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Applicability of Green Absorbents to Remove Lead (II) from Polluted Water: a Potential Low-cost Adsorbent

FATMA. M. ABOUZEID[1]*, SULTANAH ALSHAMMERY[2]
[1]Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt
[2]Department of Basic Engineering Science, College of Engineering, Imam Abdulrahman bin Faisal university, King Faisal Road, King Faisal City, Dammam, 34212, Saudi Arabia

Abstract: *The present work represent potential bio-sorbent (banana and pomegranate peel) in nano size range, with a view to for adsorption of lead(II) ions from aqueous solution. Dose, adsorbate concentration, pH, time, and temperature factors were investigated. The most favorable stipulations for Pb (II) adsorption are 50 mg /L as initial concentration, 0.2 g as pomegranate and banana peels mass and pH 5.5 and 5.23for banana and Pomegranate peel. Removal data obey the Langmuir model with* q_{max} *of 25.64 mg/g for banana and 41.66 mg/g for Pomegranate peel. The kinetics of removal process was fitted well by a second -order equation. It was observed that that the Pb (II) ion adsorption process on the both bio-sorbents is spontaneous process, endothermic for banana while exothermic for pomegranate peel. A distinct improvement in the adsorbent surface was noted after adsorption process which demonstrated via scanning electron microscope.*

Keywords: *Pb (II), banana peel, kinetic study, scanning electron microscope*

1. Introduction

Toxic heavy metals enter human beings, plant and animal soft tissue through air breathing, food and instruction manual management. Electric motor car radiations are a main resource of aerial pollutants. Water supplies (groundwater, lagoons, rivers and canals) can be contaminated via toxic heavy metals leaking from manufacturing and user trash; acid rain water may aggravate this procedure via distributing toxic heavy metals entrapped in stains.

Toxic heavy metals "may attach to essential cellular elements, for instance, nucleic acids and, enzymes and disturb their performance". Indications and consequences may differ in relation to the metal or metal complex, and the dosage concerned. Generally, prolonged-time exposure to poisonous heavy metals may have carcinogenic, significant, and secondary nervous system structure and cardiovascular influences [1].

Currently, Pb (II) ions pollution in an environments is a very considerable issue of all the world due to its extremely poisonous and non-biodegradable in nature [2-5]. When lead is released into the surrounding, it will be accrued in food chain and subsist in the scenery. Pb (II) ions can be the motive for the strict health threat even in the very low amount. For example, lead is awfully poisonous and may harm the nervous system, kidney, organ, and reproductive system [6, 7]. Furthermore it is poisonous to human being through contact with SH group of proteins, leading to disturbance of the growth and chemical process of several proteins and it also impairs hemoglobin synthesis [8]. So that control the level of Pb(II) ions emission from any sources, World Health Organization (WHO) aim to limit it in allowable concentrations. The latest sequence of the further most infection of Pb(II) ions rank in consumption water from (EPA) is 0.015 mg/L [9].

The adsorption method is considered as the main procedures for toxic metals treatment. Adsorption is an essential progression in the management of polluted solutions by physical and chemical method. Adsorption is mass transfer process in which definite contents of liquid are transferred to the plane of the solid adsorbents. When a solid plane become in contact with liquid, the particles from liquid bulkiness have a affinity to collect or assemble at solid plane [10]. Several adsorbent has been utilized

*email: fatma.abouzeid@yahoo.com

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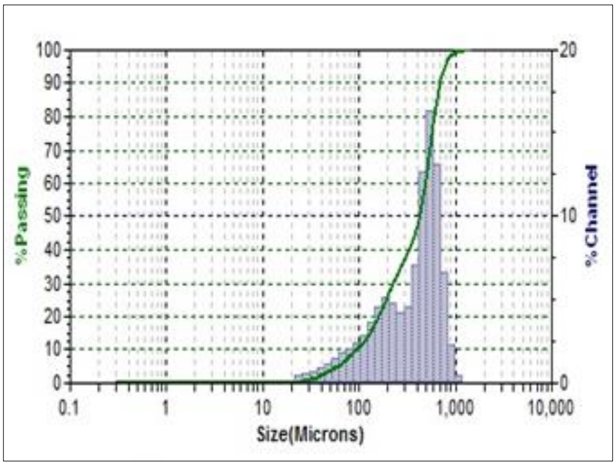
for Pb(II) ions treatment as of aqua solution. These adsorbents were used in unprocessed shape or with customized surface. Thus, there is a great insist to discover comparatively proficient, minimal price and simply accessible adsorbents for the lead adsorption [11-14].

The major purpose of research is utilizing low cost and valuable bio sorbent materials in nano size form (banana and Pomegranate peel) to treat aqueous solutions via removing Pb (II) from it. The research data has been inspected by the kinetic adsorption standards and equilibrium adsorption isotherm types.

