
INVESTIGATE THE ADSORPTION KINETICS AND ISOTHERM MODELS OF Pb(II) IONS REMOVAL BY RESINEX™ K-8 STRONG ACID CATION EXCHANGE RESIN.

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Abstract

In the present study we investigated the adsorption kinetics and isotherm models of Pb(II) removal by Resinex™ K-8 strong acid cation exchange resin at different temperatures. Adsorption kinetics is investigated to develop an understanding of controlling reaction pathways (e.g. chemisorptions versus physisorption) and the mechanisms (e.g. surface versus intraparticle diffusion) of adsorption reactions. Kinetic data can be used to predict the rate at which the target contaminant is removed from aqueous (pure water) and aqueous-organic solutions (formic, acetic, propionic) and equilibrium adsorption isotherms are used to quantify the adsorptive capacity of an adsorbent. The results can be used to assess the utility of the adsorbent for the heavy metal removal, in particular Pb(II) ions adsorption, in the field scale.

Thermodynamic parameters, the Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS), were calculated and show that adsorption of Pb(II) ions is spontaneous and endothermic in nature.

Keywords: Cation exchange resin; lead (II) ions; Adsorption kinetics; Adsorption mechanism; organic acids.

Introduction

lead(II) can be found in wastewater from metallurgical processes, galvanizing plants, stabilizers, thermoplastics, pigment formation, alloys and battery manufacturing in addition to the discharges of municipal wastewater treatment plants [1-3]. lead(II) was an essential trace element in small quantities for humans taking role in electron transfer in many enzymatic reactions [4].

However, its prolonged and excessive intake may Pb(II) ions has toxic effects such as carcinogenesis, mutagenesis and tetragenesis as a result of its bioaccumulation [5], adsorption has been developed as an efficient method for the removal of heavy metals from contaminated water and soil. A variety of adsorbents, including clays, zeolites, dried plant parts, agricultural waste biomass, biopolymers, metal oxides, microorganisms, sewage sludge, fly ash, cation and anion exchangers and activated carbon have been used for lead(II) ions removal. Ion exchange now is a well-established technology, particularly in water purification and the concentration and removal of hazardous substances at very low concentrations in chemical process industries [5-10].

For example, it has been applied for the recovery of copper from rayon spinning wastewater and the recovery of gold from cyanide solution in metallurgical industries. Besides, many studies presented covered applications in the wine industry, the separation of amino acids and nucleic acids, and therapeutic uses. However, selective removal of one or more metal ions from multi-metal mixtures using common organic cation exchange resins is generally not feasible, especially for those ions with the same valence [11-12].

The kinetics of ion exchange is frequently correlated using semi empirical pseudo first- and second-order equations. However, such models are merely correlative, which limits their application and extrapolation. An alternative approach adopts Nernst-Planck equations to describe mass transport in ionic systems, accounting for concentration and electric potential gradients induced by the different counter ions mobility [13-15].

Experimental

(1) Resin and materials:

A commercial synthetic, strongly acidic cation exchange resin in the H-form of Resinex KTM-8 of gel type structure supported from Jacob I (Swedish company). All chemicals used were of analytical reagent grade and obtained from commercial suppliers without further purification. The certified stock solution of Pb(II)ions was purchased from Merck.

(2) Methods:

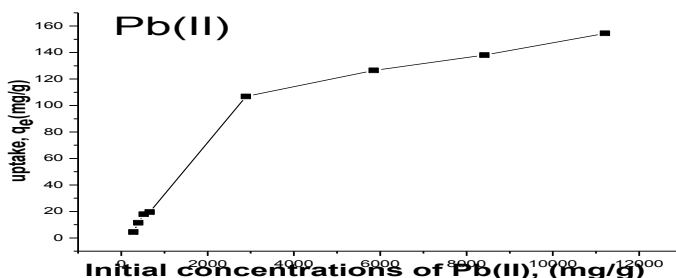
For the kinetic studies, 50 mL Pb(II) solution at a respective initial Pb(II)ions concentrations (2.82×10^2 , 3.94×10^2 , 5.25×10^2 , 6.63×10^2 , 28.92×10^2 , 58.49×10^2 , 84.13×10^2 and 112.06×10^2 mg/L) was introduced into a 100 mL conical flask containing 1.0 g of the dried cation exchanger. The flasks were capped joint-stopper and agitated at a desired temperature (19, 37 and 51°C) in separate. After different contact time intervals, aliquots of metal ion solutions were withdrawn and centrifuged to obtain the supernatants.

The supernatants were then kept to determine the Pb(II) concentrations using AAS varion 6 (Analytik Jena AG Konrad-Zuse-StraBe 107745 Jena). The amount of metal ion adsorbed q_t (mg/g), at time t (min), was calculated by equation: $[q_t = (C_i - C_t)V/m]$ where C_i and C_t (mg/L) are initial and equilibrium concentrations of metal ion, respectively, V (L) is the volume of metal ion solution, and m (g) is the mass of the adsorbent.

Results And Discussion.

(1)Effect of initial concentration of metal ions and contact times:

The influence of contact time on the adsorption of Pb(II) onto Resinex™ K-8 strong acid cation exchange resin was investigated at various concentrations of Pb(II)ions, is shown in (Fig.1). Our experiments were carried out at different concentrations(2.82×10^2 , 3.94×10^2 , 5.25×10^2 , 6.63×10^2 , 28.92×10^2 , 58.49×10^2 , 84.13×10^2 and 112.06×10^2 mg/L), a fixed adsorbent quantity of 1.0g and 19°C. It can be seen that the amount adsorbed increases (4.44, 11.5, 17.91, 19.55, 106.81, 126.53, 138, and 154.47 mg/g) with increasing initial Pb(II)ions concentration, so the removal of Pb(II)ions depends on the concentration of Pb(II)ions.



