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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<sup>2+</sup> ions from aqueous solution by nanographene (nG). The adsorption percentage of Pb<sup>2+</sup>ions onto nG samples at different initial pH, contact time (t<sub>c</sub>), adsorbent dosage (m<sub>nG</sub>) 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<sup>2+</sup>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 ( $\Delta G^0$ ,  $\Delta H^0$ ,  $\Delta S^0$ ) were also evaluated. The overall adsorption process was exothermic and spontaneous in nature. The results indicate that Pb<sup>2+</sup>ions adsorption onto nG may be chemisorption.

Keywords: Nanographene; Pb<sup>2+</sup>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  $260m^2g^{-1}$ ) [6,7]. nG as a newly emerging has unique physical, mechanical chemical. electrical and

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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<sup>2+</sup>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<sub>3</sub>)<sub>2</sub> salt in deionized water.

Adsorption isotherms were obtained by using initial  $Pb^{2+}$ ion concentration ,C<sub>o</sub>, and

equilibrium concentration, Ce, at its 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:

$$\%A = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

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<sup>-1</sup>) of  $Pb^{2+}$  adsorbed at equilibrium was calculated using the following equation:

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

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 oneatom layered structure of nG [13]. The optimum contact time was obtained as 50 min.

<b>Table 1.</b> The effect of contact time, t <sub>c</sub> , on the
adsorption percentage (%A) of $Pb^{2+}ions$ (C <sub>o</sub> =20
ppm, m <sub>nG</sub> =0.07g, T=298K, pH=6)

t <sub>c</sub> /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 ( $C_o=20$ PPm, T=298K, pH=6, m<sub>nG</sub>=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 $Pb^{2+}(C_0=20ppm)$ ,	рН=6,



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<sup>2+</sup> 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<sup>2+</sup>.

**Table 3.** The effect of initial pH of the solution on the adsorption percentage (%A) of Pb<sup>2+</sup> (C = 20 mm m = -0.07 c T=20 eV t = -60 min)

$(C_0=20ppm, m_{nG}=0.07g,$	$T=298K, t_c=60min$
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<sub>o</sub>=20PPm, t<sub>c</sub>=50 min,T=298K, m<sub>nG</sub>=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<sub>o</sub>=20ppm,

$m_{nG}=0.1$	$0g, pH=7, t_c=50 min)$
T/K	%A
298	79.71
303	72.10
308	68.80
313	67.10
318	64.50





#### **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<sup>2+</sup> adsorption onto nG (pH=7,  $t_c$ =50min,T=298K,  $m_{nG}$ =0.10g)

parameter			value		
$C_{\circ}$ /mg L <sup>-1</sup>	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 <sup>-1</sup>	1.10	0.55	0.38	0.28	0.24
$1/q_e~/{ m g~mg^{-1}}$	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 adsorbentadsorbate intraction[14]. This model is:

$$B_T = \frac{RT}{K_T} \tag{4}$$

where  $A_T$  (Lmg<sup>-1</sup>) is Temkin isotherm constant.  $A_T$  is related to binding constant and  $K_T$  (Jmol<sup>-1</sup>) 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<sub>e</sub> (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;

$$\log q_e = \log K_F + 1/n \log C_e$$
 (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<sub>e</sub> versus log C<sub>e</sub> (table 5 and fig.6 that were used to calculate the values of  $K_F$  and n (table 8)).



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:

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

where  $q_m$  (mgg<sup>-1</sup>) is the maximum adsorption capacity corresponding to complete monolayer coverage and K<sub>L</sub> (L/mg) is the Langmuire constant related to adsorption capacity and energy of adsorption [18].The slope and intercept of plot of 1/q<sub>e</sub> versus 1/C<sub>e</sub> is shown in fig.7 that were used to calculate the values of K<sub>L</sub> and q<sub>m</sub> (table 8).



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

$$\ln q_e = \ln q_m - K_D \varepsilon^2 \tag{7}$$

where  $K_D$  (mol J<sup>-1</sup>) is the D-R isotherm constant related to free energy:

$$E=-0.7 \text{ K}_{\text{D}}^{-0.5}$$
(8)

and  $\boldsymbol{\epsilon}$  is Polani potential (J/mol) ,which is defined as:

$$\varepsilon = RT \ln(1 + \frac{1}{c_e}) \tag{9}$$

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



**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:

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

$$C_s = C_o - C_e \tag{11}$$

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 isothermmodel on the basis of table 5

$\frac{c_e}{(c_s - c_e)q_e} (g/mg)$	$\frac{C_e}{C_e}$
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 <sup>+2</sup> ion adsorption onto
nG at 298K

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

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

$$R_L = \frac{1}{1 + K_L C_0} \tag{12}$$

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<sup>2+</sup> concentration are given in table 9, indicating that the Langmuire adsorption of Pb<sup>2+</sup> 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 <sub>L</sub>
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:

$$K_{0} = \frac{C_{0} - C_{e}}{C_{e}} = \frac{a_{ad}}{a_{s}}$$
(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  $(\Delta G^0)$  is calculated according to:

$$\Delta G^{\circ} = -RT \ln K_{\circ} \tag{14}$$

The average standard enthalpy change  $(\Delta H^{\circ})$  and the average standard entropy change  $(\Delta S^{\circ})$  are obtained from the plot of equation (15):

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

In order to obtain the values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$ , was plotted lnK<sub>o</sub> 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 <sub>e</sub> /mg L <sup>-1</sup>	$q_e$ /mg g <sup>-1</sup>	$\mathbf{K}_{0}$
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 ( $\Delta G^0$ ,  $\Delta H^0$ ,  $\Delta S^o$ ) are listed in table 11. Negative value of  $\Delta H^0$  suggests that the interaction of adsorbed Pb<sup>+2</sup> 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  $\Delta S^{\circ}$  indicates a decrease randomness and mobility at the adsorbent/solution interface during the adsorption of lead ion onto nG. The negative values of  $\Delta G^{\circ}$  reveals the fact that the adsorption process is spontaneous.



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

Table 11.	Therm	odynamic	parameters	fo
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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	T/K	$\Delta G^{o}/$	$\Delta H^{o}/$	$\Delta S^{o}$ /
298         -3.228         -26.4         -0.078           303         -2.387         -26.4         -0.078           308         -2.01         -26.4         -0.078		kJmol <sup>-1</sup>	kJmol <sup>-1</sup>	kJmol <sup>-1</sup>
303       -2.387       -26.4       -0.078         308       -2.01       -26.4       -0.078	298	-3.228	-26.4	-0.078
308 -2.01 -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	313	-1.842	-26.4	-0.078
318 -1.57 -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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