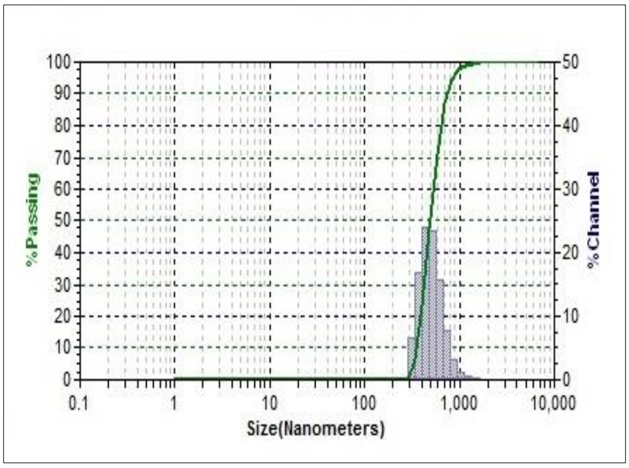
2.Material and method

2.1. Adsorbent

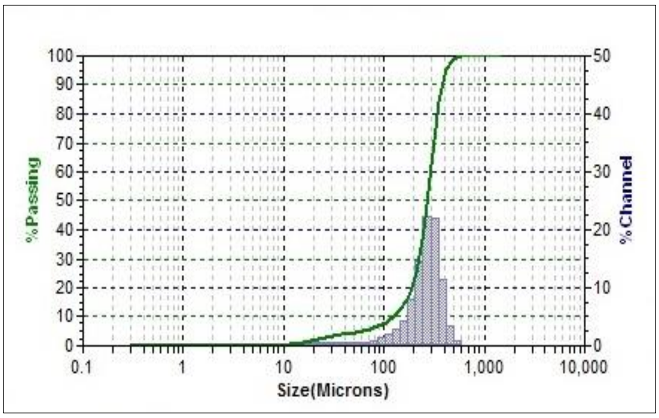
The adsorbent material banana and pomegranate peel was collected as wastes of juices shops. The different peels were rinsed with tap water firstly, double distilled water secondly and finally filtered dried at 80^{o}C for 48 h. Dried peels were ground and sieved (sieve mesh size 200, 150 and 75 µm) (sieve brand), the smallest particle size (less than 75 µm) was grinded using Microtrac, S3500Alright Ball miller device. Ball miller: were prepared the nano size of all samples after ball milling used 25g of sample, 1250 g of Zircona balls (50 balls for each 1g of sample) and high energy system, used HDDM program, the chiller with 13C, the power was 4000 m Amps and the ball mill for 6 h for each samples (Figure 1).



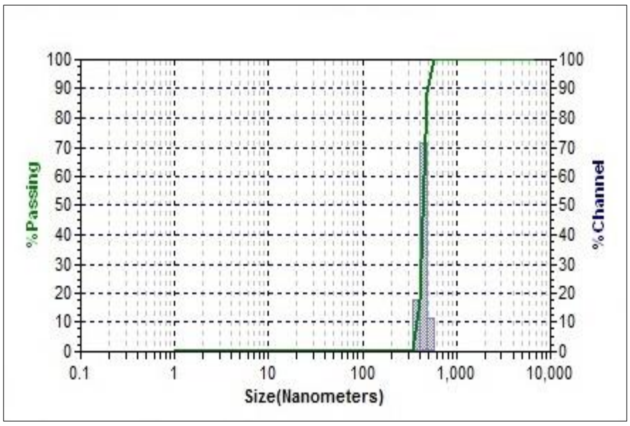
Average size (435.624µm) (peak diameter 525.80, 136.90), banana beel



Average size (544.2 nm) (peak diameter.495), banana beel



Average size (279.15µm) (peak diameter 270.5), Pomegranate beel. Before milling



Average size (448.8µm) (peak diameter 442), Pomegranate beel. After milling

Figure 1. DLS data for adsorbent samples before and after milling

2.2. Characterization

Scanning electron microscope (Inspect S50, FEI, Thermo Fisher scientific). DLS measurements, ball miller provides particle size before and after milling as shown in Figure 1. Fourier-transform infrared spectroscopy (FTIR), Shimadzu, IRAffinity-1S, sample prepared by used Potassium bromide (KBr) disk. Spectra prior to and behind bio-sorption were registered through a declaration of 2 cm^{-1} in the range 400–4000 cm^{-1}.

2.3. Preparation of adsorbate

$Pb(NO_3)_2$(Merck) was dissolved in de-ionized water with resistance > 18 mΩ.cm to prepare (1000 mg/L) solution of Pb(II). Test solutions was arranged via dilution with double distilled water, 0.1M HNO_3 & NaOH solution was used to adjusted *p*H (Metrohm pH meter (MettlerToledd.)). In order to determine Pb(II) ion in solution, atomic absorption spectrophotometer (AAS) with lead hollow cathode lamps and air acetylene flame was used (Shimadzu (AA-7000)). Adjusted water bath flask shaker was used for stirring all the tested solutions.

2.4. Adsorption and experimental procedure.

*p*H parameter were examined via changing the $Pb(NO_3)_2$ solution preliminary *p*H range between 1.2 - 7.2 at 293 K and 250 rpm 60 min for trial. The contact time influence was investigated at optimal *p*H, 0.2 g nano-size peel / 250 mL $Pb(NO_3)_2$ (50 mg/L) at 293 K. Magnetic stirrer was used for agitating (250 rpm) solution. Samples were withdrawn at 1,2,3,5,7,10,20,30,40,50,60 and 100 min. 0.2g to 2g of bio-sorbents were studied as mass influence. 10, 20, 30, 40 and 50mg/L of $Pb(NO_3)_2$ were investigated as adsorbate amount effect and (293, 303, 313, 323K) was also determined as temperature factor

2.5. Data analysis

Pb (II) % removal was calculated along with the subsequent equation:

$$\% \; Removal = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

where C_o(mg/L) is the initial Pb (II) concentration and C_t(mg/L) is the Pb (II) concentration at time t. The adsorption capacity, the amount of metal ions adsorbed per unit mass of adsorbent, was evaluated using the following equations:

a- The adsorption capacity at time *t*, q_t (mg/g):

$$q_t = \frac{(C_o - C_t)V}{m} \qquad (2)$$

b- The adsorption capacity at equilibrium, q_e(mg/g):

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (3)$$

where C_e(mg/L) is the equilibrium concentration of metal ions, *m* (g) is the mass of adsorbent and *V* (L) is the volume of metal solution.

