International Journal of Applied Chemistry.
ISSN 0973-1792 Volume 12, Number 2 (2016) pp. 157-174

http://www.ripublication.com

Evaluation of removal study of pb (II) from aqueous solution onto polyaniline nanocomposite (prepared in situ by oxidative polymerization of aniline in presence of natural Bentonite)

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Abstract

Polyaniline (PANI) nanocomposites used as a removal surface of pb(II) from aqueous solution has been prepared. A PANI nanocomposite was obtained in situ by oxidative polymerization of aniline in acidic medium using ammonium persulphate as initiator in the presence of natural Bentonite at room temperature. The PANI nanofiber and nanocomposite were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Scanning Electron Microscope (SEM).The parameters such as pH, initial conc. of pb(II),contact time and PANI dosage affecting the removal of pb(II) from aqueous solution have been investigated. The studies of kinetic models including pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich are performed. Langmuir, Freundlich and Temkin adsorption isotherm are investigated. Equilibrium data fitted the Freundlich adsorption isotherm. The thermodynamic parameters such as ΔG^o, ΔH^o and ΔS^o are calculated. The positive value of ΔH^o (18.17 $KJmol^{-1}$) indicated that the adsorption of pb (II) onto PANI nanocomposite was endothermic; The positive value of ΔS^o (69.92 $Jmol^{-1}k^{-1}$) reveals good affinity of pb (II) ions towards PANI nanocomposite.

Keywords: Polyaniline nanocomposite, adsorption kinetic, adsorption isotherms and thermodynamic,

INTRODUCTION

The pollution of water by toxic compounds, heavy metal ions and dyes imposes ecological and public problem due to hazardous and irrecoverable effects of such pollutants on human health and the environment [1-3].

Lead, one of the most common heavy metal, has been widely used in many important industrial applications. As a result, lead ions are usually found in wastewater or effluents from lead mining, battery recycling plants, printed circuit board factories and electronics assembly plants. Lead is suitable for storage-batteries, due to its conductivity, resistance to corrosion and special reversible reaction between lead oxide and sulfuric acid. Lead is well-known to be accumulative poison through water intake or food chains and can cause brain damage and dysfunction of the kidneys [4-6]. Lead in atmosphere comes mainly, 90% from exhaust of gasoline vehicle. The concentration of lead in the air varies with population or more precisely with traffic density [7].

Nowadays, a number of promising processes are used for elimination of heavy metal ions and dyes from wastewaters. Adsorption is one of these processes, in which the adsorbent may be of organic, mineral or natural source [8].Various materials such as zeolites, activated carbon, clays, agricultural wastes, biomass and synthetic polymers were used as an adsorbent [9,10].

Natural Iraqi clay minerals, e.g., kaolinite, smectite, illite, chlorite, etc., are very abundant materials useful for removal studies of pollutant from effluents. Effluent pollutants can be adsorbed either on the external surfaces of the clay or within its interlamellar spaces, by interaction with or substitution of the exchange cations in those spaces [11]. Conductive electro active polymers such as polypyrrole and polyaniline can be used for the removal of heavy metals from water and waste waters [12, 13].

Polyaniline, used in this study as a removal surface of lead from aqueous solution, has a reactive N-H group in a polymer chain flanked on either side by a phenylene ring, imparting a very high chemical flexibility. It undergoes protonation and deprotonation in addition to adsorption ability through nitrogen atoms bearing lone pair of electrons. These properties are responsible for the technologically interesting in chemistry and in physics [14].

In this our research work, a nanocomposite was prepared by the chemical polymerization of aniline in the presence of Bentonite. Its application for pb (II) Ions removal will be discussed in detail.

EXPERIMENTAL WORK

Materials

Aniline 99% (Merck) was double distilled under vacuum pressure, Ammonium peroxydisulphate (APS), hydrochloric acid, sodium hydroxide and $pb(NO_3)_2$, Acetone(BDH), Ethanol(BDH) were of analytical grade and used as received; deionized water was used throughout this work. Natural Bentonite (B) of particles size 150–200 µm was washed with deionized water and dried, then treated with acetone for 3 h and dried in the oven at 100C^o. Bentonite was supplied from the General company of Geological survey and Mining Iraq

Instrumentation

pH meter type trans BP 300, Water bath shaker type lab companion BS-11,digital scale KERN-ABBS,UV-Visible spectrometer, CARY 100 con. (SEM) model Philips XL series 30, Shimadzu 8400 FTIR, (x-ray Diffraction/SHMADZU-XRD 6000-General-Purpose X-Ray Diffractometer) were employed in this research.

Preparation of polyaniline composites

The polyaniline composites were prepared by in situ polymerization of aniline.[15] in the presence of Bentonite in hydrochloric acid solution by rapid addition of a specified amount of ammonium persulphate (APS) in 1 M HCl to the mixture then was moderately stirred using magnetic bar. After 3 h, the product was filtered and washed with distilled water then washed with ethanol and with acetone to remove unreached aniline, oligomers and impurities then dried in an oven at 80 C° for 6 h and stored in a sealed container.

Adsorption experiments

Batch adsorption experiments were carried out by shaking a known amount of adsorbent with 50 ml solution of pb^{2+} in a temperature controlled water bath shaker at different concentrations(10-60 ppm),pHs(1-8),trmperatures(25,35,45C), contact time(20-120 min)and adsorbent dosage (0.05-0.4 g)at a constant shaking rate(80 rpm).The adsorbed amount of lead ions was determined using UV-Visible spectrophotometer at ƛ max 235nm. The removal %(R %) and removal amount of pb^{2+} ions were calculated using the following equations [16].

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (1)$$

$$q_e = \frac{(C_i - C_e) \times V}{M} \qquad (2)$$

C_i and C_e are the initial and final concentration (mg/L) of pb(II), V is volume of initial pb^{2+} ions solution used and M(g) is mass of adsorbent used

RESULT AND DISCUSSION

Characterization of prepared composite by Scanning electron microscopy (SEM), FTIR spectroscopy and X-ray diffraction (XRD).