(Fig.1) Effect of initial concentration on the uptake of Pb(II)

Moreover, the amount adsorbed increased with an increase in contact time and then reached equilibrium. This may be attributed to the initial concentration which provides an important driving force to overcome all mass transfer resistances of Pb(II)ions between the aqueous and solid phases, hence a higher initial concentration of Pb(II)ions will enhance the adsorption process shown in (Tabl.1) [16,17].

(Table. 1): Effect of different initial concentrations on the uptake and removal percentage of lead(II) ions in aqueous solutions and at different temperatures.

Temp.K	282		394		525		663		2892		5849		8413		11206	
	q _e	R%	q _e	R%	q _e	R%	q _e	R%	q _e	R%	q _e	R%	q _e	R%	q _e	R%
292	21.54	37.54	35.00	39.89	67.38	58.69	70.90	49.39	365	56.49	452	34.98	618	41.22	728.0	29.90
310	22.40	39.02	48.97	55.06	71.43	62.22	77.24	53.81	380	58.81	480	37.14	852	50.89	940.0	43.22
324	25.00	43.55	54.60	61.35	72.40	63.04	93.14	64.89	395	61.13	1000	77.38	1187	63.59	1357	55.59

When equilibrium adsorption capacity of the adsorbent increased with an increase initial Pb(II)ions concentration, the percentage removal of Pb(II)ions

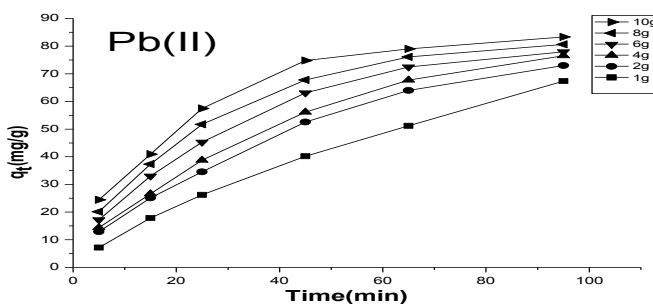
showed opposite trend. Since the percentage removal decreased in the following sequence: 76, 70, 68.75, 58, 55.71, 43.26, 32.82 to 27.56 %.

Kinetic experiments clearly indicate that adsorption of Pb(II) ions on the adsorbent followed three-step process, a rapid initial adsorption followed by a period of slower uptake of metal ions and finally no significant uptake [18]. This may be explained as follow: the first step (the rapid adsorption) observed is probably due to the abundant availability of active sites on the adsorbent surface (bulk diffusion).

The second step, exhibiting additional adsorption, is attributed to the diffusion of the adsorbate from the surface film into the macropores of the adsorbent (pore diffusion or intra-particle diffusion) stimulating further movement of metal ions from the liquid phase into the adsorbent surface, the adsorption becomes less efficient. With gradual occupancy of these sites on the adsorbent, the last stage is essentially an equilibrium stage[19].

(2)Effect of adsorbent dosage:

The effect of adsorbent quantity on the adsorption capacities and percentage removal of Pb(II) by Resinex™ K-8 strong acid cation exchange resin are depicted in (Fig.2), it can be seen that the adsorption capacity at equilibrium, q_e , increased as the adsorbent quantity increased from 1.0 to 8.0g in 50 mL solution at 19°C, and the percentage removal of Pb(II) ions increased from 68.75 to 87.62%, due to that the adsorption surface area and available adsorption sites on the adsorbent [20,21].



(Fig.2) Effect of dose for the Pb(II) adsorption by resinx K-8(8mmol/l)

Further, increase in adsorbent quantity(10 g) has shown negligible effect towards increase in percentage adsorption of Pb(II) ions from the solution. This may be due to aggregation of the adsorbent. Such aggregation may be cause the adsorption surface became saturated with Pb(II), making the adsorption capacity of Pb(II) ions nearly constant [22].

(3)Effect of acidity on the metal uptake:

The influence of different concentrations of HCl and HNO₃ ions on the position of the equilibrium of metal resin interactions are given in (Table.2) and reveals that the amount of Pb(II) ions taken by the resin sample decreased with increasing concentration of Cl⁻ and NO₃⁻ ions. However, the uptake of Pb(II) ions was depends on the nature of the electrolyte present in the solution. In the presence of nitrate ions, the uptake of Pb(II) ions is higher than that in the presence of chloride ions.

Table. 2: Effect of acidity medium (0.1M) on the uptake and removal percentage of Pb(II) ions at different temperatures (292,310 and 324 K).

Temp.K,	HCl		HNO ₃		HCOOH		CH ₃ COOH		C ₂ H ₅ COOH	
	q _e	R%	q _e	R%	q _e	R%	q _e	R%	q _e	R%
292	34.96	30.47	43.60	37.96	60.3	52.50	47.40	41.27	67.50	58.77
310	39.47	34.39	47.94	41.75	71.8	62.52	57.43	50.02	70.35	61.25
324	53.00	46.15	59.41	51.76	83.3	72.53	70.35	61.25	75.40	65.65

This may be explained in terms of the stability constants of the complexes formed by the metal ions with the anions used in the present study [23]. Nitrate ion forms a strong complex with Pb(II) ions while Pb(II) ions form stronger complex with chloride ion, i.e., if electrolyte ligand- metal ion complex is stronger than polymer-metal ion chelates, then more metal ions form strong complexes with electrolyte ligand itself which results in the reduction of metal uptake capacity of the resin. This trend has also been observed by other investigators in this field [24].