2.6. Point of the zero charge (pHpzc)

The nano size adsorbents pHpzc has been established using certain procedure. 0.1 mol/ L NaCl (50 mL) containing 0.2 g adsorbent have been transmitted in several beakers; solution *p*H range of 2–7 has been regulated via 0.1 M HNO_3 or/and 0.1 M NaOH, then, the solutions were shaken for 5 days at 25°C. the final solution *p*H has been determined. pH_{PZC} value can be estimated from crossing line of the plot Δ*p*H versus pH_0 [14 ,15]

3. Result and discussions

3.1. Time influence

Figure 2 demonstrates the result of Pb(II) adsorption amount onto nano size banana and pomegranate peel for 1–100 min at 50 ppm initial concentration, 293 K, 250 rpm and sorbent dosage of 0.2 g/250 mL. It is apparent which the adsorption uptake rises quickly at the first stage of adsorption process, an extra raise in trial time, there is no achieve on the uptake percent. The adsorption amounts of bio-sorbent reached equilibrium at 60 min, the rate of Pb (II) uptake diminish through time could be down to accumulation of Pb(II) on nano banana and pomegranate peels particles surface. This accumulation might hinder the adsorbate immigration, moreover, as the adsorption active sites covered completely, confrontation to the distribution of lead ions in the adsorbents enlarge [16].

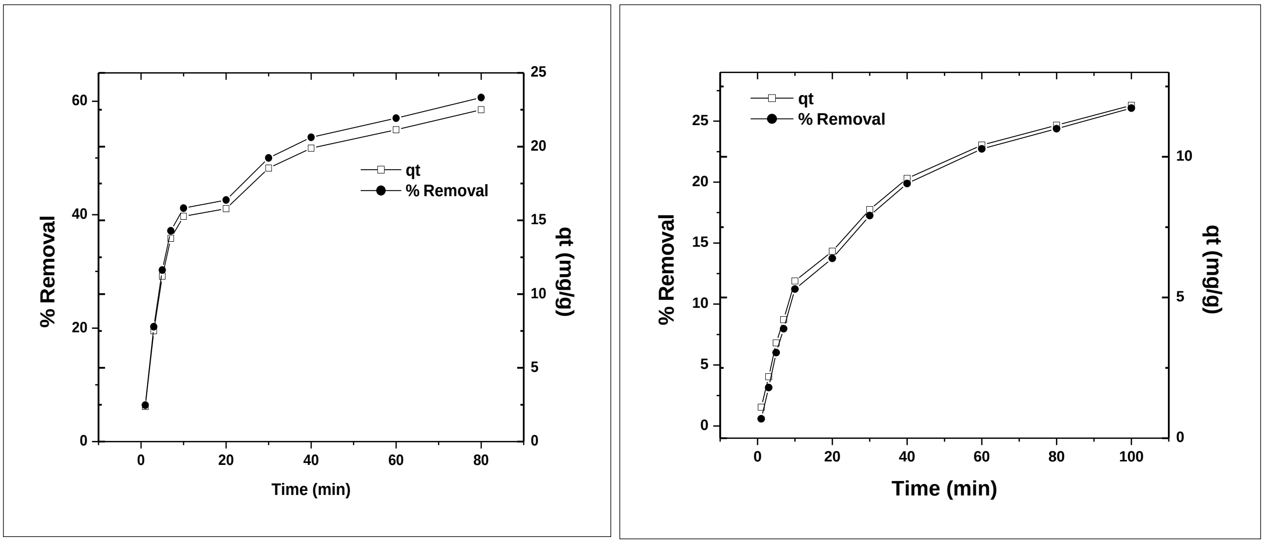


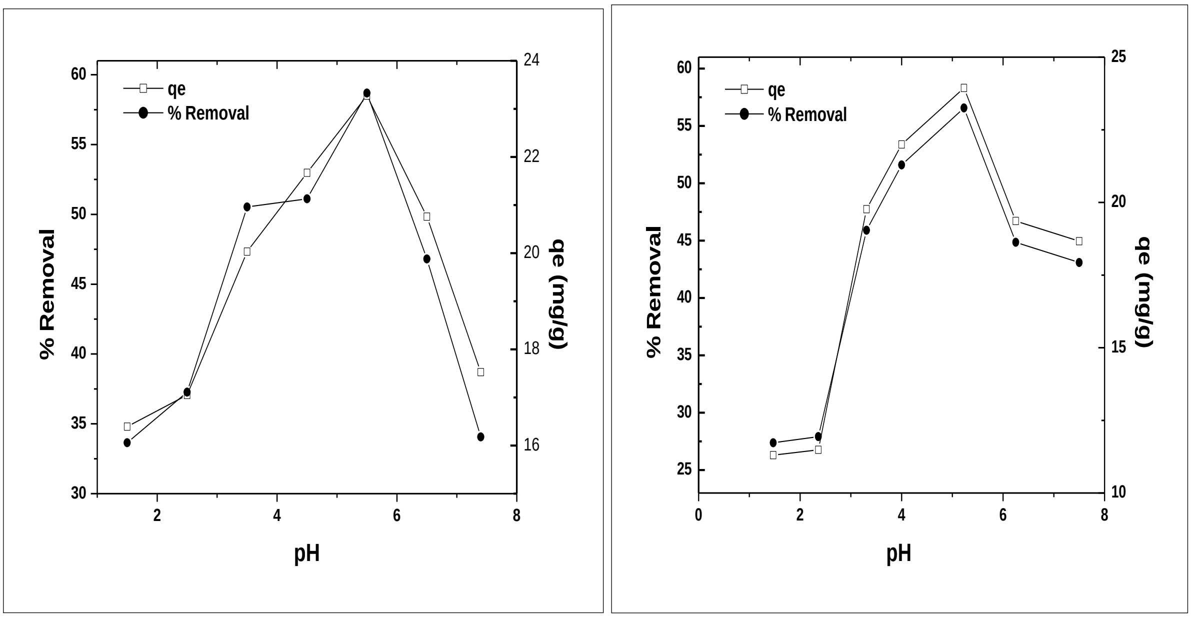
Figure 2. Time effect on the % removal of Pb(II) ions onto a) banana, b) Pomegranate peel (T=293K, 250rpm, C_o=50mg/L and 0.2g of bio-sorbent

3.2. *p*H effect

As shown in Figure 3, *p*H parameter ranging from 1.48 to 7.4 of the lead ions solution was examined. It is apparent that the removal efficiency % and qe increases very quickly from *p*H 1.47 to 5.5 banana peel which record 58.5 as maximum removal percentage while Pomegranate peel record 58.32 as maximum removal percentage at *p*H 5.23.