Scanning electron microscope (SEM)

Scanning electron microscope (SEM) image gave information about the structure of the PANI nanofiber with respect to its shape. The dark areas are micropores and the pale grey areas are due to the PANI nanofiber matrix as shown in Figure.1

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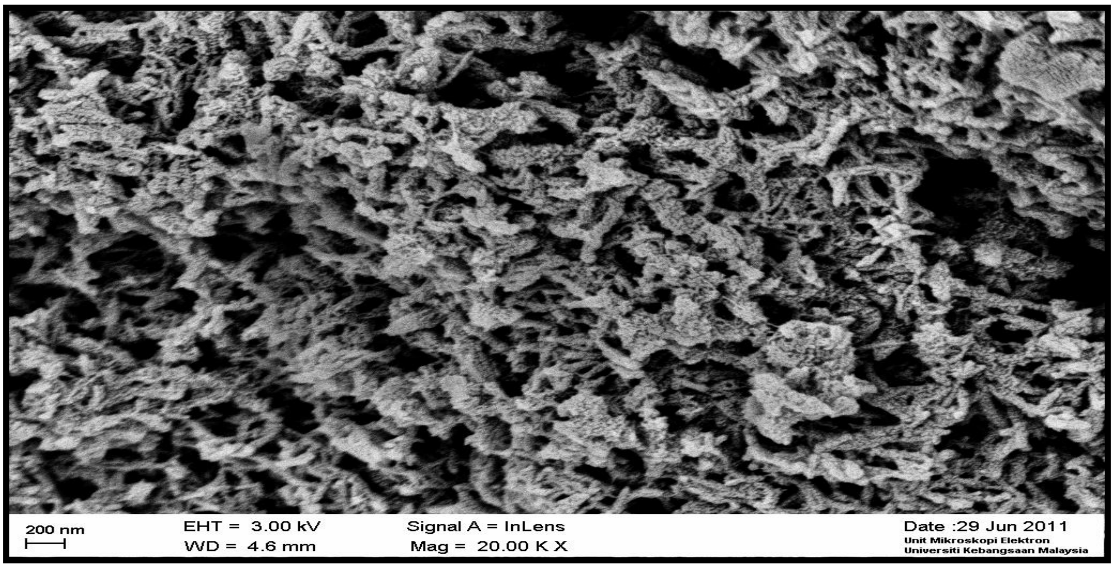

Figure 1. SEM image of polyaniline nanofiber with diameter of 30-80- nm.

Whereas SEM image of polyaniline nanocomposite (fig.2) gave information about the remarkable change in the shape, structure and texture which is due to the nanocomposite formation.

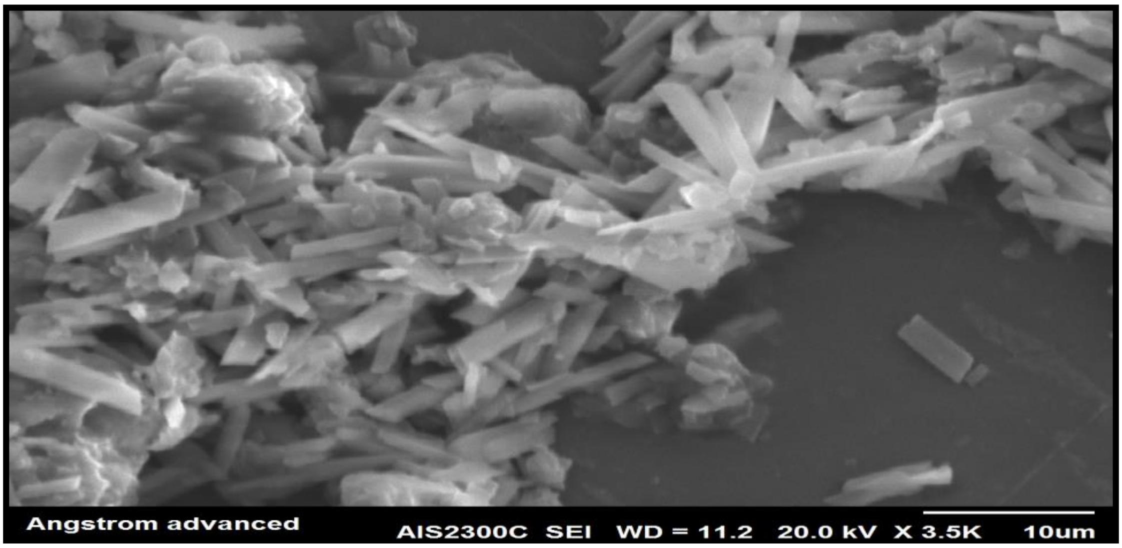

Figure 2. SEM image of polyaniline nanocomposite (PANIB).

FTIR spectroscopy

FTIR analysis was done to identify the characteristic peaks of polyaniline nanofiber. Figure 3 illustrates the presence of characteristic absorption bands at 1563 cm^{-1} (C=C stretching vibration of the quinoid ring), 1468 cm^{-1} (stretching vibration of C=C of the benzenoid ring), 1294 cm^{-1} (C-N stretching vibration), 1119 cm^{-1} (C-H in-plane deformation) and782 cm^{-1} (C-H out-of-plane deformation) [17].

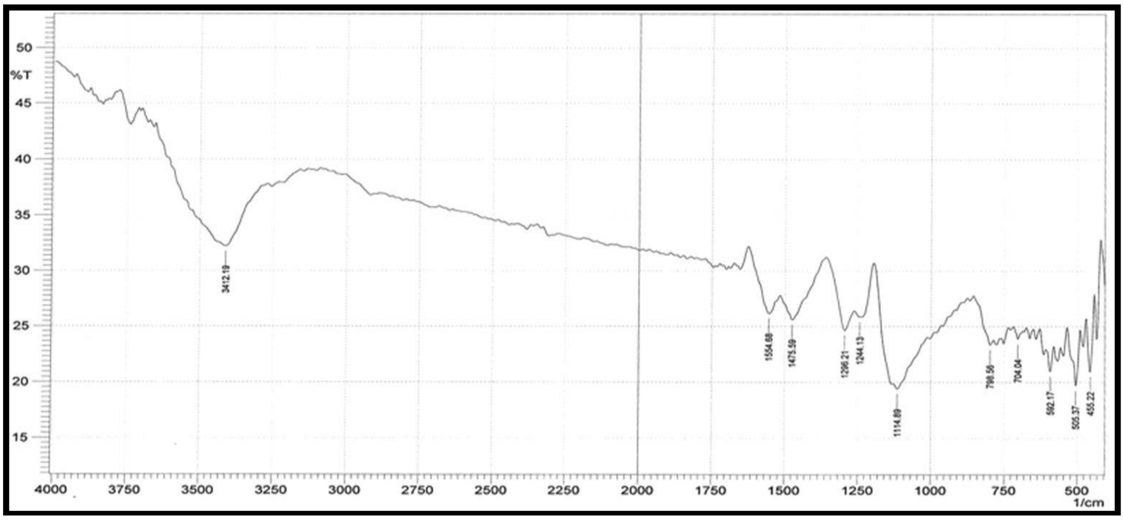

Figure 3. FTIR spectrum of PANI nanofiber.

