

## ADSORPTION OF $Pb^{2+}$ IONS FROM AQUEOUS SOLUTIONS ONTO BAEI TREE LEAF POWDER: ISOTHERMS, KINETICS AND THERMODYNAMICS STUDY

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### Abstract

In this study, bael tree (BT) leaf powder was used as an adsorbent for removal of  $Pb^{2+}$  ions from aqueous solutions through batch equilibrium technique. The influence of pH, equilibrium time, temperature, adsorbent dosage and initial concentration of metal ions on adsorbed amount of metals ions were investigated. Studies showed that the pH of aqueous solutions affected  $Pb^{2+}$  ions removal as a result of removal efficiency increased with increasing solution pH. The experimental isotherm data were analyzed using the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich equations. The monolayer adsorption capacity is 4.065 mg/g with the correlation coefficient of 0.993. The experiments showed that highest removal rate was 84.93% at solution pH 5, contact time 60 min and initial concentration of 50 mg/L. Thermodynamic parameters such as Gibbs free energy, enthalpy, and entropy have also been evaluated and it has been found that the sorption process was feasible, spontaneous and exothermic in nature. Three simplified kinetic models including a pseudo-first-order equation, pseudo-second-order equation and intraparticle diffusion equation were selected to follow the adsorption process. Kinetic parameters, rate constants, equilibrium sorption capacities and related correlation coefficients, for each kinetic model were calculated and discussed. It was shown that the adsorption of  $Pb^{2+}$  ions could be described by the pseudo-second order equation, suggesting that the adsorption process is presumable a chemisorption.

Keywords: Lead ( $Pb^{2+}$ ), Bael Tree, Isotherms, Kinetics, Thermodynamics.

<b>Nomenclatures</b>	
$A$	Temkin constant, L/g
$B$	Temkin constant
$C_{Ae}$	Solid-phase concentration at equilibrium, mg/L
$C_e$	Equilibrium concentration of $Pb^{2+}$ solution, mg/L
$C_i$	Initial lead concentration, mg/L
$C_f$	Final lead concentration, mg/L
$E$	Mean free energy, kJ/mg
$h$	Initial adsorption rate, $mg\ g^{-1}\ min^{-1}$
$K_c$	Equilibrium constant, mg/mg
$k$	Rate constant of pseudo-second-order adsorption, $g\ mg^{-1}\ min^{-1}$
$k_{ad}$	Rate constant of the pseudo-first-order adsorption process, $min^{-1}$
$K_L$	Langmuir constant, L/mg
$K_f$	Freundlich constant, $(mg/g)(L/mg)^{(1/n)}$
$K_p$	Intraparticle diffusion rate constant, $mg/gmin^{1/2}$
$n$	Freundlich constant
$q_e$	Amount of lead adsorbed per unit mass of adsorbent at equilibrium, mg/g
$q_m$	Langmuir constant, mg/g
$q_{m,DR}$	Dubinin-Radushkevich monolayer capacity, mg/g
$q_t$	Amount of lead adsorbed per unit mass of adsorbent at time $t$ , mg/g
$R$	Gas constant, 8.314 J/mol/K
$T$	Temperature, K
$t$	Time, min
<i>Greek Symbols</i>	
$\beta$	Constant related to sorption energy, $mg^2/J^2$
$\varepsilon$	Polanyi potential, J/mol
$\Delta G^\circ$	Change in Gibbs free energy, kJ/mol
$\Delta H^\circ$	Change in Enthalpy, kJ/mol
$\Delta S^\circ$	Change in Entropy, kJ/mol/K

## 1. Introduction

Lead is one of the potentially toxic heavy metals when adsorbed into the body [1]. For the last few decades the pollution of water resources due to indiscriminate disposal of lead metals has been creating worldwide threat. Lead is non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain and can be readily absorbed into the human body [2]. The presence of lead in drinking water even at low concentration level may cause diseases such as anemia, encephalopathy, hepatitis and nephritic syndrome [3]. Lead is released into the environment in number of ways, including lead acid batteries, pulp and paper, petrochemicals, refineries, printing, pigments, photographic materials, explosive manufacturing, ceramic, glass, paint, oil, metal, phosphate fertilizer, electronic goods, wood production and also combustion of

fossil fuel, forest fires, mining activity, automobile emissions, sewage wastewater and sea spray [4-6].