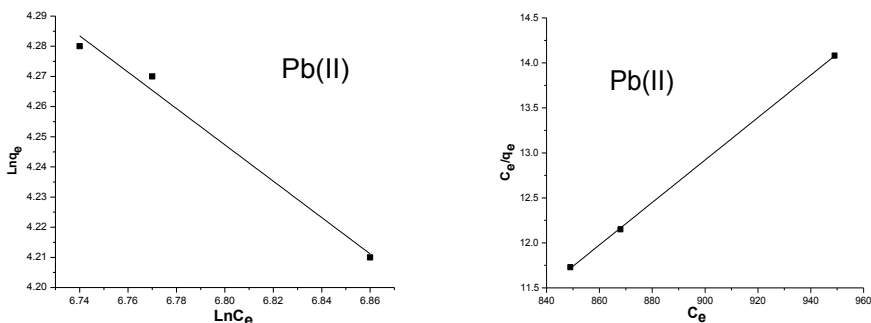
(4)Equilibrium isotherms:

Langmuir, Freundlich, Temkin and Dubinin-Radushkevich(D-R) equations were used to analyze the equilibrium data by [25-27] means of the adsorbent. Langmuir and Freundlich isotherm models can be expressed by the following equations (1) and (2) respectively.

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (1) \quad \& \quad q_e = k_f C_e^{1/n} \quad (2)$$

$$C_e q_e = (1/Q_0 b) + (C_e/Q_0) \quad (3) \quad \& \quad \text{Log } q_e = \text{log } k_f + \frac{1}{n} \text{log } C_e \quad (4)$$

Langmuir and Freundlich adsorption isotherms of lead Pb(II) ions on the cation exchange resin are shown in (Figs.3 and 4). The model parameters and the statistical fits of the adsorption data to these equations are given in (Table.3). The results show that Langmuir model describes the adsorption data with a correlation factor R² values <0.996. According to the saturated monolayer adsorption capacity Q₀ (434 mg/g) and b (7.02x10⁻⁴L/g), in the aqueous solution system.



(Fig.3) Freundlich plot for the Pb(II) adsorption by resin K-8 (Fig.4) Langmuir plot for Pb(II) adsorption by resin K-8 (8mmol/L)

(Table. 3): Freundlich, Langmuir, Temkin, and D-R isotherm model parameters and correlation coefficients for adsorption of lead ions ($C_0=525, \text{mg/L}$) in aqueous and acidic media.

Isotherm model Adsorption medium	Freundlich		Langmuir				Temkin		D-R				
	n	k_f	R^2	Q_0	b	R^2	R_L	B	A	R^2	X_m	β	R^2
Pure water	1.54	5845	0.99	42.37	3.63×10^{-3}	0.999	0.12	45.76	241×10^{-3}	0.999	85.97	0.0208	0.904
HCl	0.64	3912472	0.986	16.58	0.06	0.996	0.02	68.94	3.75×10^{-4}	0.999	23.84	0.1689	0.992
HNO_3	0.85	227325	0.992	23.02	0.07	0.997	0.03	62.54	3.94×10^{-4}	0.997	33.02	0.098	0.999
HCOOH	1.71	3685.83	0.97	43.73	0.14	0.983	3.12×10^{-3}	42.28	2.18×10^{-4}	0.985	54.96	0.02337	0.929
CH_3COOH	1.1	34926.11	0.970	29.27	0.05	0.975	8.78×10^{-3}	10.68	1.09×10^{-3}	0.987	39.92	0.06327	0.914
$\text{CH}_3\text{CH}_2\text{COOH}$	1.65	4317.19	0.998	44.46	0.14	0.998	3.12×10^{-3}	43.63095	2.25×10^{-4}	0.998	58.49	0.02162	0.999

On the other hand, the equilibrium data were analysed using Freundlich isotherm model and R^2 values (1.00) were estimated. The values of $1/n$ ($1/2 < 1$) generally indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the adsorbent by the lead Pb(II) ions; thus infinite surface coverage is expected to occur indicating multilayer adsorption on the surface.

It can be concluded from (Table.3) that the Freundlich isotherm was more suitable than the Langmuir one as in most cases the correlation coefficient was higher ($1.000 > 0.994$) as seen in (Table.3). Thus, indicating the applicability of multilayer coverage of the lead Pb(II) ions on the surface of adsorbent. This can be explained by the fact that the adsorbent has a high surface area for metal adsorption. Therefore, only multilayer adsorption occurred on their surface, in spite of any surface modification.

According to the literature, the essential characteristics of Langmuir isotherm can be explained in terms of a dimensionless constant separation factor, R_L , defined by equation :

$$R_L = 1/(1 + bC_0) \quad (5)$$

In general, the values of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L=0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). In this study the calculated value of $R_L(0.73)$ shown in (Table.3) indicating that adsorption of Pb(II) ions into Resinex™ K-8 strong acid cation exchange resin was favourable.

The Temkin and Pyzhev isotherm model contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This model assumes the following facts; (i) the heat of adsorption of all molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and then (ii) the adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy. The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation.