X-ray Diffraction

The crystalline PANI was determined from XRD analysis. The XRD patterns of PANI nanofiber is shown in Figure 5. The X-ray diffraction confirms the formation of PANI nanofiber, two characteristic peaks around 2ϴ = 20 and 2ϴ = 25 presented in the XRD pattern of the PANI nanofiber.The same XRD pattern was obtained by other researchers which is concur with our data analysis. The average crystallite size was estimated from the integral intensity of the XRD using the Scherer's equation [18]

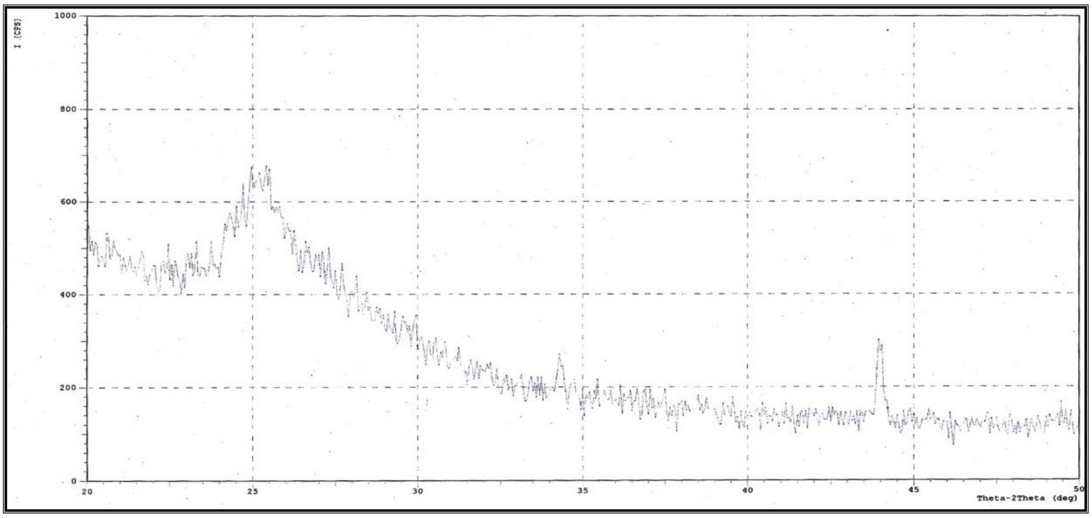

Figure. 5. XRD of polyaniline nanofiber.

Effect of contact time

Figure 6 shows the effect of contact time on the adsorption of pb^{2+} on the surface of PANI-nanocomposite.The amount of pb (II) adsorbed increases rapidly with the increase in contact time at the first 20 min.. More than 90% of the equilibrium for the removed amount of pb^{2+} occurred at the first 40 mins. After 120 min.the removed amount becomes constant and the equilibrium attained So 120 min. was chosen as the contact time for the removal study of pb^{2+} onto the PANI- nanocomposite.

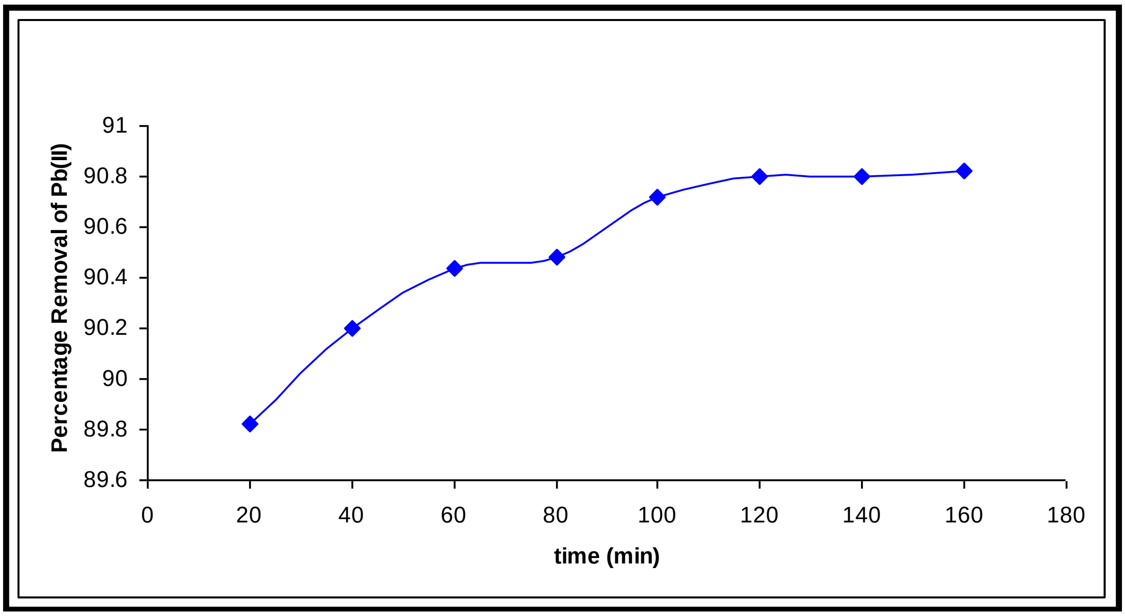

Figure. 6 Effect of contact time on adsorption of pb(II) ions

Effect of pH

The pH of the solution is one of factors that can influence the uptake process of pb^{2+} ions in aqueous solution. Figure 7 shows the effect of pH on the removal of pb^{2+} ions onto PANInanocomposite.lt can be observed that the pb^{2+} removal increases gradually with increase of pH from pH1till it reaches it's maximum at pH4.0 and then decreases remarkably at pH 4.5-8.0. At pH values higher than 7precipitation of pb $(OH)_2$ occurs which leads to inaccurate interpretation of adsorption.[19]