The presence of high levels of lead in the environment may cause long-term health risks to humans and ecosystems. It is therefore mandatory that their levels in drinking water, waste water and water used for agricultural and recreational purposes must be reduced to within the allowable concentrations recommended by national and international health authorities such as the World Health Organization. Lead removal from the wastewater prior to discharge into environment is, therefore, necessary. Current Environmental Protection Act (EPA) drinking water standard for lead are 0.05 mg/L, but a level of 0.02 mg/L has been proposed and is under review [7]. According to the Indian Standard Institution, the tolerance limit for discharge of lead into drinking water is 0.05 mg/L and in land surface waters is 0.1 mg/L [8]. Increasingly stringent legislation on the purity of drinking water has created a growing interest in the development of the conventional treatment processes. Various chemical and physico-chemical methods for the treatment of wastewaters containing lead wastes are known, such as chemical precipitation, electrochemical reduction, ion exchange, biosorption and adsorption [9-13]. The choice of treatment depends on effluent characteristics such as concentration of lead, pH, temperature, flow volume, biological oxygen demand, economics involved and social factor like standard set by the government agencies. Many methods of wastewater treatment were examined and adsorption emerged as one of the most promising technique [14] as it is generally preferred for the removal of lead due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness.

The use of activated carbon (AC) is still very popular and different grades are available, but are quite expensive and the regeneration of the carbon is not always possible. Activated carbon has been chosen as an adsorptive media for the removal of lead, by many researchers [15-18]. But the process has not been used extensively due its high cost. For that reason, the uses of low cost materials as sorbent for metal removal from the wastewater have been highlighted. More recently, great effort has been contributed to develop new adsorbents and improve existing adsorbents like granular activated carbon, other adsorbents such as iron oxide coated sand [19], porous cellulose carrier modified with polyethyleneimine [20], iron coat granular activated carbon [21], modified chitosan [22] and so on. One of the exploitation is the use of natural wastes. Materials investigated are cotton [23], walnut waste [24], peanut skin [25], sugar cane waste and onion skin [26], coffee grounds [27], apple waste [28], wool fibers [29], bark and other cellulosic material [30-34], cottonseed hulls, rice straw, soybean hulls [35] and linseed flax straw [36]. Because of the low cost and high availability of these materials, it is not essential to have complicated regeneration process. This low cost adsorption method has been attracting many scientists and engineers.

The main objective of this research is to develop inexpensive and effective metal ion adsorbents from plentiful sources of natural wastes, such as tree leaves, to replace the existing commercial materials. In this paper, BT leaf powder as a new low-cost adsorbent were introduced and it was examined for their sorption properties towards  $Pb^{2+}$  ions removal. The influence of experimental parameter such as pH, contact time, temperature, adsorbent dosage and initial  $Pb^{2+}$

concentrations were studied at 30°C. The adsorption process is studied from isotherm, kinetic and thermodynamic standpoints.

## **2. Experimental**

### **2.1. Adsorbent**

The bael tree leaves were collected from Vaalmel Nandantha Amman Koil-Temple, Ilayangudi, Sivagangai District, Tamilnadu, India. They were gathered from twigs into clean plastic bags. Washed with triple distilled water and laid flat on clean table to dry. Dry leaves were grounded with grinder. After grounded, the leaf particles were sieved and stored into plastic bag by size, and ready to use. 40 mesh size of BT leaf particles were used as adsorbent for these studies.

### **2.2. Adsorbate**

Stock solution of lead (100 mg/L) was prepared by dissolving  $\text{Pb}(\text{NO}_3)_2$  salts (procured from Merck, India) in double distilled water. The concentration range of lead prepared from stock solution varied between 10 to 100 mg/L. All the chemicals used were of analytical reagent grade.

### **2.3. Analysis**

The concentrations of lead in the solutions before and after equilibrium were determined by Perkin-Elmer 3100 Atomic absorption spectrometer. The pH of solution was measured with a Hanna pH meter using a combined glass electrode. The shaking was carried out in a water bath shaker.

### **2.4. Adsorption experiment**

Adsorption experiments were conducted by varying pH, contact time, adsorbent dose, temperature and lead concentration. The experiments were carried out in 250 mL Erlenmeyer flasks and the total volume of the reaction mixture was kept at 100 mL. The pH of solution was maintained at a desired value by adding 0.1 M NaOH or HCl. The flasks were shaken for the required time period in a water bath shaker. The kinetics study was carried out by agitating 250 mL flasks containing 2 g of BT leaf powder and 100 mL lead solutions in water bath shaker. The mixture was agitated at 120 rpm at 30°C. The contact time was varied from 0 to 60 minutes. At predetermined time, the flasks were withdrawn from the shaker and the reaction mixtures were filtered through Whatman filter paper No. 40. For thermodynamic study, the experiment was performed using 2 g BT leaf powder added to 100 mL of lead solution in 250 mL flasks. The flasks were shaken at 120 rpm for 60 min at pH 5. The initial lead concentration used in this study was 50 and 100 mg/L. The isotherm study was performed using various concentrations of lead solutions. A 2 g BT leaf powder with 100 mL lead solutions of various initial concentrations was shaken at 120 rpm for 60 min at 30°C. The initial pH of the solution was adjusted to 5. All the experiments were performed in duplicates. The filtrate samples were analyzed by Atomic absorption spectrometer. The percentage

removal of lead from the aqueous solution was calculated according to the following equation:

