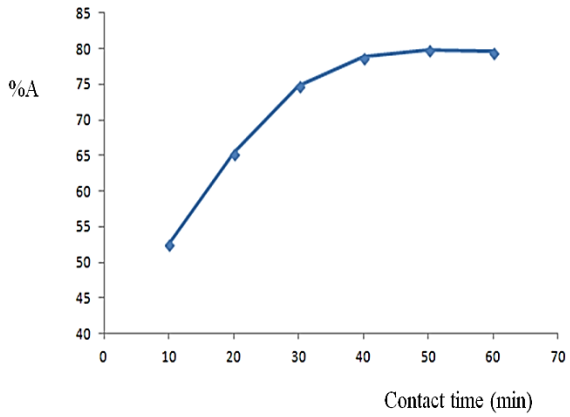

Fig. 1. The effect of contact time on the adsorption percentage of Pb2+ ion onto nG (C_o=20PPm, T=298K, pH=6, m_{nG}=0.07g).

The effect of dosage

The effect of nG dosage on the adsorption percentage of Pb^{2+} ion are shown in table 2 and ploted in fig. 2. We concluded that the dosage of 0.10g of nG was the most suitable. After optimum dosage, all active sites are entirely exposed and the adsorption on the surface is saturated.

Table 2. The effect of nG dosage on the adsorption percentage (%A) of Pb^{2+}(C_o=20ppm, pH=6, T=298K, t_c=50 min)

m_{nG}/g	%A
0.025	50.00
0.050	59.20
0.075	70.40
0.100	79.72
0.150	78.30

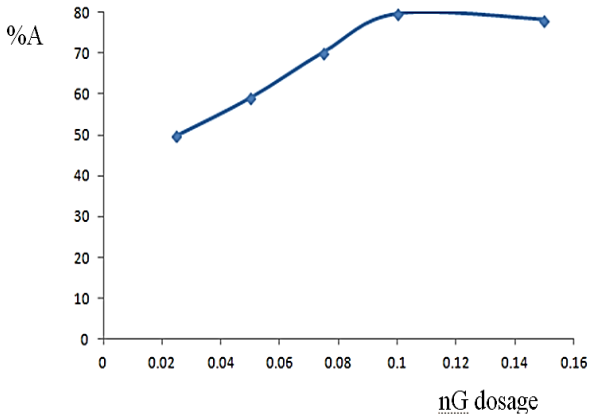

Fig. 2. The effect of nG dosage on the adsorption percentage of lead ion onto nG (C_o=20PPm, T=298K, pH=6, t_c=50min).

The effect of pH

Solution pH is one of the most important parameters to determine the adsorption property of an adsorbent that it controled the kind and amount surface charge of the adsorbent [11]. Table 3 and fig.3 illustrate the effect of the pH of the solution on the adsorption percentage of Pb^{2+} ion adsorbed onto nG. The adsorption percentage was increased with pH and optimum pH was 7.0, which is much higher than isoelectric point (IEP) of nG (IEP nG=5.5) [12]. The decrease of the adsorption percentage in acidic pH can be attributed to the repulsion between positive charge surface of nG and Pb^{2+}.

Table 3. The effect of initial pH of the solution on the adsorption percentage (%A) of Pb^{2+} (C_o=20ppm, m_{nG} =0.07g, T=298K, t_c=60min)

pH	%A
2	41.3
4	50.90
6	63.40
7	74.03
8	73.07
9	71.15

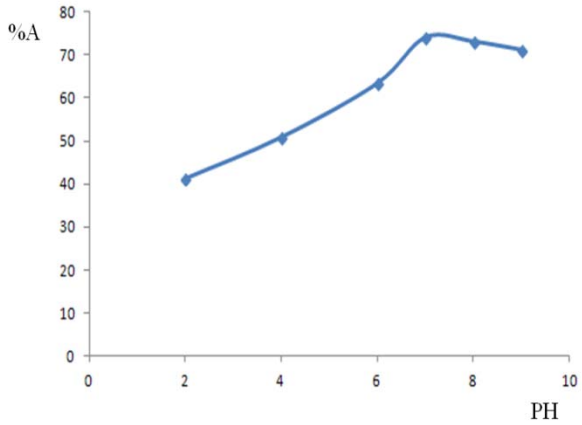

Fig. 3. The effect of initial pH of the solution on the adsorption percentage of Pb^{2+} ion onto nG (C_o=20PPm, t_c=50 min,T=298K, m_{nG}=0.10g).