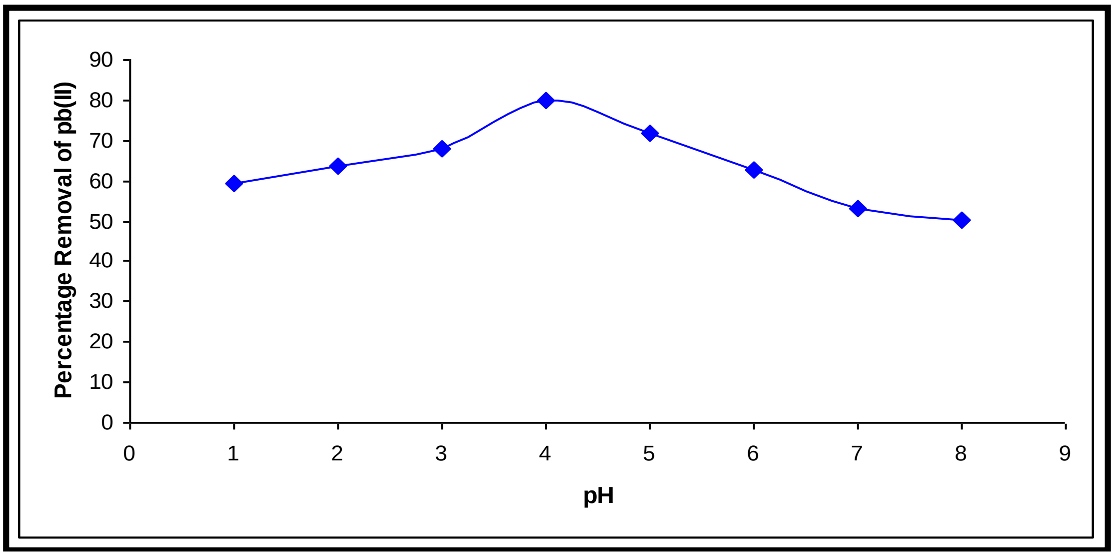

Figure. 7: Effect of pH on adsorption of pb(II) ions.

Effect of Adsorbent Dosage

The effect of loading quantity of adsorbent on the pb^{2+} removal has been processed (fig.8).Various amount of the adsorbent was shaked with the optimum concentration of the metal ion solution under the experimental conditions. The uptake of pb^{2+}ions gradually increased from 89.5% to 92.5% when the nanocomposite dose was increased from 0.05 to 0.4g respectively. This is due to the fact that as the adsorbent dosage is increased, more adsorption sites are accessible for adsorbate enhancing the pb^{2+} uptake.

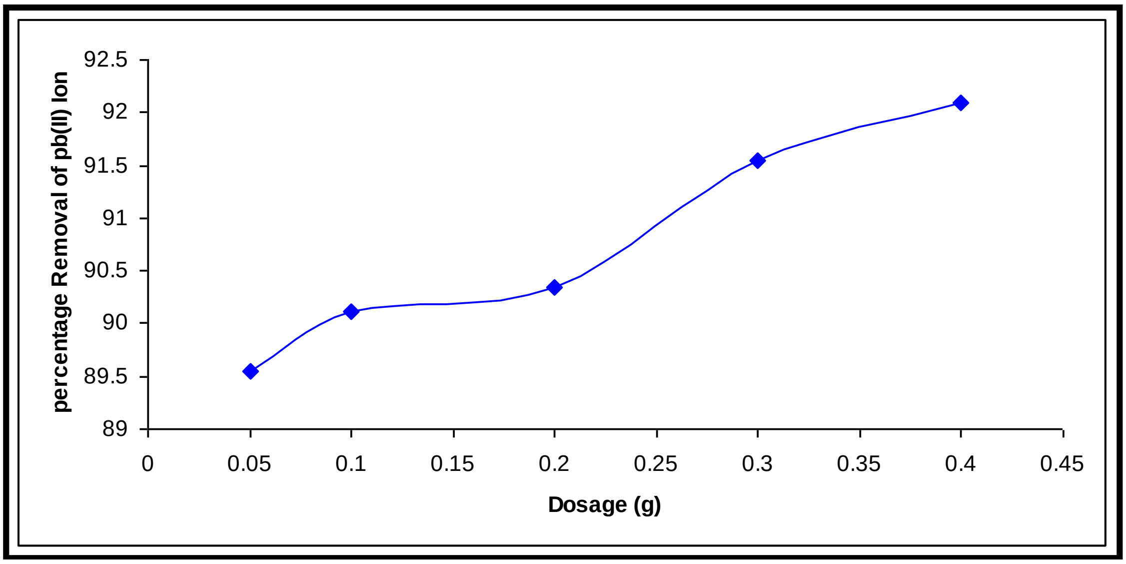

Figure. 8: Effect of adsorbent dosage on adsorption of pb(II) ions

Effect of initial pb(II) ions Concentration

lnitial Concentration of pb^{2+} ions can affect equilibrium of sorbent/sorbate system. Fig.9 illustrates the effect of initial pb^{2+} ions concentration on the removal percent of pb^{2+} ions.lt is noticed that the adsorption progress rapidly with the increase in initial pb^{2+} ions at the first stage then gradually increases until the equilibrium attained at 60 mg/l of metal ion concentration. This finding may be due to the fact that, the sorbent surface area is high and more active sites are accessible for pb^{2+}ions to be uptake [20] Whereas at high metal ion concentration the biosorbent uptake capacity attained plateau (leveled off) leading to the saturation of accessible active binding sites on PANI-nanocomposite and metal ion solution un able to release more pb^{2+} ions to adsorbate on the biosorbent surface [21]

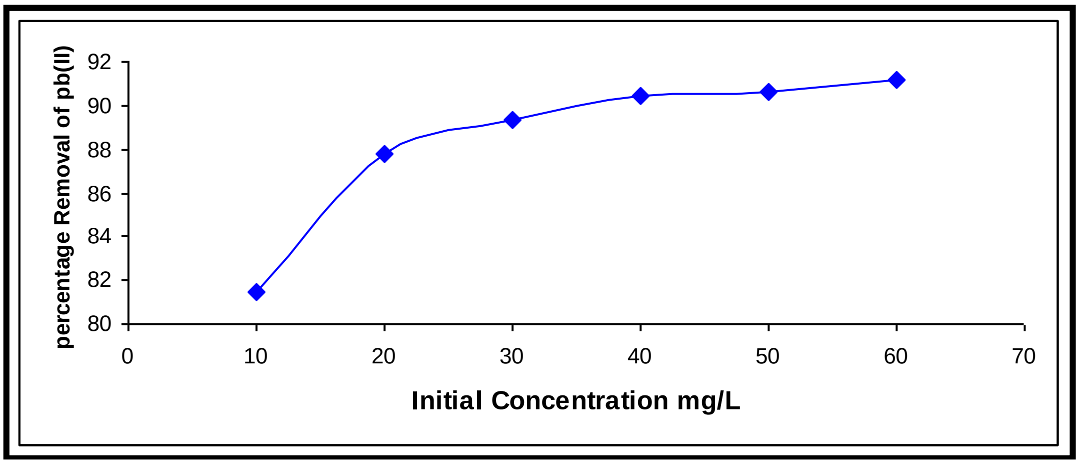

Figure. 9: Effect of initial concentration on adsorption of pb(II) ions

ADSORPTION ISOTHERMS

Langmuir isotherm

Langmuir model is applied to describe the monolayer pb^{2+} adsorption onto biosorbent homogeneous active sites. Langmuir isotherm can be expressed as;

$$\frac{1}{q_e} = \left(\frac{1}{K_L Q_m}\right)\frac{1}{C_e} + \frac{1}{Q_m} \quad \ldots\ldots \qquad \ldots..(4)$$

Ce is the equilibrium concentration of the metal ions (mg/L), qe is the amount ofpb^{2+} adsorbed per unit mass of biosorbent (mg/g). Q_m and K_L are Langmuir constants related to adsorption capacity and rate of adsorption [22]. Maximum adsorption capacity (mg·g-1) determined by the intercept and slope of the linear plot of 1/qe versus 1/Ce (Fig.10).