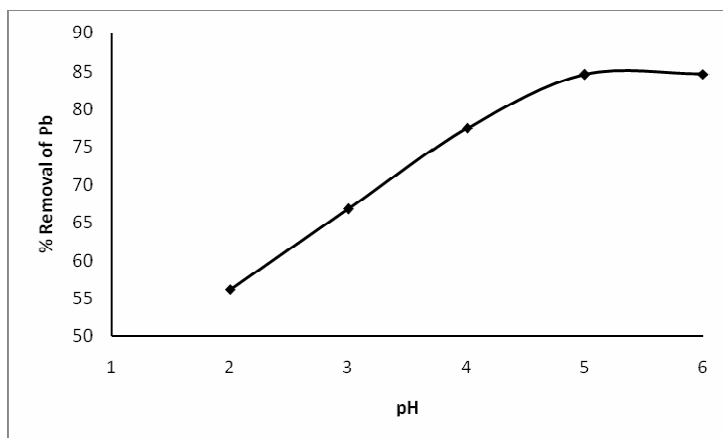
$$\% \text{ Removal} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where  $C_i$  and  $C_f$  are the initial and final lead concentration (mg/L), respectively.

### 3. Results and Discussion

#### 3.1. Effect of pH

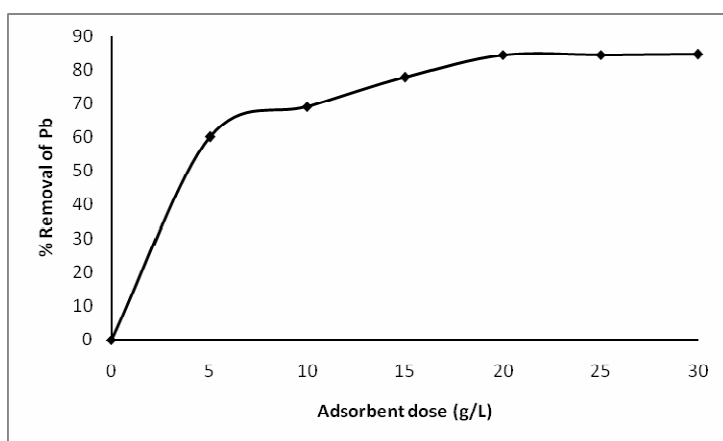
The adsorption of  $Pb^{2+}$  ions was found to be strongly dependent on the pH of the solution. Figure 1 demonstrates that the optimum pH for the adsorption  $Pb^{2+}$  ions was about 5 which were rather acidic. At low pH (below 3), there was excessive protonation of the active sites at BT leaf powder surface and this often refuses the formation of links between  $Pb^{2+}$  ions and the active site. At moderate pH values (3-6), linked  $H^+$  is released from the active sites and adsorbed amount of metal ions is generally found to increase. At higher pH values (above 6), the precipitation is dominant or both ion exchange and aqueous metal hydroxide formation may become significant mechanisms in the metal removal process. This condition is often not desirable as the metal precipitation could lead to a misunderstanding for the adsorption capacity. And in practice, metal precipitation is generally not a stabilized form of heavy metal as the precipitation can some time be very small in size, and upon the neutralization of the effluent from the wastewater treatment plant, the solubility of the metals increases resulting in a re-contamination of the waste outlet stream.



**Fig. 1. Effect of pH on Pb Removal onto BT Leaf Powder (Pb Concentration=50 mg/L, Adsorbent Dose=2 g/100 mL and Equilibrium Time=1 h).**

### 3.2. Effect of adsorbent dose

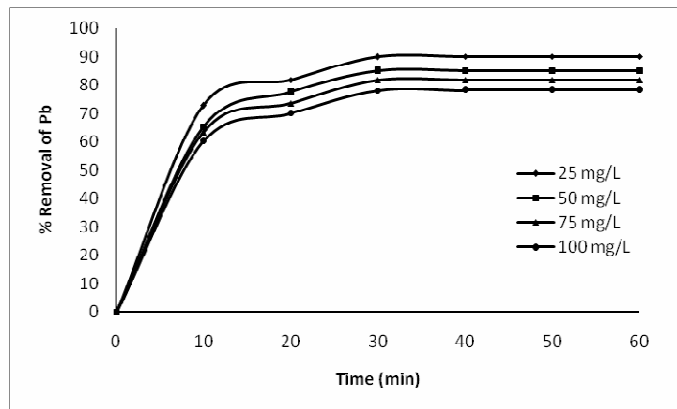
The effect of the adsorbent dose was studied at room temperature (30°C) by varying the adsorbent amounts from 5 to 30 g/L. For all these runs, initial concentration of  $Pb^{2+}$  ions was fixed as 50 mg/L. Figure 2 shows the adsorption of  $Pb^{2+}$  increases as the adsorbent dosage increases from 5 to 30 g/L due to the limited availability of the number of adsorbing species for a relatively larger number of surface sites on the adsorbent at higher dosage of adsorbent. It is plausible that with higher dosage of adsorbent there would be greater availability of exchangeable sites from metals ions [37]. The significant increase in uptake was observed when the dose was increased from 5 to 20 g/L. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles [38]. The maximum removal of  $Pb^{2+}$  was obtained in the adsorbent dose of 20 g/L. On considering this fact for the subsequent studies, the amount of adsorbent was taken as 20 g/L.