The small lead ions elimination percentage at low *p*H values, may be clarified via the statistic that the lower solution *p*H range, H^+ is predominant ; consequently, there is a competition between protons & Pb(II) on active surface spots but by raising the solution *p*H , the struggle diminishes, therefore, the deletion of Pb(II) (as dominant species) enlarges [17].

The pHpzc of nano size banana and pomegranate peel is 5.06 and 5.25 which reflect that the nano size peel surface became carry positive charge when *p*H of solution beneath about *p*H 5 so, Pb (II) ions keep away from nano size adsorbent surface which leads to decline of Pb (II) uptake. When *p*H become more higher pHpzc value, the surface of nano size powder can be free from protons



(a) (b)

Figure 3. *p*H effect on removal % and qe of Pb(II) ions on a) banana and b) Pomegranate peel (T= 293K, 250 rpm as stirring rate, $[C]_o$=50mg/L and 0.2 g nano size peel)

3.3. Dose effect

Banana and pomegranate peel mass influence on Pb(II) uptake % of 50 ppm is displayed in Figure 4. As usual, uptake proportion enlarged with raising the nano size banana and pomegranate mass at certain initial Pb(II) concentration. This can be elucidated as, the area and of the adsorption active sites number raise when the banana and pomegranate peel mass enlarge. Additional, the binding of Pb (II)onto functional groups present on the nano size banana and pomegranate surface enlarges. Alternatively, when the bio-sorbent mass enhanced, the adsorption capacity declined. The diminish in uptake capability through raising in the banana and pomegranate peel mass is primarily as result of enhancing the free active uptake sites in the metal removal process [18]. The optimum dosages of nano size banana and pomegranate peel is 2 g and 0.7 g respectively

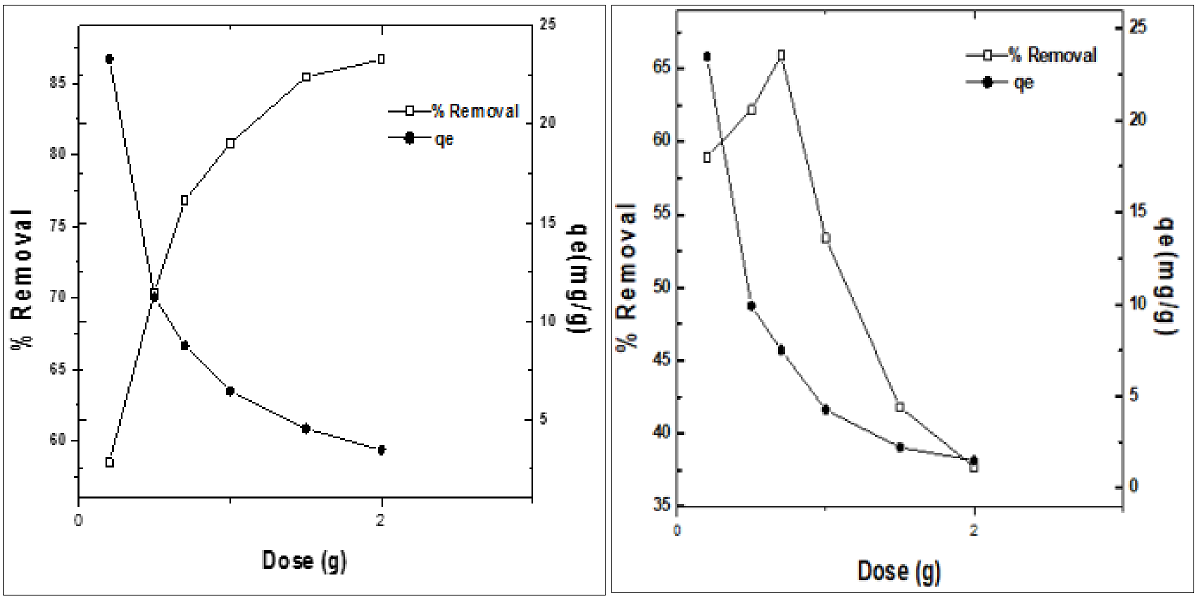


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Figure 4. Influence of biosorbent a) banana and b) Pomegranate peel mass on the elimination % & qe of Pb(II) ions(T=293K, 250rpm, *p*H= maximum value for every adsorbent and C_O=50 mg/L

3.4. Initial concentration of metal ion influence

Pb(II) ions initial concentration influence on adsorption was tested between 10 and 50 mg/L at an initial concentrations for all samples and the removal efficiency increases also.

As demonstrated in Figure 5, Pb(II) ions subtraction on nano size banana and pomegranate peel surface is $[Pb(II)]_o$ ions concentration dependent and is enlarging with raising of Pb(II) ions concentration. It could be clarified as, improvement in the rousing incline power is depend on the original of metal concentration. Within certain sorbent quantity, the raise in metal ions amount requires a superior motivating power to carry metal ions from aqueous phase bulk to adsorbent surface, and consequently, there is a great opportunity for the interaction between the active binding sites and metal ions [19].