Freundlich isotherm

Freundlich model suggest that the adsorption occurs in the form of a monolayer on the heterogeneous distributed active sites of the adsorbent, also there exists an interaction between adsorbed molecules [23]. Freundlich isotherm can be represented in the following linearized formulae (5).

$$\log\ Q_e = \log\ K_f + \frac{1}{n}\ \log C_e\ \cdots\cdots\cdots \qquad \ldots(5)$$

qe is the amount of the metal ions adsorbed per unit weight of the adsorbent at equilibrium (mg/g); Ce =concentration of metal ions in bulk solution at equilibrium after binding (mg/L); kf = Freundlich constant related to adsorbent sorption capacity; n = Freundlich constant related to adsorbent sorption intensity. “n” and “kf” are Freundlich isotherm constants, were calculated from slope and intercept of the linear plot of log qe versus log Ce (Fig. 11)

Temkin Isotherm

The Temkin isotherm [24,25] have been given by the following linear formulas:Eq (6,7,and 8).

$$q_e = \frac{RT}{b_T}\ln(A_T C_e)\ \cdots\cdots\cdots\cdots \qquad (6)$$

$$q_e = B_T \ln A_T + B_T \ln Ce \ldots \qquad (7)$$

$$B_T = \frac{RT}{b_T} \qquad (8)$$

The adsorption data can be analyzed according to equation (7). Therefore a plot of qe versus ln *Ce* enables us to determine the constants *A* and b (fig.12).