**Fig. 2. Effect of Adsorbent Dose on Pb Removal onto BT Leaf Powder (Pb Concentration=50 mg/L, Volume of Sample=100 mL, pH=5 and Equilibrium Time=1 h).**

### 3.3. Effect of contact time

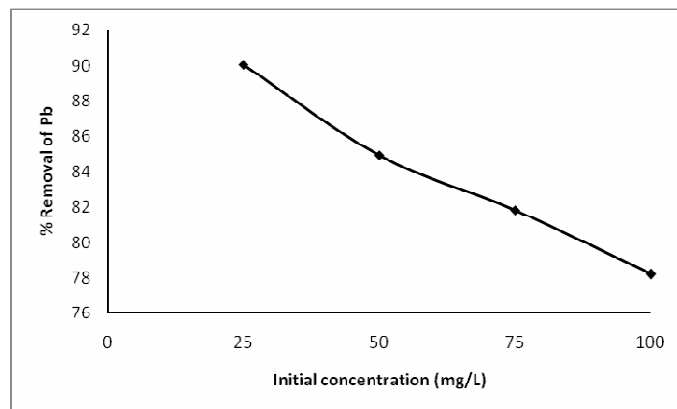
Adsorption of  $Pb^{2+}$  was measured at given contact times for four different initial  $Pb^{2+}$  concentrations of 25, 50, 75 and 100 mg/L. From Fig. 3 the plot reveals that the rate of percent lead removal is higher at the beginning. This is probably due to larger surface area of the leaves being available at beginning for the adsorption of  $Pb^{2+}$  ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. Most of the maximum percent lead removal was attained after about 60 min of shaking time at different initial concentrations. The increasing contact time increased the  $Pb^{2+}$  adsorption and it remains constant after equilibrium reached in 30 min for different initial concentrations.



**Fig. 3. Effect of Contact Time on Pb Removal onto BT Leaf Powder (Pb Concentration=25-100 mg/L, Adsorbent Dose=2 g/100 mL, pH=5 and Equilibrium Time=1 h).**

### 3.4. Effect of initial concentration

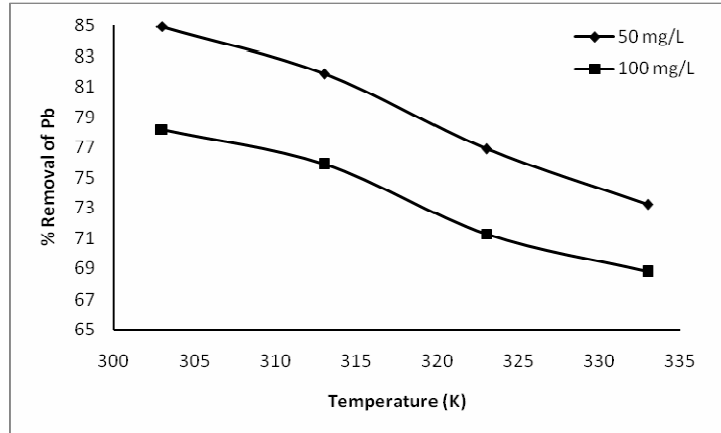
Lead adsorption is significantly influenced by the initial concentration of  $Pb^{2+}$  ions in aqueous solutions. In the present study, the initial  $Pb^{2+}$  concentration is varied from 25 to 100 mg/L while maintaining the adsorbent dosage at 20 g/L. Figure 4 shows the effect of initial concentration on percentage removal of  $Pb^{2+}$  ions. The percentage removal decreases from 90.07% (for 25 mg/L) to 78.21% (for 100 mg/L) at the same contact time and adsorption temperature. The percentage removal of  $Pb^{2+}$  ions decreases with an increase in initial  $Pb^{2+}$  ions concentration. It may be due to an increase in the number of  $Pb^{2+}$  ions for the fixed amount of adsorbent.



**Fig. 4. Effect of Initial Concentration on Pb Removal onto BT Leaf Powder (Pb Concentration=25-100 mg/L, Adsorbent Dose=2 g/100 mL, pH=5 and Equilibrium Time=1 h).**

### 3.5. Effect of temperature

The adsorption of lead on BT leaf powder was investigated as a function of temperature and maximum removal of lead was obtained at 30°C. Experiments were performed at different temperatures of 30, 40, 50 and 60°C for the initial lead concentrations of 50 and 100 mg/L at constant adsorbent dose of 20 g/L and pH of 5. The adsorption decreased from 84.91 to 73.21% and 78.21 to 68.78% for the initial lead concentrations of 50 and 100 mg/L respectively with the rise in temperature from 30 to 60°C (Fig. 5). This is mainly due to the decreased surface activity suggesting that adsorption between lead and BT leaf powder was an exothermic process.