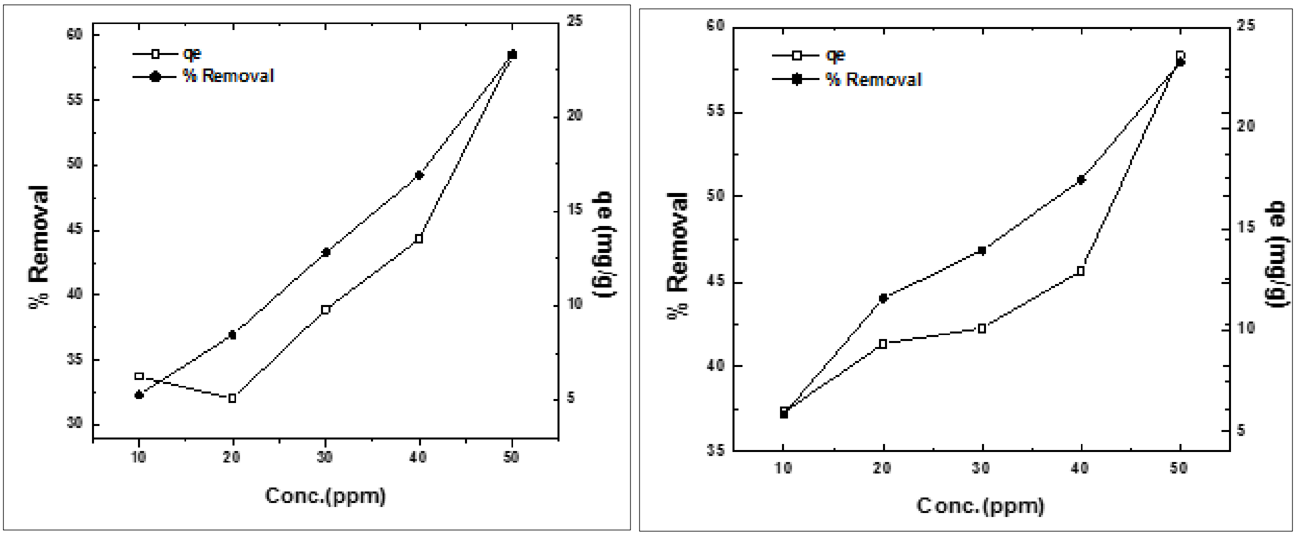

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Figure 5. Initial concentration influence on uptake % & qe of Pb(II) ions in a) banana and b) Pomegranate peel (T=293K, 250rpm, 0.2g of adsorbent and maximum *p*H for each adsorbent)

3.5. Temperature effect

The temperature effect on lead deletion by nano size biomass was inspected and this reliance is explained by Figure 6. It can simply be monitored that qe and removal % enhance with rise of temperature in case of banana peel, reflecting the endothermic behavior for up take process, this characteristic being typical for a chemical interaction between banana peel active sites and lead ions so an elevated temperature could reinforce that chemical interaction. Also an elevated temperature leads to diminish in liquid viscosity and encourages extra particles mobility, consequently the attraction of lead ions on banana peel is superior at elevated temperature. In another word, the up take metal % enlarges with temperature enhancing arise from generation of new active sites due to break down in a little interior bond for banana peel active sites.

While in case of pomegranate peel, it can observed that qe and removal % increase with rise of temperature till reach to 303 K but at 313 and 323 K, there is a diminish in both removal % and qe which reflect that, at high temperature there is desportion process was happened and the capability of pomegranate peel adsorbent to eliminate lead (II) ions affected in negative way [20, 21].

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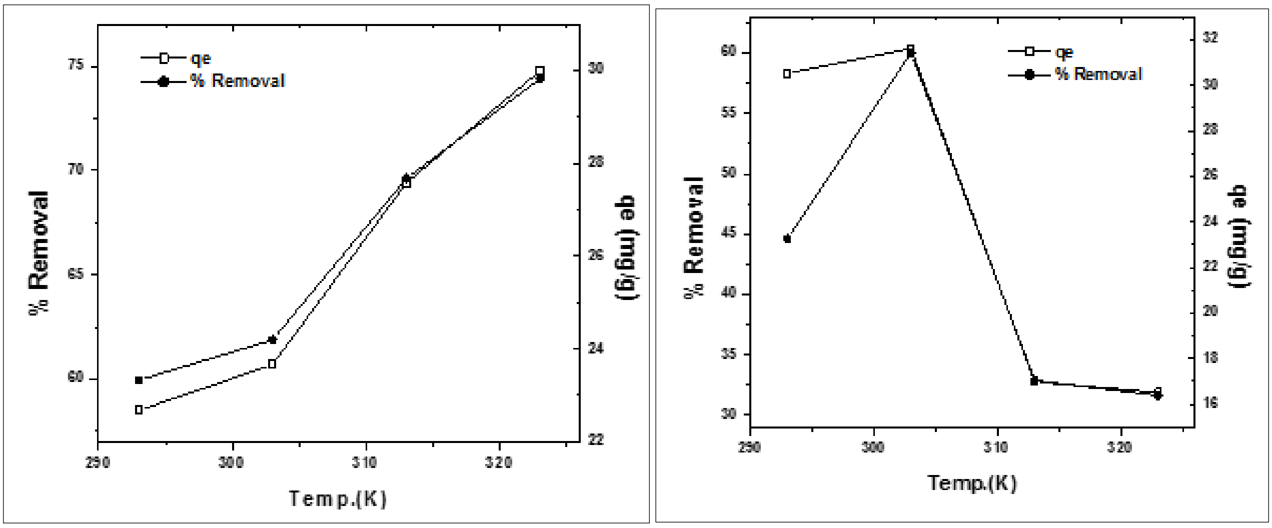

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Figure 6. Temperature effect on uptake % & qe of Pb(II) ions onto a) banana and b) Pomegranate peel (T=293K, 250rpm, 0.2g of adsorbent and maximum *p*H for each adsorbent)