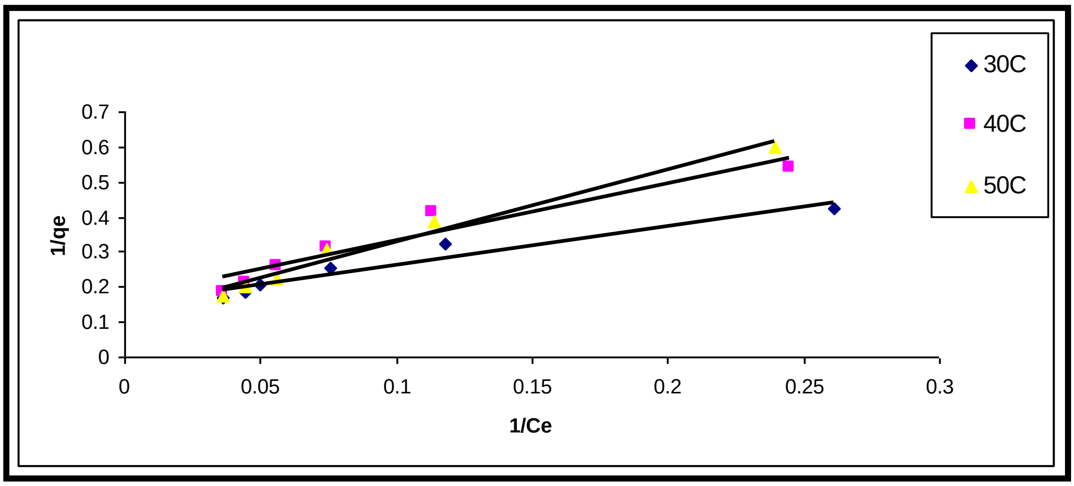

Figure 10. Langmuir adsorption isotherm for pb (II) ions

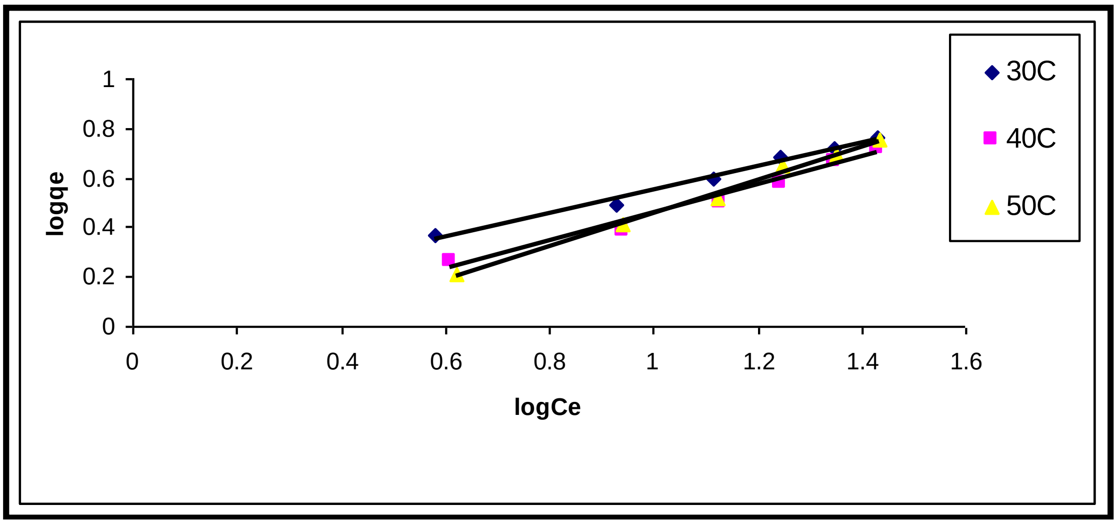

Figure 11: Freundlich adsorption isotherm for Pb (II) ions

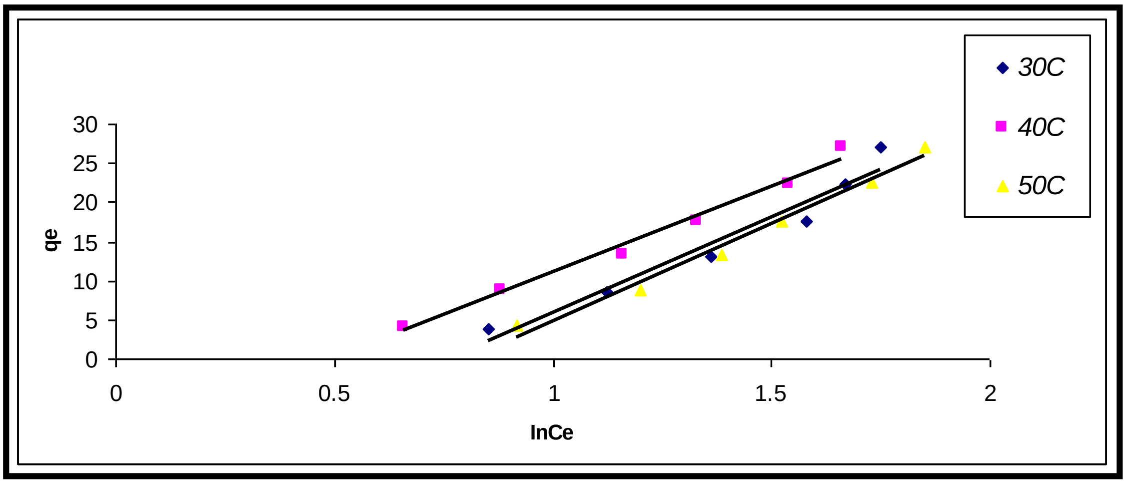

Figure. 12: Temkin adsorption isotherm for Pb (II)

The isotherms experimental data obtained from equations (4), (5) and(7) are tabulated in table 1.From the correlation coefficient determined, the adsorption process was found to fit well to the freundlich model than the Langmuir. So that the adsorption of pb^{2+} ions on the PANI-nanocomposite occurred heterogeneously in majority whereas homogeneous adsorption surface participated in minority.Freundlich exponent 1/n indicates favorable condition of adsorption of pb^{2+} onto the PANI-nanocomposite since $0 < 1/n < 1$ [26].

Table 1: Values for Langmuir, freundlich and Temkin adsorption isotherm parameters.

Isotherm model	Isotherm parameter	Temperature ºC		
		30	40	50
Langmuir	Q_m (mg / g)	6.531	5.97	8.176
	b L mg $^{-1}$	0.1384	0.10322	0.0592
	R^2	0.9392	0.9789	0.9783
Freundlich	K_F	1.190	0.779	0.6137
	n	2.098	1.77	1.491
	R^2	0.9849	0.9731	0.9929
Tempkin	A_T	0.267	0.135	0.288
	B_T	24.34	22.09	24.71
	b_T	103.49	117.80	108.67
	R^2	0.980	0.9934	0.9833

Kinetics studies

The kinetic of adsorption process of pb2+ onto PANI nanocomposite was investigated according to the pseudo- first-order model and pseudo-second-order kinetic model. The pseudo-first order equation can be expressed as;

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \cdots\cdots \qquad \ldots(9)$$

where qt is the amount of pb2+ ions adsorbed at time *t* (mg g^{-1}), *q*e (mg g^{-1}) is equilibrium solid phase concentration and k_1 is first order rate constant for adsorption(min^{-1}).. The rate constant can be calculated from the slope the plot of log *(*qe−qt*)* *vs*. *t* as shown in fig.13

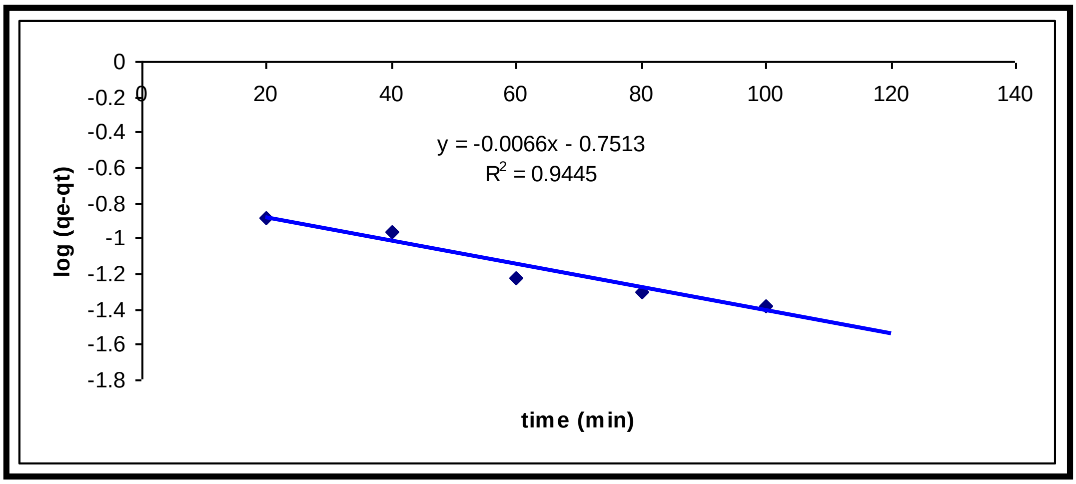

Figure 13: Pseudo-first-order kinetic model for adsorption of Pb (II) ions.

.Kinetic data can also be analyzed using pseudo-second-order kinetic model. Contrary to other models, it predicts the behavior over the whole range of adsorption [27].it can be expressed as:

$$\left(\frac{t}{q_t}\right)=\frac{1}{k_2 q_e{}^2}+\frac{1}{q_e}(t) \tag{10}$$

qe and *qt* represent the sorption capacities at equilibrium and at time t, respectively (mgg^{-1}) and k_2 is the rate constant of pseudo-second order adsorption (g mg^{-1} min^{-1}). The rate constant, k_2 and qe are calculated from the slopes and intercepts of the linear plot of (t/qt) against t as shown in (Figures 14).The parameters of the two kinetic models are represented in table(2).From table 2,it can be noticed that; for pseudo-second order kinetic model (R^2>0.999) and the Qe (Q_{cal}) value calculated was found to be in consistent with the Qe (Q_{exp}).These finding, suggest that the adsorption process of pb2+ onto PANI-nanocomposite was controlled by chemisorptions [26].