**Fig. 5. Effect Temperature on Pb Removal onto BT Leaf Powder (Pb Concentration=50 and 100 mg/L, Adsorbent Dose=2 g/100 mL, pH=5 and Equilibrium Time=1 h).**

### 3.6. Thermodynamic study

Thermodynamic parameters such as Gibbs free energy  $\Delta G^\circ$ , enthalpy,  $\Delta H^\circ$  and entropy, and  $\Delta S^\circ$ , change of adsorption can be evaluated from the following equations

$$K_c = \frac{C_{Ae}}{C_e} \quad (2)$$

$$\Delta G^\circ = -RT \ln K_c \quad (3)$$

$$\log K_c = \frac{\Delta S^\circ}{2.303 R} - \frac{\Delta H^\circ}{2.303 RT} \quad (4)$$

where  $K_c$  is the equilibrium constant,  $C_e$  is the equilibrium concentration in solution (mg/L) and  $C_{Ae}$  is the solid-phase concentration at equilibrium (mg/L).  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol/K), respectively,  $R$  is the gas constant (8.314 J/mol/K)



and  $T$  is the temperature (K). The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are determined from the slope and the intercept of the plots of plots of  $\log K_c$  versus  $1/T$  (Fig. 6.). The  $\Delta G^\circ$  values were calculated using Eq. (3). The plots were used to compute the values of thermodynamic parameters (Table 1). The negative  $\Delta G^\circ$  value indicates the feasibility and spontaneous nature of the adsorption process; negative  $\Delta H^\circ$  value suggests the exothermic nature of adsorption and the  $\Delta S^\circ$  can be used to describe the randomness at the BT leaf powder-solution interface during the sorption.

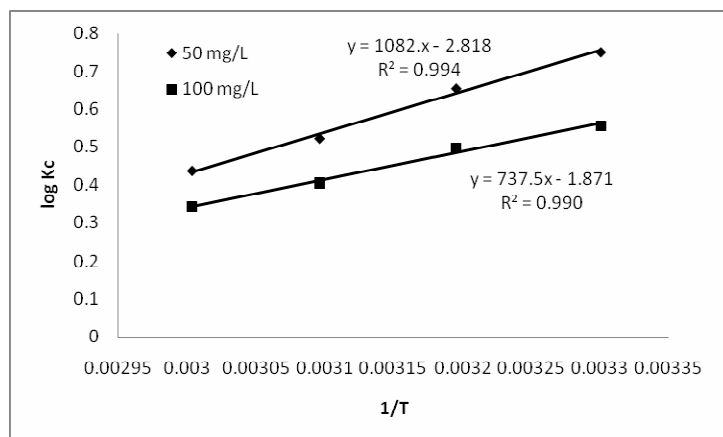


Fig. 6. Thermodynamic Study.

Table 1. Thermodynamic Parameters for the Adsorption of  $Pb^{2+}$  Ions onto Bael Tree Leaf Powder.

Initial $Pb^{2+}$ Concn. (mg/L)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol/K)	$\Delta G^\circ$ (kJ/mol)			
			30°C	40°C	50°C	60°C
50	-20.717	-53.957	-4.352	-3.919	-3.228	-2.783
100	-14.121	-35.824	-3.219	-2.982	-2.442	-2.187

It has been reported that  $\Delta G^\circ$  up to -20 kJ/mol are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption), while  $\Delta G^\circ$  values more negative than -40 kJ/mol involve charge sharing or transfer from the biomass surface to the metal ion to form a coordinate bond (chemical adsorption) [39]. The  $\Delta G^\circ$  values obtained in this study for the  $Pb^{2+}$  ions are <-10 kJ/mol, which indicates that physical adsorption was the predominant mechanism in the sorption process [40].

### 3.7. Adsorption isotherms

Adsorption isotherms, which are the presentation of the amount of solute adsorbed per unit of adsorbent, as a function of equilibrium concentration in bulk

solution at constant temperature, were studied. In order to optimize the design of a sorption system to remove lead from aqueous solutions, it is important to establish the most appropriate correlation for the equilibrium curve. Four isotherm equations have been tested in the present study, namely, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich.

### 3.7.1. The Langmuir isotherm

The Langmuir model [41] is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The Langmuir isotherm is given by:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where  $C_e$  is the equilibrium concentration in solution (mg/L),  $q_m$  and  $K_L$  are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.