The effect of temperature

Table 4 and fig.4 show that the adsorption percentage decrease with increasing temperature. Therefore, it may be concluded that the interaction between Pb^{2+} ions and nG is exothermic in nature. Adsorption decrease may be due to increase the electrostatic repulsion between of the Pb^{2+} ions.

Table 4. The effect of temperature on the adsorption percentage (%A) of Pb^{2+} (C_o=20ppm, m_{nG}=0.10g, pH=7 , t_c=50 min)

T/K	%A
298	79.71
303	72.10
308	68.80
313	67.10
318	64.50

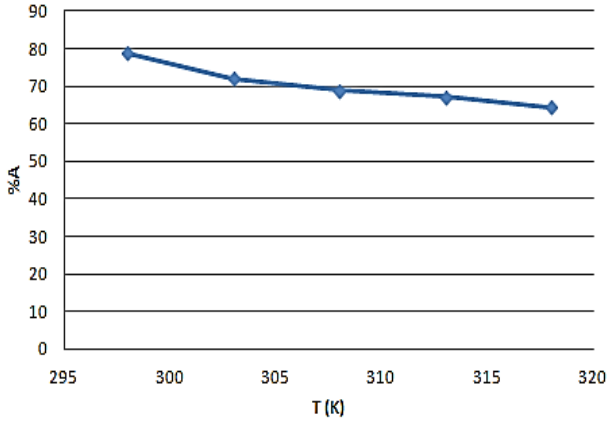

Fig. 4. The effect of temperature on the adsorption percentage of lead ion onto nG (C_o=20PPm, m_{nG} =0.10g, pH=7, t_c=50min).

Adsorption isotherm

An adsorption isotherm is characterized by certain constant values, which express the surface properties of the adsorbent and so on the percentages adsorption of Pb^{2+} ion onto nG as a function of initial concentration of Pb^{2+} ions are given in table 5.

Table 5. Adsorption data for Pb^{2+} adsorption onto nG (pH=7, t_c=50min,T=298K, m_{nG}=0.10g)

parameter	value				
C_o /mg L^{-1}	2	5	10	15	20
%A	55	64	74	76.6	79.8
C_e / mg L^{-1}	0.90	1.80	2.60	3.5	4.04
q_e / mg g^{-1}	1.10	3.20	7.40	11.50	15.96
log Ce	-0.04	0.25	0.41	0.54	0.60
log q_e	0.04	0.50	0.86	1.06	1.20
ln Ce	-0.10	0.58	0.96	1.25	1.40
1/Ce /L mg^{-1}	1.10	0.55	0.38	0.28	0.24
1/ q_e /g mg^{-1}	0.90	0.31	0.13	0.08	0.06

Equilibrium data of adsorption process can be analyzed on the basis of Temkin, Freundlich, Langmuire, Dubini-Radushkevich (D-R) and Brunauer, Emmett and teller (BET) models.

Temkin model assumes that the adsorption energy decreases linearly with

the surface coverage due to adsorbent-adsorbate intraction[14]. This model is:

$$B_T = \frac{RT}{K_T} \qquad (4)$$

where A_T (Lmg^{-1}) is Temkin isotherm constant. A_T is related to binding constant and K_T ($Jmol^{-1}$) is the Temkin constant that is related to the heat of sorption. K_T and A_T are determined from the slope and intercept of a plot of q_e versus lnc_e (table 5 and fig. 5). We used these results to calculate the values of K_T and A_T (table 8).

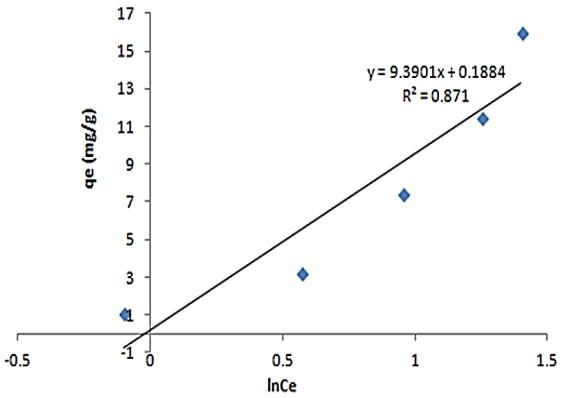

Fig. 5. Temkin isotherm for lead ion adsorption onto nG.