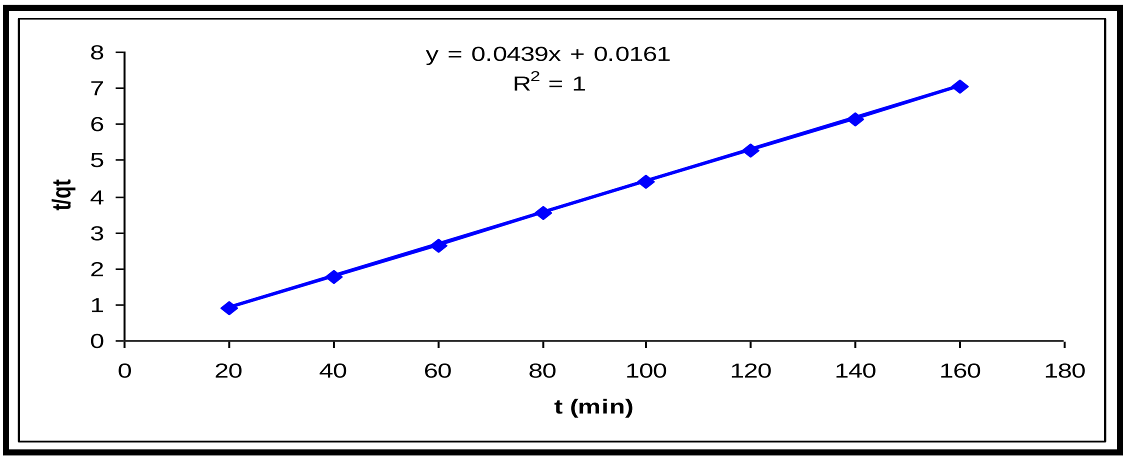

Figure 14: Pseudo-second-order kinetic model for adsorption of Pb (II) ions.

Intra-particle diffusion

The intra-particle diffusion model can be expressed by the following equation ;

$$q_t=K_{dif}\, t^{1/2} \tag{11}$$

k_{dif} is the intra-particle diffusion rate constant. According to this model the plot of q_t *vs.* $t^{1/2}$ should be linear if intra-particle diffusion is involved in the sorption process (fig 14).The linear plot did not pass through the origin, suggesting that the Intra-particle diffusion is not the rate-controlling step for over all mass transfer of adsorption process [28]. In table 2,the value of R^2 of the intra-particle diffusion model is 0.968,showing that the intra-particle diffusion was not the only rate-controlling step of the adsorption process.

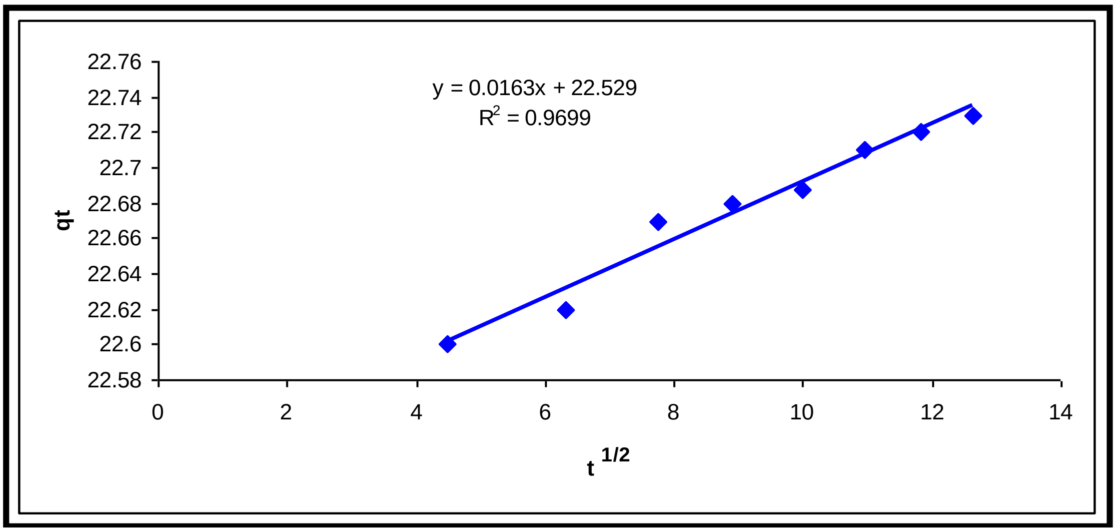

Figure. 15. Intra-particle diffusion kinetic model for adsorption of Pb (II) ions.

Elovich Kinetic equation

Second order kinetic model can be describe by applying the Elovich equation, assuming that the actual solid surfaces are energetically heterogeneous [29]. Chemisorptions' process can be described by the following linear form [30].;

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad (12).$$

The Elovich coefficients could be computed from the plots qt versus ln t. The initial adsorption rate, α (mg/g min) and the desorption constant, β (g/mg) were calculated from the intercept and slope of the plots of qt against ln. Elovich equation constants obtained are given in table (2). It can be noticed that the values of α and β varied as a function of the solution temperature. Thus, on increasing the solution temperature from 30 to 50 C^o, the value of β decreased from 15.384 to 5.690g/mg. This may be due to the less available surface adsorption sites for pb2+ ions. On the other hand, the raising in the solution temperature from 30 to 50 C^o leads to a decrease in the value of α from 22.397to 21.55mg/g min. This means that adsorption lowered down while desorption raised up during increasing solution temperature. However, the experimental data did not give a good correlation for these results at high solution temperature.

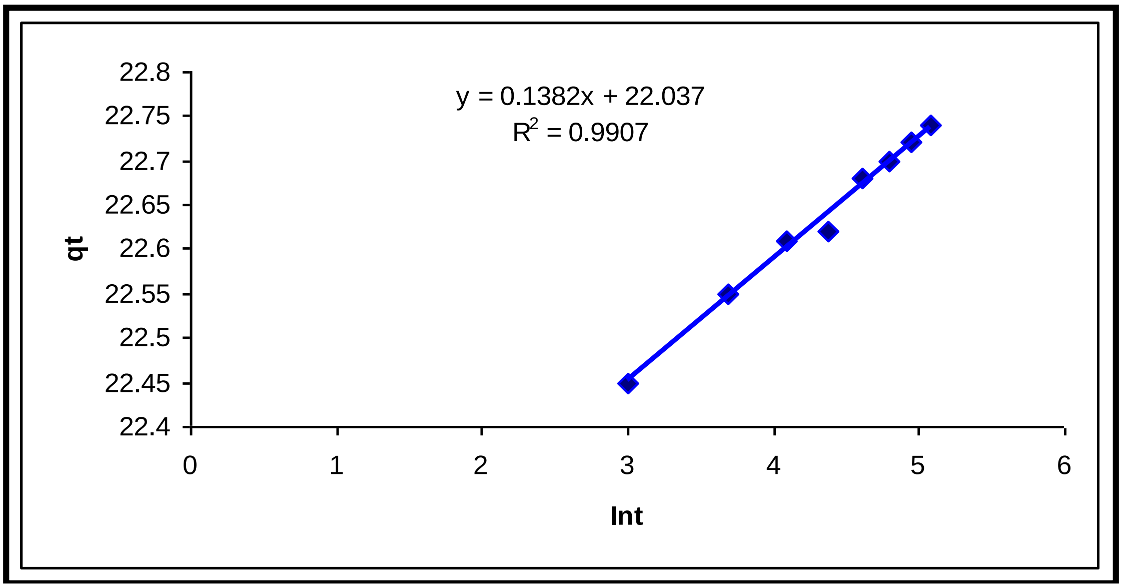

Figure. 16: Elovich kinetic model for adsorption of Pb (II) ions.