### 3.7.2. The Freundlich isotherm

The Freundlich isotherm model [42] is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of lead adsorbed per unit mass of adsorbent,  $q_e$ , and the concentration of the lead at equilibrium,  $C_e$ .

$$q_e = K_f C_e^{1/n} \quad (6)$$

where  $K_f$  and  $n$  are the Freundlich constants, the characteristics of the system.  $K_f$  and  $n$  are the indicator of the adsorption capacity and adsorption intensity, respectively.

### 3.7.3. The Temkin isotherm

The Temkin isotherm [43] has been used in the following form:

$$q_e = B \ln(A C_e) \quad (7)$$

where  $A$  and  $B$  are Temkin isotherm constants.

Temkin isotherm contains a factor that explicitly takes into the account adsorbing species-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.

**3.7.4. Dubinin-Radushkevich isotherm**

The Dubinin-Radushkevich [44] has the following form

$$q_e = q_{m,DR} e^{-\beta \epsilon^2} \tag{8}$$

where  $q_{m,DR}$  is the Dubinin-Radushkevich monolayer capacity (mg/g),  $\beta$  is a constant related to sorption energy, and  $\epsilon$  is the Polanyi potential which is related to the equilibrium concentration as follows

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \tag{9}$$

where  $R$  is the gas constant (8.314 J/mol K) and  $T$  is the absolute temperature.

The constant  $\beta$  gives the mean free energy,  $E$ , of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship

$$E = \frac{1}{\sqrt{2\beta}} \tag{10}$$

The experimental data on the effect of an initial concentration of lead on the BT leaf powder of the test medium were fitted to the isotherm models and graphical representations of these models are presented in Fig. 7. All of the constants are presented in Table 2.

**Table 2. Isotherm Models Constants and Correlation Coefficients for Adsorption of Pb<sup>2+</sup> Ions onto Bael Tree Leaf Powder.**

Langmuir Isotherm			Freundlich Isotherm			
$q_m$ (mg/g)	$K_L$	$R^2$	$K_f$	$n$	$R^2$	
4.065	0.183	0.993	0.741	1.805	0.948	
Temkin			Dubinin-Radushkevich			
$A$ (L/g)	$B$	$R^2$	$q_{m,DR}$ (mg/g)	$\beta$ (mg <sup>2</sup> /J <sup>2</sup> )	$E$ (kJ/mg)	$R^2$
2.344	0.328	0.988	2.068	$7.5 \times 10^{-8}$	2.582	0.902

Since the value of  $R^2$  nearer to 1 indicates that the respective equation better fits the experimental data. The representations of the experimental data by all models equation result in non-linear curve with  $R^2$  values of a least 0.902 as tabulated in Table 2. Langmuir isotherm was concluded to be preferred model for the adsorption process. The observations confirm the capacity of BT leaf powder to adsorb lead fit: the Langmuir model fits well with  $R^2$  value of 0.993.

### 3.8. Kinetic study

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the data. Any kinetic or mass transfer representation is likely to be global. From a system design point of view, a lumped analysis of kinetic data is hence sufficient for practical operations.

#### 3.8.1. Pseudo-first-order model

The sorption kinetics may be described by a pseudo-first-order equation [45]. The differential equation is the following

$$\frac{dq}{dt} = k_{ad} (q_e - q) \quad (11)$$

After integration by applying the initial conditions  $q = 0$  at  $t = 0$  and  $q = q_t$  at  $t = t$ , Eq. (11) becomes:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_{ad}}{2.303} t \quad (12)$$

Equation (12) can be rearranged to obtain a linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \quad (13)$$

where  $q_t$  and  $q_e$  are the amount of lead adsorbed (mg/g) at time  $t$  and at equilibrium respectively and  $k_{ad}$  is the rate constant of the pseudo-first-order adsorption process ( $\text{min}^{-1}$ ).

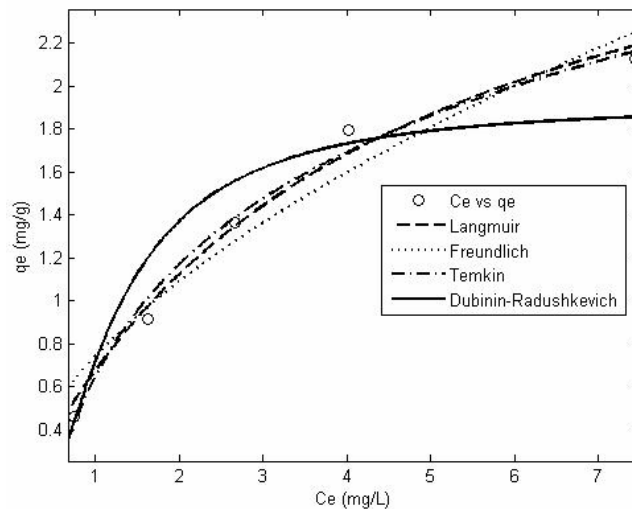


Fig. 7. Adsorption Isotherms.