The Temkin and Pyzhev isotherm has commonly applied in the following equation (6):

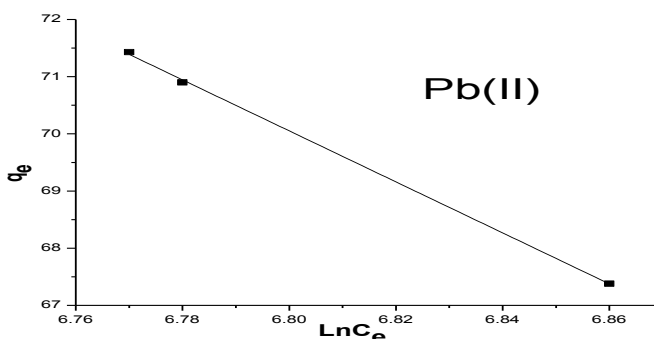
$$q_e = (RT/b) \ln(AC_e) \text{ ----- (6)}$$

This equation can be expressed in its linear form as:

$$q_e = (RT/b) \ln A + (RT/b) \ln C_e \text{ ----- (7)}$$

where $B = RT/b \text{ ----- (8)}$

where A and B are Temkin isotherm constants, R is the gas constant (8.314 j/mol K) T is the absolute temperature. The Temkin and Pyzhev isotherm for Pb(II) is shown in (Fig.5) the related parameters are given in (Table.3), B related to heat of adsorption. Values higher than 8 indicates strong interaction between metal and the adsorbent. However, lower value of B (7.77) for Pb(II) ions indicates presence of relatively stronger cohesive forces in between the adsorbent and lead Pb(II) ions. Process, as indicated by B can be expressed as physical adsorption [25].



(Fig.5) Temkin plot for the Pb(II) adsorption by resin K-8.

Although the Freundlich isotherm provides the information about the surface heterogeneity and the exponential distribution of the active sites and their energies, it does not predict any saturation of the surface of the adsorbent by the adsorbate.

Hence, infinite surface coverage could be predicted mathematically. In contrast, Dubinin-Radushkevich (D-R) isotherm relates the heterogeneity of energies close to the adsorbent surface. If a very small sub-region of the adsorption surface is chosen and assumed to be approximately by the Langmuir isotherm.

The Dubinin-Radushkevich (D-R) isotherm was employed to find out the adsorption mechanism based on the potential theory assuming a heterogeneous surface. Dubinin-Radushkevich isotherm is expressed as follows:

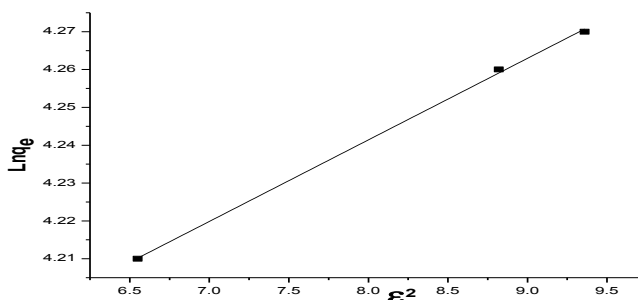
$$q_e = X_m e^{-\beta \varepsilon^2} \quad (9)$$

$$\text{The linear form was : } \text{Log} q_e = \text{log} X_m - \beta \varepsilon^2 \quad (10)$$

Where (X_m) is the Dubinin-Radushkevich (D-R) monolayer capacity (mg/g), β is a constant related to adsorption energy, and ε is the Polanyi potential [33] which is related to the equilibrium concentration as follows :

$$\varepsilon = RT \ln (1 + 1/C_e) \quad (11)$$

Where R is the gas constant (8.314 J/mol K) and T is the absolute temperature. A plot of q_e vs. ε^2 in (Fig. 6) gave a straight line of slope, (β) and intercept, (X_m) of different systems were calculated.



(Fig.6) D-R plot for the Pb(II) adsorption by resin X-K-8.

The difference in the free energy between the adsorbed phase and the saturated liquid adsorbate is referred to as the potential, a term first advanced by Polanyi [26] and later developed by Dubinin and his co-workers [19].

Thus, the adsorption space in the vicinity of the solid surface may be characterized by a series of equipotential surfaces with a given adsorption potential. The adsorption potential is independent of temperature but varies according to the nature of the adsorbent and adsorbate. In the present study, Dubinin-Radushkevich

(D-R) isotherm constants, monolayer capacity (X_m) and adsorption energy (β) are tabulated in (Table.3). The magnitude of β is used to determine the type of adsorption mechanism.

When one mole of ions is transferred the adsorbent surface, its value is higher than 8 kJ/mol which indicates chemical adsorption [27], the calculated values of E for the present study is higher than 8 kJ/mol for the adsorption of Pb(II) ions, which suggest that adsorption process of Pb(II) onto the surface of the adsorbent is chemical adsorption type.

(5) Comparison of adsorption isotherms:

The experimental data of the effect of an initial concentration of copper ions on the adsorbent surface of the test medium were fitted to the different four isotherm models, namely, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherms. The constants obtained from Langmuir and Freundlich isotherms had very high correlation coefficients (R^2) (Table.3). Comparisons between correlation coefficients, with the adsorption correlation values for the adsorbent, fit the Langmuir model better than the Freundlich model. These values indicated a strong positive correlation.

The results indicated that adsorption of lead Pb(II) ions in aqueous solution is a better system than aqueous-organic systems, it was observed from (Table.3) that the best fitted adsorption isotherms considering the correlation coefficient obtained were to be in the order of prediction precision; Langmuir > Freundlich > Temkin > Dubinin-Radushkevich (D-R) isotherms. Comparing the correlation coefficients which obtained from the adsorption isotherms shows the best fits to the experimental values using the different isotherm equations and were also generally very good for Langmuir and Freundlich isotherm equations.