The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. This isotherm is applicable to both monolayer (chemisorption) and multilayer (physisorption) adsorption [15]. The linear form of the Freundlich isotherm model is described as;

$$\log q_e = \log K_F + 1/n \log C_e \qquad (5)$$

where K_F (L/g) and n are the Freundlich constants related to adsorption capacity and adsorption intensity [16].The values of K_F and n are determined from the intercept and slope of a plot of log q_e versus log C_e (table 5 and fig.6 that were used to calculate the values of K_F and n (table 8)).

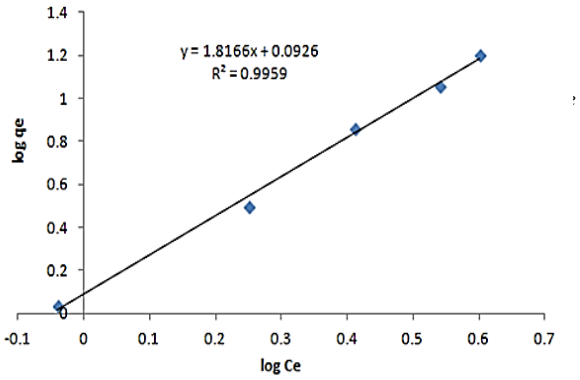

Fig. 6. Freundlich isotherm for lead ion adsorption onto nG.

The Langmuire isotherm assumes monolayer adsorption on a homogeneous surface without any interaction between adsorbed ions and with uniform binding sites and equivalent sorption energies [17]. The linear form of Langmuire equation is expressed as:

$$\frac{1}{q_e} = \frac{1}{K_L q_m}\left(\frac{1}{C_e}\right) + \frac{1}{q_m} \qquad (6)$$

where q_m (mgg^{-1}) is the maximum adsorption capacity corresponding to complete monolayer coverage and K_L (L/mg) is the Langmuire constant related to adsorption capacity and energy of adsorption [18].The slope and intercept of plot of $1/q_e$ versus $1/C_e$ is shown in fig.7 that were used to calculate the values of K_L and q_m (table 8).

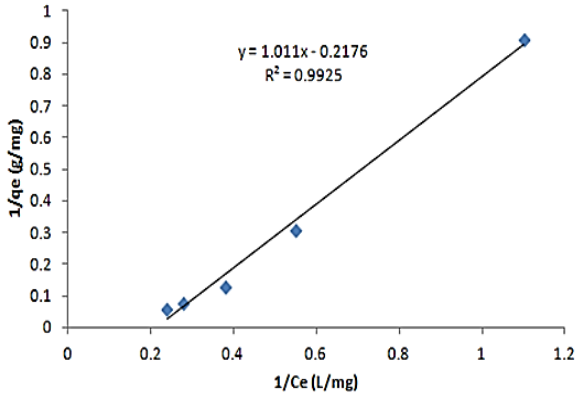

Fig. 7. Plot of ($1/q_e$) versus ($1/C_e$) for Pb^{+2} adsorption onto nG.

The D-R isotherm model is a semi-empirical equation. It assumes that the adsorption has a multilayer character and physisorption [19].The leaner form of D-R equation is expressed as:

$$\ln q_e = \ln q_m - K_D\varepsilon^2 \quad (7)$$

where K_D (mol J^{-1}) is the D-R isotherm constant related to free energy:

$$E=-0.7\ K_D^{-0.5} \quad (8)$$

and ε is Polani potential (J/mol) ,which is defined as:

$$\varepsilon = RT\ln(1+\frac{1}{C_e}) \quad (9)$$

q_m and K_D are determined from the intercept and slope of a plot of $\ln q_e$ versus ε^2 (table 6 and fig.8 that were used to calculated the values of K_D and q_m (table 8)).