Figure 8 shows a plot of linearized form of pseudo-first-order at all concentrations studied. The slopes and intercepts of plots of  $\log(q_e - q_t)$  versus  $t$  were used to determine the first-order rate constant  $k_{ad}$  and equilibrium adsorption density  $q_e$ . However, the experimental data deviated considerably from the theoretical data. A comparison of the results with the correlation coefficients is shown in Table 3. The correlation coefficients for the pseudo-first-order kinetic model obtained at all the studied concentrations were low. Also the theoretical  $q_e$  values found from the pseudo-first-order kinetic model did not give reasonable values. This suggests that this adsorption system is not a first-order reaction.

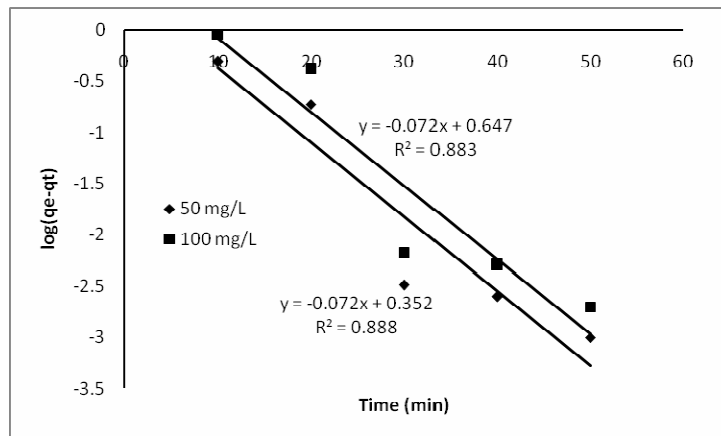


Fig. 8. Pseudo-first-order Reaction for Lead Adsorbed onto BT Leaf Powder at Different Concentrations.

Table 3. Comparison between the Adsorption Rate Constants,  $q_e$ s, Estimated and Correlation Coefficients Associated with Pseudo-first-order and to the Pseudo-second-order Rate Equations and Intraparticle Diffusion.

Initial $Pb^{2+}$ Concn. (mg/L)	Pseudo-first-order rate equation			Intraparticle diffusion	
	$k_{ad}$ ( $min^{-1}$ )	$q_e$ (mg/g)	$R^2$	$k_p$ ( $mg/g \cdot min^{1/2}$ )	$R^2$
50	0.166	2.249	0.888	0.445	0.986
100	0.166	4.436	0.883	0.813	0.990

Initial $Pb^{2+}$ Concn. (mg/L)	Pseudo-second-order rate equations				
	$k$ ( $g \cdot mg^{-1} \cdot min^{-1}$ )	$q_e$ , cal. (mg/g)	$R^2$	$h$ ( $mg \cdot g^{-1} \cdot min^{-1}$ )	$q_e$ , exp. (mg/g)
50	0.142	2.262	0.998	0.728	2.125
100	0.071	4.184	0.998	1.248	3.913

### 3.8.2. Pseudo-second-order model

The adsorption kinetics may also be described by a pseudo-second-order equation [46]. The differential equation is the following:

$$\frac{dq}{dt} = k(q_e - q)^2 \quad (14)$$

Integrating Eq. (14) and applying the boundary conditions, gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \quad (15)$$

Equation (15) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \quad (16)$$

Where  $h = kq_e^2$  ( $\text{mg g}^{-1}\text{min}^{-1}$ ) can be regarded as the initial adsorption rate as  $t \rightarrow 0$  and  $k$  is the rate constant of pseudo-second-order adsorption ( $\text{g mg}^{-1}\text{min}^{-1}$ ). The plot  $t/q_t$  versus  $t$  should give a straight line if pseudo-second-order kinetics is applicable and the  $q_e$ ,  $k$  and  $h$  can be determined from the slope and intercept of the above plot. The straight lines in plot of  $t/q_t$  versus  $t$  (Fig. 9.) shows the good agreement of experimental data with the second-order kinetic model for different initial concentrations. Table 3 lists the computed results obtained from the second-order kinetic model. The correlation coefficients for the second-order kinetic model obtained were greater than 0.998 for all concentrations. The calculated  $q_e$  values also agree very well with the experimental data. These indicate that the adsorption system studied belongs to the pseudo-second-order kinetic model. The similar phenomena are also observed in adsorption of copper onto cedar sawdust and crushed brick [47] and in adsorption of copper and lead on tea waste [48].