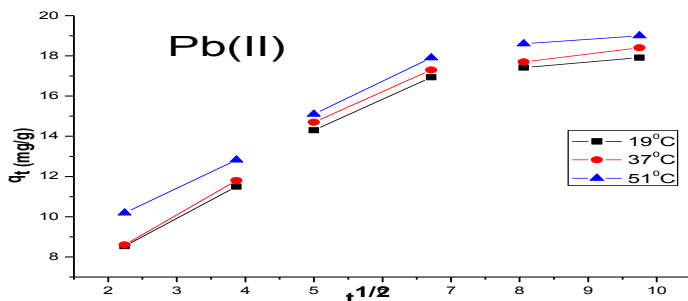
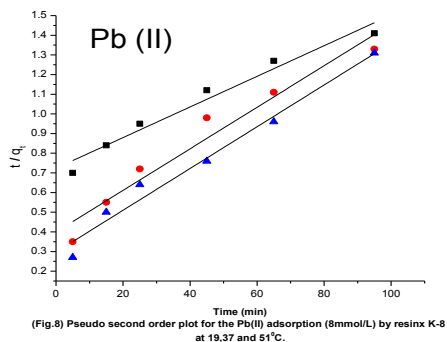
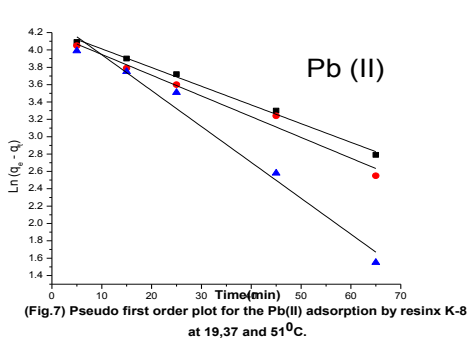
The applicability of Langmuir and Freundlich isotherm equations to the lead Pb(II) ions-Resinexcation exchange resinsystem indicated that the monolayer adsorption and heterogeneous surface conditions exist under the studied experimental conditions. The adsorption of lead Pb(II) ions into the adsorbent surface is thus complex, involving more than one mechanism [28].

The comparison of maximum monolayer adsorption capacity of copper ions onto various adsorbents was presented in (Table.3). It shows that the aqueous system studied in this work has larger adsorption capacity.

(6) Adsorption kinetics modeling :

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid/solution

interface. In this part of study, the data of the kinetics of Pb(II) adsorbed from aqueous solution onto Resinex™ K-8 strong acid cation exchange resin as illustrated in (Figs. 7-9), were analyzed using pseudo first-order, pseudo second-order and intraparticle diffusion kinetic models, respectively. The conformity between experimental data and each model predicted values was expressed by the correlation coefficient (R^2). A relatively high R^2 values indicates that the model successfully describes the kinetics of metal ion adsorption removal.



The adsorption kinetics of metal ions from liquid phase to solid is considered as a reversible reaction with an equilibrium state being established between two phases. A simple Pseudo first-order model was therefore used to correlate the rate of reaction and expressed as follows:

$$dq_t/dt = k_1(q_e - q_t) \text{ ----- (12)}$$

Where q_e and q_t are the concentrations of ion in the adsorbent at equilibrium and at time t , respectively (mg/g) and k_1 is the Pseudo first-order rate constant (min^{-1}).

After integration and applying boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t = q_t$, the integrated form of Eq.(12) becomes:

$$\text{Log}(q_e - q_t) = \text{log } q_e - k_1 t / 2.303 \text{ ----- (13)}$$

Plots for (Eq.13) were made for Pb(II) adsorption at different studied temperatures, and shown in (Fig.7). Approximately linear fits were observed for the Pb(II) ions, over the entire range of shaking time explored and at all temperatures, with low correlation coefficients (Table. 4a and b), indicating that the Pseudo first-order kinetic model is not valid for the present systems.

(Table 4-a): Parameters of pseudo first-order kinetic models of lead(II) -adsorbent systems at different temperatures.

Parameter	Temp.,K	Initial concentration of Pb(II), mg/L							
		282	394	525	663	2892	5849	8413	11206
K ₁ (min ⁻¹)	292	0.03108	0.01686	0.02155	0.0276	0.03669	0.03461	0.03631	0.03638
	310	0.03221	0.03203	0.02391	0.0262	0.04502	0.05024	0.0278	0.02843
	324	0.02264	0.05382	0.04137	0.0291	0.04564	0.0292	0.02264	0.02012
q _{ei} (mg/g)	292	24.62	36.12	68.59	509.27	694.80	794.5	71.79	395.99
	310	21.59	44.57	65.85	72.11	392.89	517.74	830.35	848.41
	324	21.39	44.27	78.14	69.15	390.26	934.57	1008.06	1053.36
R ²	292	0.965	0.8766	0.9569	0.9831	0.9554	0.9820	0.9707	0.8643
	310	0.945	0.8721	0.9660	0.9642	0.9880	0.9483	0.9669	0.9002
	324	0.992	0.9972	0.9504	0.9992	0.9453	0.8453	0.9750	0.9673

(Table 4-b): Parameters of pseudo first-order kinetic models of leadPb(II) ions adsorbent systems at different media, C₀=525 mg/L.