3.6. Activated parameters

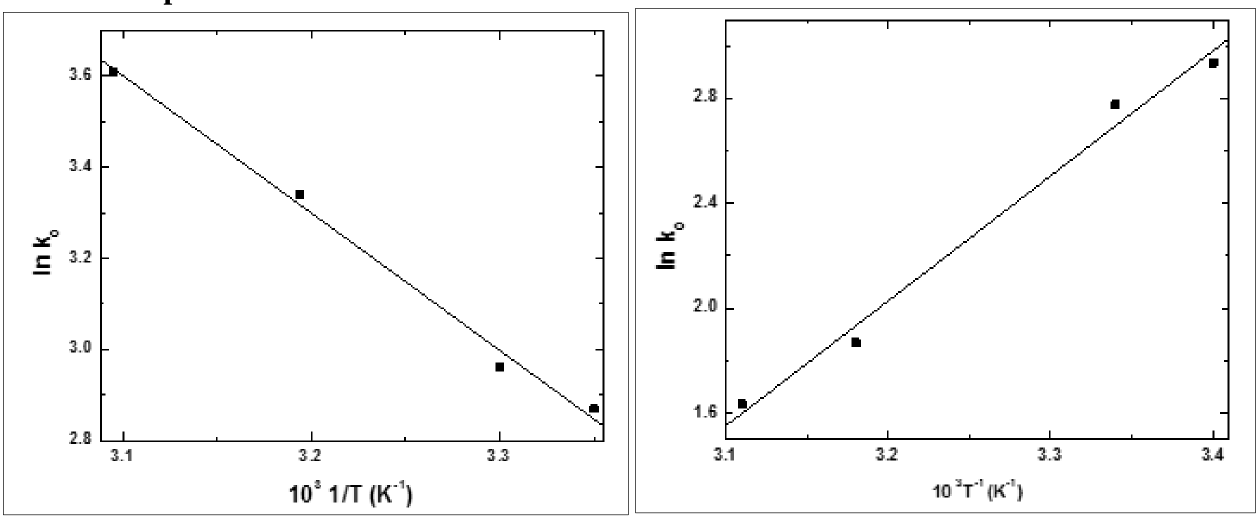

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Figure 7. Temperature effect on the adsorption thermodynamic comportment for Pb(II) ions onto a) banana and b) Pomegranate peel (50 ppm, 250rpm, 0.2g of adsorbent and maximum *p*H for each adsorbent)

Table 1. Thermodynamic constraints for Pb(II) adsorption onto different biosorbent

T (K)	ΔG^o(kJ/mol)	Adsorbent	ΔH^o(kJ/mol)	ΔS^o(J/mol.K)
293	-6.79	**Banana peel**	20.82	94.19
303	-7.72			
313	-8.66			
323	-9.60			
293	-7.43	**Pomegranate peel**	**-37.79**	**-103.59**
303	-6.40			
313	-5.36			
323	-4.33			

The thermodynamic parameters, Gibbs free energy change (ΔG^O), enthalpy (ΔH^O) and entropy (ΔS^O) for lead ion adsorption onto banana and pomegranate peel surface were calculated through the following equations

$$K_o = qe / C_e \quad (4)$$

$$\Delta G^o = \Delta H^o - T\,\Delta S^o \quad (5)$$

where K_O is equilibrium constant *(L/g)*, T: temperature (K) and R: gas constant

Table 1 show that negative values of ΔG^o indicates Pb(II) adsorption onto banana and Pomegranate peel is spontaneous ,also there is great attraction for lead ion binding on peels surface [22].

In case of banana, the spontaneity of Pb(II) adsorption increase by temperature raising which reflect that Pb(II) ions adsorption on banana peel surface is constructive at elevated temperature. The ΔH^o positive value signifies that the uptake procedure is endothermic, also ΔS^o has positive value which indicates arbitrariness at solid-liquid boundary was increased throughout adsorption procedure (Figure 7). In case of pomegranate the reduce in ΔG^o values by means of temperature amplifying reflects that the metal uptake was unconstructive when temperature became higher, the negative value of ΔH^o reflected that metal uptake process was accompanied with heat release. The ΔS^o were −103.59 J/mol K which means that lead ions solution bulk is distributed in disordered random way more than that at peel surface [23].

3.7. Adsorption isotherm

The Langmuir isotherm is typically utilized to examine the solute sorption as of a fluid solution. which has the following formula

$$C_e/q_e = 1/(q_{max}b) + (1/q_{max})C_e \quad (6)$$

The plot of C_e/q_e verses *Ce.* (Figure 8), straight plot is attained and q_{max} **(**saturated monolayer sorption capacity) and b (the energy of adsorption) are estimated through slope and intercept values. The higher R^2 values recommend that the Langmuir isotherm affords an excellent sorption system model. q_{max} and b values are represented in Table 2 [24].

R_L (separation factor) was estimated by the following equation.

$$R_L = 1/(1 + bCe) \quad (7)$$

It was found that values of R_L were less than one, which reflects that lead ions adsorption on nano size banana and pomegranate peel is favorable.