Table 2: Kinetic constants for the adsorption of pb (II) onto PANIB

Kinetic Model	Parameter	30 ºC	40 ºC	50 ºC
First- Order Kinetic Model	q_e exp. (mg/g)	22.73	22.40	22.45
	$k_1 \times 10^2$(min.$^{-1}$)	0.0153	0.0165	0.0283
	q_e calc. (mg/g)	0.1772	0.2857	0.9815
	R^2	0.9445	0.9032	0.9841
Second- Order Kinetic Model	$k_2 \times 10^2$ (g mg^{-1} min^{-1})	0.344	0.119	0.07
	h (mgg^{-1} min^{-1})	178.35	62.11	35.50
	q_e calc.(mg/g)	22.72	22.77	22.52
	R^2	1.0	0.9994	0.9997
Elovich Model	β (g mg^{-1})	15.384	7.235	5.690
	α (mg g^{-1} min^{-1})	22.397	22.037	21.55
	R^2	0.968	0.9907	0.907
Intraparticle Diffusion	$K_{diff.} \times 10^2$ (mg g^{-1} min$^{-1/2}$)	0.0163	0.0340	0.045
	B_L (mg/g)	22.52	22.322	21.09
	R^2	0.968	0.9907	0.9529

Thermodynamic studies

Thermodynamic parameters such as change in ΔG^o, change in ΔH^o *and change in* ΔS^o are used to evaluate the adsorption mechanism of pb2+ ions onto PANI-nanocomposite

The Gibb's energy change ΔG^{o}can be calculated using the following equation [31].

$\Delta G^o = RTIn\ Kc$…… ….(13)

Where T is the temperature in (K), R is the gaz constant and K is the Langmuir constant (1/mol).

The values of ΔH° and ΔS°can be estimated using Van't Hoff equation;

$$\ln K = \Delta S/R - \Delta H/RT \quad \ldots\ldots \qquad \ldots.(14)$$

ΔH° and ΔS° were obtained from the slope and intercept of the linear plot of lnK vs. 1/T respectively (Fig.17).
Table 3 presents the values of ΔG°, ΔH ° and ΔS °. The negative values of ΔG° indicated that the adsorption process was favorable and spontaneous in nature.

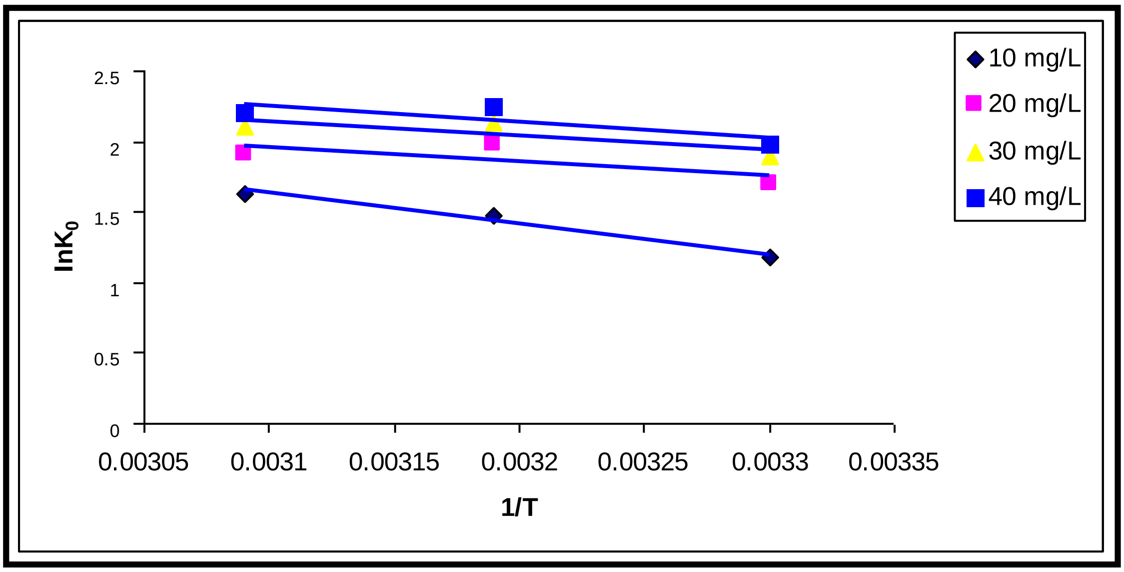

Figure. 17. Van't Hoff plot for the adsorption of pb (II) ions.

Table 3. Thermodynamic data for pb (II) ions adsorption onto PANIB.

pb (II) Con. mg/L	ΔH° KJmol^{-1}	ΔS° Jmol^{-1}k^{-1}	ΔG°KJmol^{-1}			
			30°C	40°C	50°C	R^2
10	18.171	69.924	-2.967	-3.851	-4.39	0.9758
20	8.248	41.816	-4.287	-5.144	-5.115	0.5341
30	8.476	44.039	-4.763	-5.545	-5.642	0.6708
40	9.572	48.401	-4.975	-5.855	-5.695	0.6586

The positive value of ΔH° suggests the endothermic nature of the adsorption process of pb^{2+} onto PANI nanocomposite under the experimental conditions. Moreover positive value of ΔS° also indicates the irreversibility and stability of the adsorption process.

CONCLUSION

The removal of pb^{2+} ion from aqueous solution onto PANI nanocomposite was studied using batching adsorption method under different experimental factors. The equilibrium data agreed with Freundlich adsorption isotherm with $R^2>0.999$. Freundlich exponent 1/n indicates favorable condition of adsorption. Experimental reading of adsorption process was found that the adsorption kinetic could be explained by pseudo second order kinetic model with $R^2>0.999$. The negative value of ΔG^o affirms the spontaneity of adsorption process. The PANI nanocomposite prepared was successfully applied for the removal of pb2+ ions from aqueous solution.

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