Parameter	Temp.K	Pseudo-first order					
		Pure water	HCl (0.1M)	HNO ₃ (0.1M)	HCOOH (0.1M)	CH ₃ COOH (0.1M)	CH ₃ CH ₂ COOH (0.1M)
K ₁ (min ⁻¹)	292	0.052	0.02043	0.01859	0.02995	0.0265	0.03016
	310	0.046	0.02098	0.01859	0.0334	0.03062	0.03606
	324	0.050	0.01942	0.02312	0.04271	0.3755	0.04516
q _{ei} (mg/g)	292	1.14	38.22	45.81	59.41	51.0	78.76
	310	1.18	43.66	49.62	65.45	95.58	83.92
	324	1.24	51.21	58.25	79.837	5.8	92.93
R ²	292	0.983	0.980	0.956	0.977	0.993	0.977
	310	0.964	0.949	0.970	0.994	0.977	0.988
	324	0.950	0.987	0.986	0.977	0.974	0.989

A pseudo second-order rate model is also used to describe the kinetics of the adsorption of ions adsorbent materials. The differential equation for chemisorptions kinetic rate reaction is expressed as:

$$dq_t/dt = k_2(q_e - q_t)^2 \text{ -----} \tag{14}$$

where k_2 is the rate constant of pseudo second-order equation (mg/g).

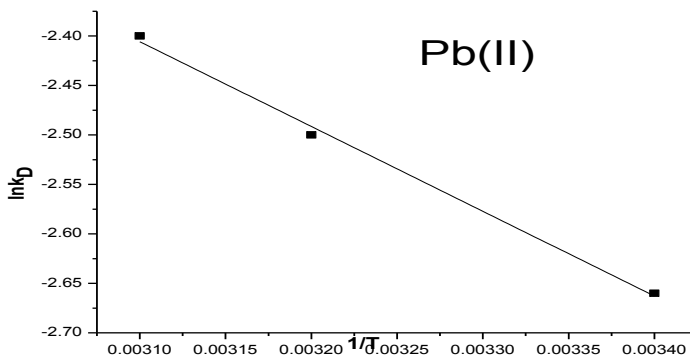
For the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t = q_t$, the integrated form of (Eq.14) becomes :

$$1/(q_e - q_t) = 1/q_e + k_2 t \text{-----} \quad (15).$$

This equation can be rearranged to obtain a linear form equation as:

$$t/q_t = (1/k_2 q_e^2) + (1/q_e)t \text{-----} \quad (16)$$

The kinetic plots of t/q_t versus t for Pb(II) adsorption at different temperatures are present in (Fig.8). The relationships are linear, and the values of the correlation coefficient (R^2), suggest a strong relationship between the parameters and also explain that the process of adsorption of Pb(II) ions follows pseudo second-order kinetic model. From (Table5a and b), it can be shown that the values of the rate constant ' k_2 ' were increased with increase in temperature.



(Fig.10) Van't Hoff plots for the adsorption of Pb(II) from aqueous solutions at different temperatures

(Table. 5-a): Parameters of pseudo second-order kinetic models of lead(II) -adsorbent systems at different temperatures(292,310and 324K), $C_0=525$ mg/L.

Parametr	Temp.,K	Initial concentration of Pb(II), mg/L							
		282	394	525	663	2892	5849	8413	11206
K_2 (g/mg min)	292	3.25×10^{-4}	8.43×10^{-5}	8.39×10^{-5}	1.53	2.65×10^{-4}	2.56×10^{-4}	2.22×10^{-4}	2.49×10^{-4}
	310	1.11×10^{-3}	6.13×10^{-4}	2.8×10^{-4}	2.69×10^{-4}	9.06×10^{-4}	9.06×10^{-4}	2.05×10^{-4}	2.92×10^{-4}
	324	1.41×10^{-3}	1.42×10^{-3}	3.79×10^{-4}	4.36×10^{-4}	1.02×10^{-4}	2.1×10^{-4}	2.14×10^{-4}	2.92×10^{-4}
q_e (mg/g)	292	39.59	81.23	128.25	113.37	625.00	719	943	1029
	310	29.17	61.73	94.67	102.61	473.93	578	1202	1202
	324	30.58	61.88	94.11	108.61	487.80	1303	1470	1535
R^2	292	0.987	0.821	0.998	0.960	0.914	0.992	0.989	0.982
	310	0.985	0.993	0.967	0.943	0.990	0.996	0.963	0.963
	324	0.997	0.996	0.972	0.971	0.994	0.991	0.934	0.882

(Table. 5-b): Parameters of kinetic models of lead(II) - adsorbent system at different media, C₀=525 mg/L.

Pseudo-second order							
Parameter	Temp (K)	Pure water	HCl (0.1M)	HNO ₃ (0.1M)	HCOOH (0.1M)	CH ₃ COOH (0.1M)	CH ₃ CH ₂ COOH (0.1M)
K ₂ (g/mg min)	292	8.39x10 ⁻⁵	7.09 x10 ⁻⁵	1.41 x10 ⁻⁴	3.53 x10 ⁻⁴	1.22 x10 ⁻⁴	6.21 x10 ⁻⁵
	310	2.8x10 ⁻⁴	8.1 x10 ⁻⁵	6.6 x10 ⁻⁵	4.62 x10 ⁻⁴	2.68 x10 ⁻⁴	8.82 x10 ⁻⁴
	324	3.79x10 ⁻⁴	2.11 x10 ⁻⁴	2.94 x10 ⁻⁴	5.33 x10 ⁻⁴	3.04 x10 ⁻⁴	8.91 x10 ⁻⁴
q _{e2} (mg/g)	292	128.25	99.8	88.11	80.939	1.91	148.15
	310	94.67	100.91	121.07	89.138	3.47	137.74
	324	94.11	88.18	91.839	5.79	95.79	146.2
R ²	292	0.998	0.492	0.344	0.948	0.96	20.962
	310	0.967	0.546	0.721	0.990	0.989	0.989
	324	0.972	0.915	0.949	0.993	0.950	0.950

The correlation coefficient R² has an extremely high value (>0.99), and the theoretical q_e values agree with the experimental ones. These results suggest that the pseudo second-order adsorption mechanism is predominant and that the overall rate constant of each ion appears to be controlled by the chemisorptions process.