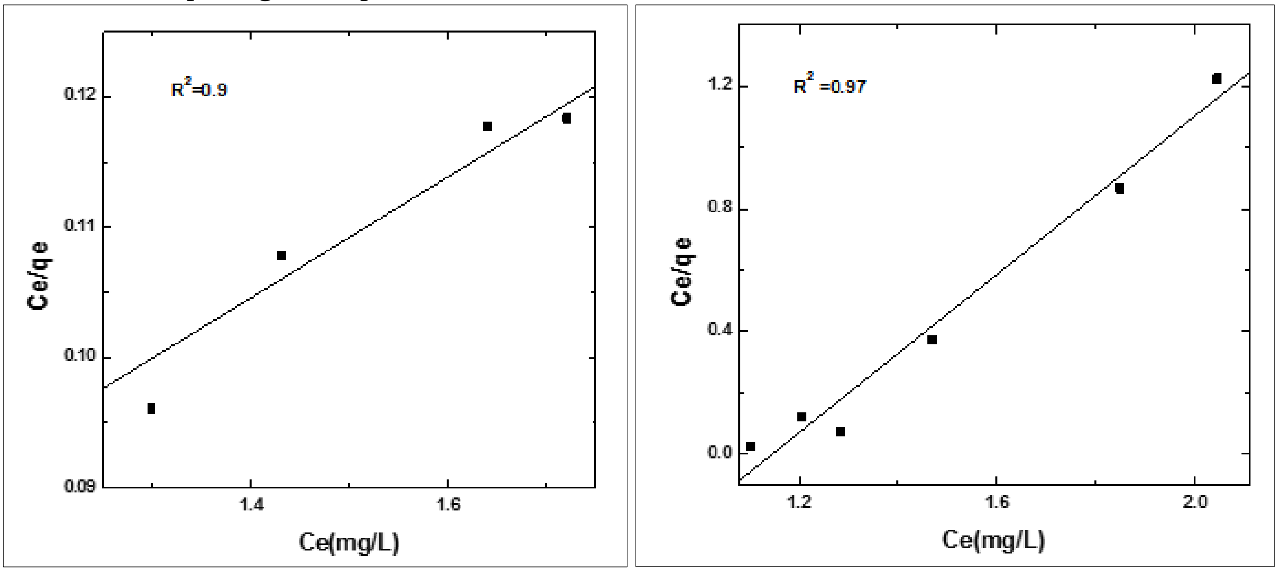

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Figure 8. linearized Langmuir model for Pb(II) ions in a) banana and b) Pomegranate peel (T=293K, 250rpm and maximum *p*H for each adsorbent)

The Freundlich isotherm illustrate dissimilar system. The Freundlich equivalence is conveyed as

$$\log q_e = \log k_f + 1/n \log C_e \quad (8)$$

k_f is the Freundlich constants related to the adsorption capability and n is adsorption intensity, plot of ln qe versus ln Ce (Figure 9) will produce intercept and slope and from them experimental kf and n will be estimated (Table 2), the experimental statistics equipped good to Freundlich. This behavior reflect that Pb (II) ions adsorption on nano size banana and pomegranate peel is monolayer-type [25].

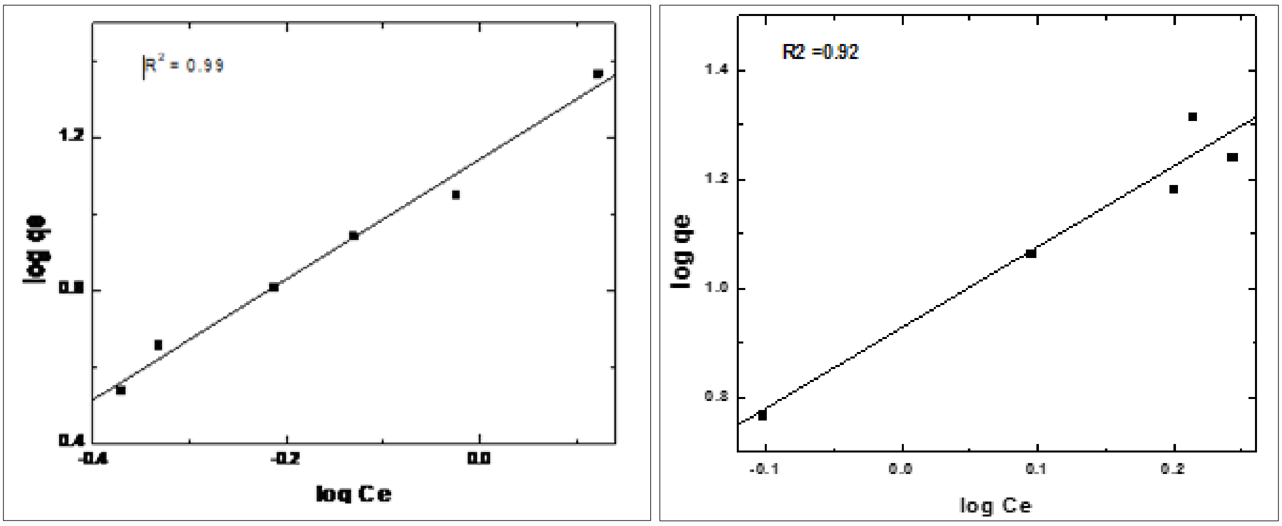

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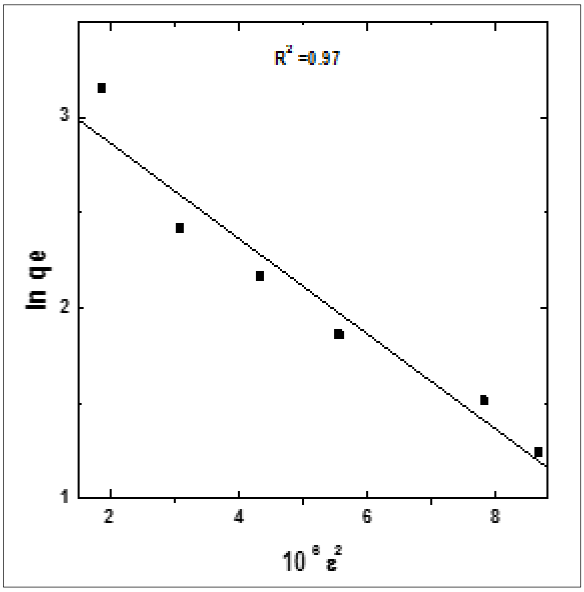
Figure 9. Freundlich adsorption model for Pb(II) ions onto a) banana and b) Pomegranate peel (T=293K, 250rpm and maximum *p*H for each adsorbent)

In order to estimate the adsorption energy per adsorbate unit and a highest adsorption capability of the adsorbent, the Dubinin– Radushkevich (D–R) adsorption isotherm standard must be applied which have the following form:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (9)$$
$$\varepsilon \text{ (Polanyi potential)} = RT\ln(1 + 1/Ce) \quad (10)$$

The adsorption energy, β ($kJmol^{-1}$) is reported to average adsorption energy as ε. Plot of ln qe versus ε^2at 298K were represented as (Figure 10). In our investigation, the mean adsorption energy (E) values were initiate to be 1.09 and 1.41 kJ mol^{-1} (Table 2), that is lesser than the adsorption reaction range, 8–16 kJ mol^{-1}. So we can conclude that lead ion adsorption on nano size banana and pomegranate peel is physical adsorption type [26].