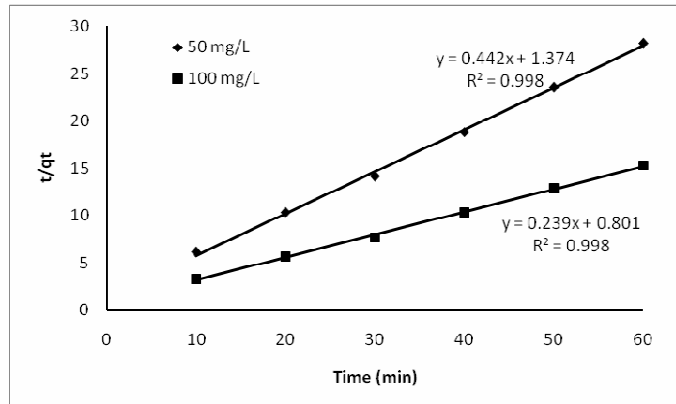


Fig. 9. Pseudo-second-order Reaction for Lead Adsorbed onto BT Leaf Powder at Different Concentrations.

### 3.8.3. Intraparticle diffusion model

Because Eqs. (12) and (15) can not identify the diffusion mechanisms, the intraparticle diffusion model [49] was also tested. The initial rate of the intraparticle diffusion is given by the following equation:

$$q_t = f(t^{1/2}) \quad (17)$$

The rate parameters for intraparticle diffusion ( $k_p$ ) at different initial concentrations are determined using the following equation.

$$q_t = k_p t^{1/2} \quad (18)$$

where  $k_p$  is the intraparticle diffusion rate constant, ( $mg/gmin^{1/2}$ ). Such plots may present a multilinearity [50, 51], indicating that two or more steps take place. The first, sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where intraparticle diffusion is rate-controlled. The third portion is the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution.

Figure 10 shows a plot of the linearized form of the intraparticle diffusion model at all concentrations studied. As shown in Fig. 10, the external surface adsorption (stage 1) is absent. Stage 1 is completed before 5 min, and then the stage of intraparticle diffusion control (stage 2) is attained and continues from 5 min to 30 min. Finally, final equilibrium adsorption (stage 3) starts after 30 min. The lead is slowly transported via intraparticle diffusion into the particles and is finally retained in the micropores. In general, the slope of the line in stage 2 is called as intraparticle diffusion rate constant,  $k_p$ . The rate parameters,  $k_p$ , together with the correlation coefficients are also listed in Table 3.

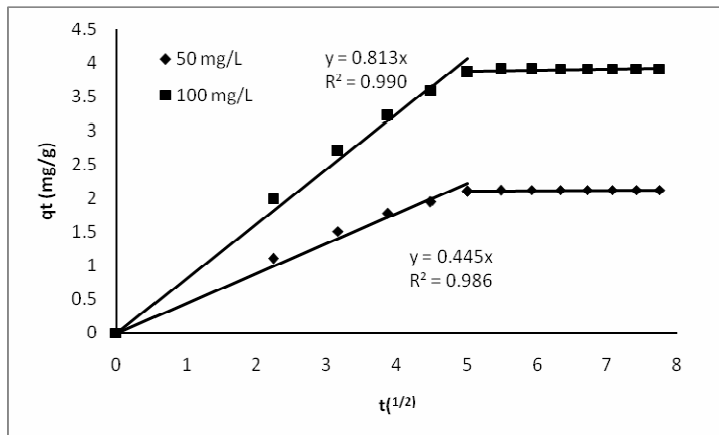


Fig. 10. Intraparticle Diffusion Model for Lead Adsorbed onto BT Leaf Powder at Different Concentrations.

The pseudo second-order kinetic model provides the best correlation for all of the adsorption process, whereas the intraparticle diffusion model fits the experimental data well for an initial period of the adsorption process only. Hence it was concluded that the intraparticle diffusion was found to be rate limiting, followed by the pseudo second-order kinetic model. Similar phenomena are also observed in adsorption of phenols on fly ash [52], in adsorption of lead (II) on cypress leaves [53], and in adsorption of chrome dye (OCRME) on mixed adsorbents-fly ash and coal [54].

#### 4. Conclusions

Equilibrium, kinetic and thermodynamic studies were made for the adsorption of  $Pb^{2+}$  ions from aqueous solution onto BT leaf powder at pH 5. The equilibrium data have been analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Langmuir isotherm was demonstrated to provide the best correlation for the sorption of  $Pb^{2+}$  ions onto BT leaf powder. The suitability of the pseudo first- and second-order equations and intraparticle diffusion kinetic model for the sorption of  $Pb^{2+}$  ions onto BT leaf powder is also discussed. The adsorption of lead can be described by the intraparticle diffusion model up to 60 min. The intraparticle diffusion model indicates that the external surface adsorption (stage 1) is absent because of completing before 5 min, and final equilibrium adsorption (stage 3) is started after 30 min. The  $Pb^{2+}$  is slowly transported via intraparticle diffusion into the particles and is finally retained in micropores. The pseudo second-order kinetic model agrees very well with the dynamical behavior for the adsorption of  $Pb^{2+}$  ions onto BT leaf powder for different initial  $Pb^{2+}$  ions concentrations over the whole range studied. It may be concluded that BT leaf powder may be used as a low-cost, natural and abundant source for the removal of  $Pb^{2+}$  ions from the wastewater.

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