Intraparticle diffusion model:

For the process design and control of adsorption systems, it is important to understand the dynamic behavior of the system. At the present time Morris and Weber's pore-diffusion is the most widely used models for studying the mechanism of adsorption. On the other hand, Weber and morris' s pore-diffusion model assumes that;

- (i) The external resistance to mass transfer is only significant for a very short period at the beginning of diffusion;
- (ii) The direction of diffusion is radial and the concentration;
- (iii) The pore diffusivity is constant and does not change with time,

The pore diffusion parameter, k_i (mg/gmin^{0.5}) is expressed as;

$$q_t = k_i t^{0.5} + C \tag{17}$$

where q is the amount adsorbed (mg/g) at time t.

The k_{id} values were obtained (Table. 6-a) from the slope of the linear portions of the curve of different initial concentrations of leadPb(II) ions in aqueous solution and shown in (Fig.9). According to this model, the plot of uptake, q_t against the square root of time (t^{0.5}) must give a straight line and intercept equal to zero if intraparticle diffusion involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step.

(Table. 6-a): Thermodynamic parameters for Pb(II)ions uptake at different aqueous systems.

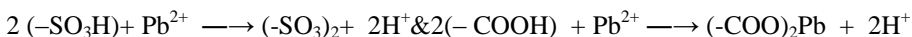
parameter	Initial concentrations of Z(II), (mg/L)								
	282	394	525	663	2892	5849	8413	11206	
E _a (KJ/mol)	42223	78745	43055	28327	39610	2732	29990	4751	
ΔH (KJ/mol)	6829	24466	7126	15737	5166	43589	33493	28445	
ΔS (J/molK)	6.16	54.86	2.09	28.05	5.24	116.22	82.61	64.01	
-ΔG (kJ/mol)									
Temp.,K	292	8521	8278	6357	7331	6627	8763	8958	9371
	310	8866	7242	6443	7242	6855	9046	8170	8943
	324	8727	6815	6464	6815	6815	4848	6492	7435
K _d (mg/gmin ^{0.5})									
Temp.,K	292	2.64951	4.20638	8.01778	8.31443	44.85	54.56	72.51	83.69
	310	2.37468	5.08365	7.627	8.25214	39.37	48.30	94.18	95.51
	324	2.49979	5.20346	7.6305	8.48901	39.72	107.51	120.52	123.19

In the present studies, the plots do not pass through the origin, this is indicative of some degree of boundary layer control and these further shows that the intraparticle diffusion is not the only rat-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. The values of intercept give an idea about the boundary layer thickness such as the larger the intercept, the greater the boundary layer effect.

(7) Mechanism of adsorption:

From the adsorption diagram that has been reported the predominant ionic species is Pb(II) at pH <7, whereas Pb(II) is present mainly as Pb(II)ions and Pb(OH)₂, and in lesser quantity as Pb(OH)⁺ at pH between 8 and 9 [29]. Since all the experiments were carried at a maximum pH of 7, the predominant Pb(II)ions species found in solution and adsorbed on the adsorbent surface was Pb(II)ions.

Due to the increased Pb(II) adsorption at high pH values until pH 7 with the release of protons with the ratio of [H⁺] release/[Pb²⁺] adsorbed ~2, it can be concluded that Pb(II) was adsorbed mostly via ion exchange. The cation exchange resin possesses acidic functional groups on surface such as (-SO₃H) that are responsible for the cation exchange property as expressed in the following equations.



At low pH values, excess H⁺ present in solution competes with Pb(II) ions for active sites leading to less Pb(II) removal. However, when the pH was increased the concentration of H⁺ decreases, but the concentration of Pb(II) ions remains the same leading to increased uptake.

(8) Effect of organic acids:

In comparison, It is observed that, the addition of organic acids to aqueous medium modifies the selectivity of cation exchange resin. In order to explore the uptake potentiality of ResinexTMK-8 strong acid cation exchange resin, adsorption behavior of Pb(II) was studied and the values obtained are given in (Table3).

It was found that the increase in dielectric constant of solvents causes decrease in Pb(II) uptake. The sequence of the values of q_e for the exchange systems under study are as follows, pure water (17.91)>formic (16)< acetic (14)< propionic (13.2)< HNO₃(12) < HCl (11) .this sequence of q_e values can be illustrated on the basis of the higher affinity of the cationic exchanger towards Pb(II) ions in the absence of organic acids [30].

The increase in polarity of the solvent increases the interaction between metal ion and solvent due to ion-dipole interaction as a result exchange of metal ion between solvent phase and exchanger phase will be less. Usually less polar organic acids enhance complex formation or other side-interactions as ion-pair formation.

In conclusion, one can say that adsorption process in mixed solvents can be completely described by last equations. A combination of data in aqueous and mixed solvents can be used as has been done here in estimating the contribution of solvent activity terms.

(9) Effect of temperature:

The thermodynamic assumptions of the best fitting isotherm provide insight into the surface properties and the mechanism of adsorption. The experimental results obtained (Fig.10) from a series of contact time studies for metal ion adsorption with an initial concentration of 525.84 mg/L at pH 7.0 in which temperature was varied from 19 to 51°C. The adsorption of metal ions has been found to increase with an increase in temperature from 19 to 51°C.