Table 6. corresponding results for D-R isotherm model on the basis of table 5

$\varepsilon^2/(Jmol^{-1})^2$	ln qe
3378244	0.09
1178101	1.16
636792	2.00
373695	2.44
262600	2.77

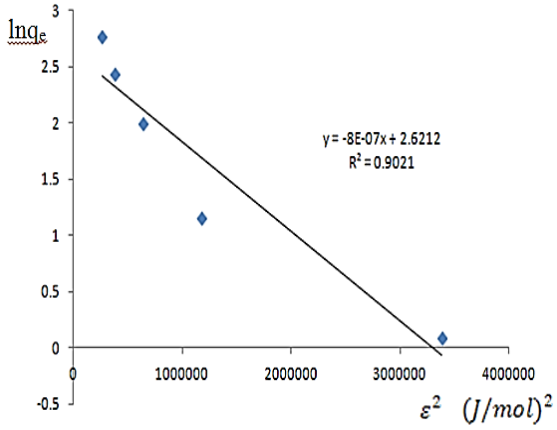

Fig. 8. D-R isotherm for lead ion adsorption onto nG.

The BET isotherm model is assumed to be multilayer and physical adsorption. The linear form of the BET isotherm is described as:

$$\frac{C_e}{(C_s - C_e)q_e} = \frac{1}{K_B q_m} + \frac{K_B - 1}{K_B q_m}\left(\frac{C_e}{C_s}\right) \quad (10)$$

$$C_s=C_o- C_e \quad (11)$$

where C_S is adsorbed concentration (ppm) and K_B (g/mg) is BET isotherm constant.K_B and q_m are determined from the intercept and slope of a plot of $\frac{C_e}{(C_s- C_e)q_e}$ versus $\frac{C_e}{C_s}$ (table 7 and fig.9 that were used to calculate the values of K_B and q_m (table 8)).

Table 7. corresponding values for BET isotherm model on the basis of table 5

$\frac{C_e}{(C_s- C_e)q_e}$ (g/mg)	$\frac{C_e}{C_s}$
4.09	0.81
0.40	0.56
0.07	0.35
0.03	0.30
0.02	0.25

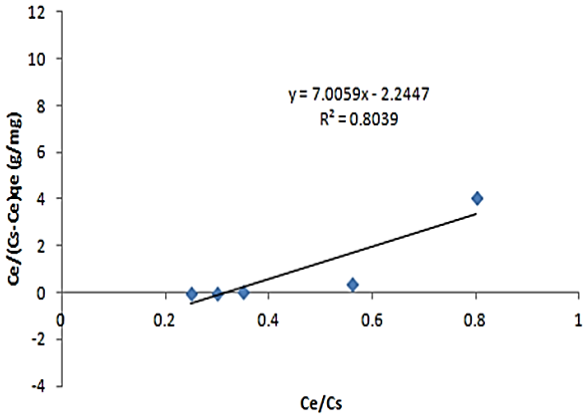

Fig. 9. BET plot for lead ion adsorption onto nG.

The resultant values for all studied isotherms are given in table 8.

As can be seen, the experimental data is nearly well described by Freundlich and Langmuire isotherms but it is fitted with Freundlich model more than the

Langmuire model. This suggests that the Pb^{2+} adsorption onto nG may be chemical adsorption. The magnitude of the correlation coefficient for the BET isotherm is the lowest one compared to the others (table 8).

Table 8. The resultant values for the studied isotherms in connection to Pb^{+2} ion adsorption onto nG at 298K

Isotherm	Parameter	Value
Temkin	K_T / (J mol^{-1})	263.8
	A_T / (L mg^{-1})	1.02
	R^2	0.871
Freundlich	K_F /(L g^{-1})	1.23
	n	0.55
	R^2	0.9959
Langmuire	K_L / (L mg^{-1})	0.21
	q_m /(mg g^{-1})	4.6
	R^2	0.9925
D-R	K_D / (mol J^{-1})	0.0000008
	$q_{m\,/}$ (mg g^{-1})	13.73
	R^2	0.9021
BET	K_B /(g mg^{-1})	4.10
	q_m /(mg g^{-1})	0.10
	R^2	0.8039

The essential characteristic separation constant factor, R_L, for the Langmuire adsorption is defined as follows:

$$R_L = \frac{1}{1+K_L C_0} \qquad (12)$$

The value of R_L illustrate the shape of the isotherm to be either unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1) or irreversible (R_L=0). The calculated R_L values versus initial Pb^{2+} concentration are given in table 9, indicating that the Langmuire adsorption of Pb^{2+} onto nG is favorable.

Table 9. Separation factor for the adsorption of Pb^{2+} onto nG in terms of initial concentration of Pb^{2+}

$C_{o\,/}$ mg L^{-1}	R_L
2	0.7
5	0.5
10	0.33
15	0.25
20	0.2

Thermodynamic Parameters

The thermodynamic parameters of adsorption process can be determined from the variation of thermodynamic equilibrium constant, K_o [20]. where K_o is defined as follow:

$$K_0 = \frac{C_0 - C_e}{C_e} = \frac{a_{ad}}{a_s} \qquad (13)$$

where a_{ad} and a_s are the activity of adsorbed Pb^{2+} and the activity of Pb^{2+} in solution at equilibrium, respectively. The adsorption standard free energy change (ΔG^0) is calculated according to:

$$\Delta G^\circ = -RT \ln K_\circ \qquad (14)$$

The average standard enthalpy change (ΔH^o) and the average standard entropy change (ΔS^o) are obtained from the plot of equation (15):

$$\ln K_0 = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (15)$$

In order to obtain the values of ΔH^o and ΔS^o, was plotted $\ln K_o$ against 1/T (table 10, fig.10).

Table 10. The effect of temperature on K_o values (C_o=20ppm, pH=7, m_{nG}=0.10g, t_c=50min)

T/K	%A	C_e /mg L^{-1}	q_e /mg g^{-1}	K_0
298	78.8	4.24	15.78	3.68
303	72.1	5.58	14.42	2.58
308	68.8	6.24	13.76	2.2
313	67.1	6.58	13.42	2.03
318	64.5	7.1	12.9	1.81

The obtained values of thermodynamic parameters (ΔG^0, ΔH^0, ΔS^o) are listed in table 11. Negative value of ΔH^0 suggests that the interaction of adsorbed Pb^{+2} with nG is an exothermic process, which is supported by the decreasing the amount of lead ion adsorption with increasing

temperature. The negative value of ΔS^o indicates a decrease randomness and mobility at the adsorbent/solution interface during the adsorption of lead ion onto nG. The negative values of ΔG^0 reveals the fact that the adsorption process is spontaneous.

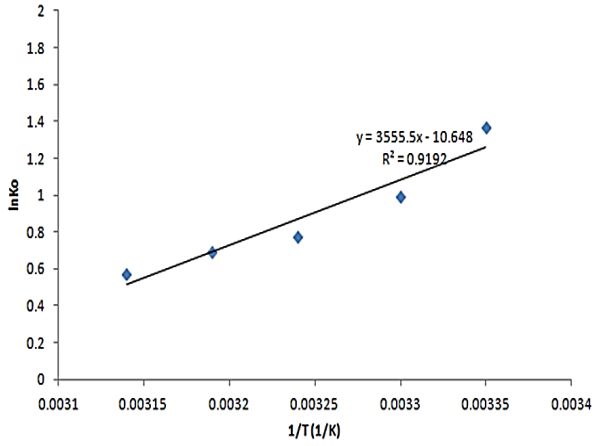

Fig. 10. The effect of temperature on equilibrium constant values.

Table 11. Thermodynamic parameters for adsorption Pb^{+2} ions onto nG

T /K	ΔG^o/ kJmol^{-1}	ΔH^o/ kJmol^{-1}	ΔS^o / kJmol^{-1}
298	-3.228	-26.4	*-0.078*
303	-2.387	-26.4	*-0.078*
308	-2.01	-26.4	*-0.078*
313	-1.842	-26.4	*-0.078*
318	-1.57	-26.4	*-0.078*

CONCLUSION

The results of this research show that nanographene particles is an effective adsorbent for removal of Pb^{2+} ion from aqueous solution. The experimental data can be fitted with the Freundlich and Langmuire isotherms, thus indicating the applicability of monolayer coverage of Pb^{2+} ion on nG surface. The experimental data for the BET model showed that the adsorption of Pb^{2+} ions onto nG is not a physical process. Thermodynamic analysis showed that the adsorption process is exothermic and spontaneous in nature.

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