The increase in adsorption capacity of the adsorbent with temperature indicates an endothermic process (Table 6-a). The increase in adsorption with temperature may be attributing to either change in pore size of the adsorbent causing inter-particle diffusion within the pores or to enhancement in the chemical affinity of the metal cations to the surface of adsorbent leading to some kind of chemical interaction to take during adsorption process which results into increase in adsorption capacity.

At higher temperatures, the possibility of diffusion of solute within the pores of the adsorbent may not ruled out as reported by earlier workers [31], the adsorption of cations on activated carbon. Since diffusion is an endothermic process, greater

adsorption will be observed at higher temperature. Thus the diffusion rate of ions in the external mass transport process increases with temperature.

The above results were further substantiated by the various thermodynamic parameters evaluated for adsorption. The effect of temperature on adsorption is further confirmed by the van't Hoff plots (Fig.10) based on the equations [32,33];

$$K_D = q_e / C_e \text{-----} \quad (18) \quad \Delta G = -RT \ln K_D \text{-----} \quad (19)$$

$$\Delta G = \Delta H - T\Delta S \text{-----} (20) \quad \ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \text{-----} \quad (21)$$

Where T is absolute temperature in Kelvin (K), R is the gas constant (8.314J/mol K) and K_D is the distribution coefficient (ml/g). The thermodynamic parameters namely enthalpy change (ΔH) and the entropy change (ΔS) can be calculated from the slope and intercept of the straight line plotted by $\ln K_D$ versus $1/T$, (Fig10) respectively.

The Gibbs free energy change was determined at 292, 310 and 324 K. The obtained thermodynamic parameters were listed in (Table 6a and b). By adsorption abundant Pb(II) ions onto the surface of the adsorbent, the number of H^+ ions attached to activate sites of the adsorbent decreased.

(Table. 6-b): Thermodynamic parameters for Pb(II) ions uptake at different systems ($C_0=525$ mg/L).

Parameters	Adsorption system					
	Pure water	HCl	HNO ₃	HCOOH	CH ₃ COOH	CH ₃ CH ₂ COOH
$-\Delta G_{292K}$ (kJ/mol)	12.70	9492	8521	7055	8411	6679
ΔH (KJ/mol)	8.311	8765	13836	32008	34087	2078
ΔS (J/molK)	8.79	31.19	17.77	81.87	84.47	14.97
E_a (KJ/mol)	23.12	26.66	40.14	65.77	67.99	52.86

Therefore the positive value of (ΔS) suggested some structure changes in the adsorbent and adsorbate. In fact, the positive value of enthalpy (ΔH) further confirmed the endothermic nature of the processes, so increasing temperature supplied with a more favorable adsorption of Pb(II) ions onto the adsorbent.

The positive Gibbs free energy value for leadPb(II) adsorption process on the adsorbent at 292 K indicates the presence of an energy barrier in this process [34], while, the increase of temperature results in the decreasing values of these thermodynamic parameters indicating the feasibility of the process.

(10) Activation energy:

The activation energy E_a was calculated by the linearized Arrhenius equation [35]

$\ln(k) = \ln(A) - (E_a/RT)$ ----- (22) Where (E_a) is the activation energy of adsorption (kJ/mol), k is the rate constant which control the process, (A) is Arrhenius constant, (R) is the ideal gas constant (8.314J/mol K), and (T) is the absolute temperature (K).

From the pseudo-second-order kinetic studies, k_2 is the rate constant which control the process. In this study, activation energy value of different systems under study (kJ/mol) was obtained from the plot of $\ln k_2$ versus $1/T$ (Figs.11). In physical adsorption, the activation energy usually more than 8.0 kJ/mol, since the forces involved in chemical adsorption is high.

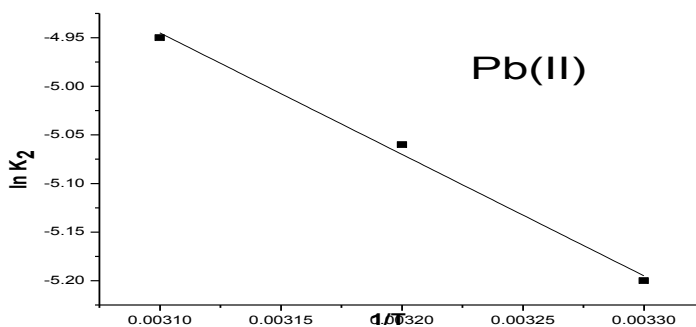


Fig.11) Arrhenius plots for the adsorption of Pb(II) from aqueous solutions and at different temperatures

Chemical adsorption involves forces much stronger than in physical adsorption and the activation energy is between 8.4 and 83.7 kJ/mol [36]. Li et al. [32] noted that chemical adsorption includes activated and nonactivated forms. Activated chemical adsorption means that the rate varies with temperature according to finite activation energy (between 8.4 and 83.7 kJ/mol) in the Arrhenius equation, but the activation energy for nonactivation chemical adsorption is near zero.

The results show that the process is one of activated chemical adsorption and the positive value of the activation energy suggested that the rise in solution temperature favors Pb(II) adsorption onto the cation exchange resin.

The values of the activation energy have been calculated using Eq.22. The E_a values in pure aqueous solution (Table 6a) are usually low as compared with those values obtained for the exchange of lead Pb(II) ions in presence of organic acids

(Table 6b). This may be due to the low swelling of the resin particles in presence of organic acids.

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