$$E = 1 /(2\beta^{)-1/2} \quad (11)$$



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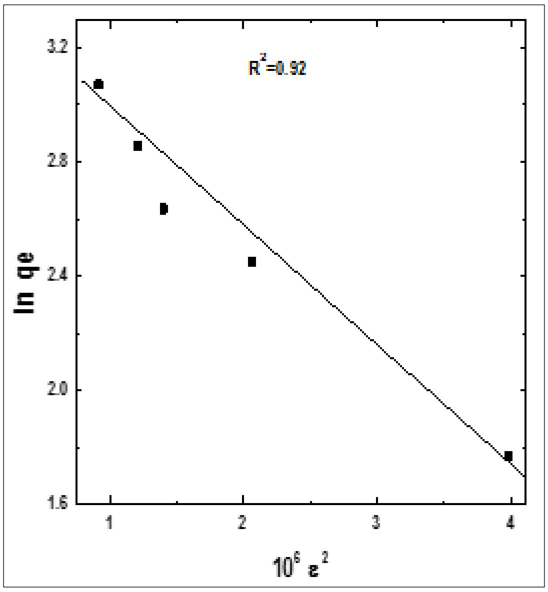

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Figure 10. D-R isotherm adsorption scheme for Pb(II) ions in a) banana and b) Pomegranate peel (T=293K, 250rpm and maximum *p*H for each adsorbent)

Table 2. Langmuir, Freundlich and Dubinin-Radushkevich(D-R) isotherms parameters for Pb^{2+} ions adsorption on banana and pomegranate peel

Adsorption isotherm model											
	Langmuir				Freundlich			Dubinin-Radushkevich (D-R)			
Adsorbent	q_{max} (mg/g)	b (L/mg)	R_L	R^2	N	K_f (L/g)	R^2	X_m (mg/g)	β(mol^2/J^2)	E (kJ/mol)	R^2
Banana peel	25.64	0.735	0.51 0.59 0.65 0.69 0.74 0.76	0.99	0.633	13.90	0.99	28.95	2.50 ×10^{-7}	1.41	0.97
Pomegranate peel	41.66	0.067	0.90 0.91 0.92 0.91 0.88 0.87	0.97	0.675	8.317	0.92	30.47	4.19 ×10^{-7}	1.09	0.92

3.8. Adsorption kinetics

In pseudo-first-order type kinetic model, reaction rate increase as qe & qt difference increase. The Lagergren pseudo-first-order model can be expressed by equation (12) [27]:

$$ln(q_e - q_t) = ln(q_e) - k_1 t \tag{12}$$

where k_1 (1/min) is the pseudo-first-order rate constant.

Table 3 demonstrates the calculated the pseudo-first-order constant (k_1) values which estimated from Figure 11. The lead(II) ions pseudo-first-order model of adsorption correlation coefficient (R^2) subtracted was in the range 0.84–0.985 for the concentrations used. This assigns which the investigational data obtained fits comparatively good to the pseudo-first order kinetics model. (qe,cal) calculated since the kinetics model of pseudo-first-order in adsorption diverged significantly from the investigational ideals (qe,exp). The model of pseudo-second-order, as will be explained in the subsequent sector represent much better fitting.

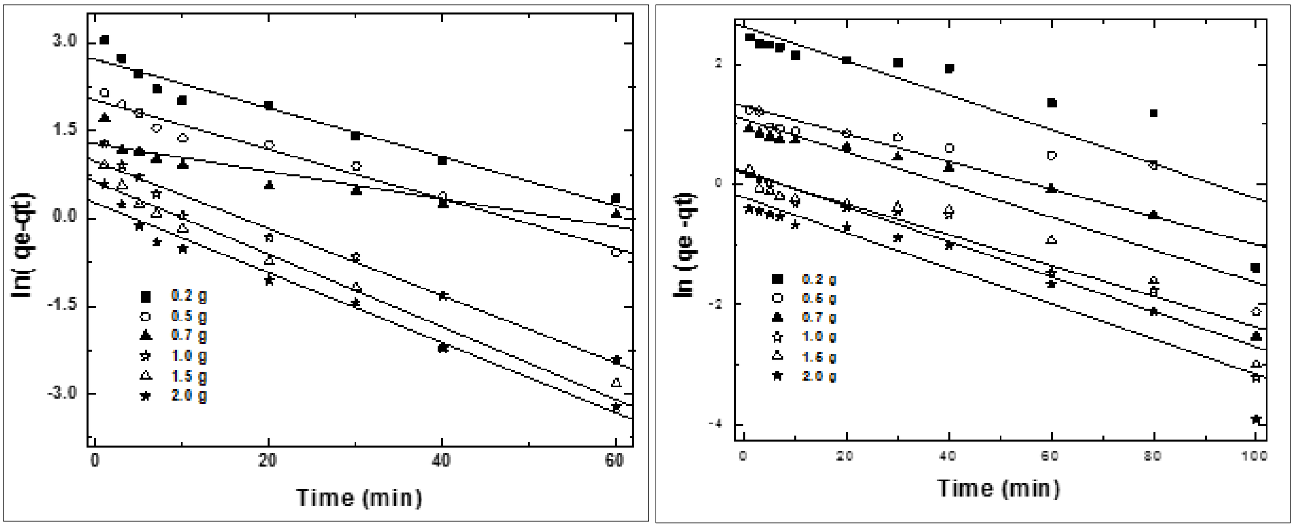

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Figure 11. Kinetic model of pseudo first order fitting for the adsorption of Pb(II) ions onto a) banana and b) Pomegranate peel (T=293K, 250rpm and maximum *p*H for each adsorbent)

Kinetic model of Ho pseudo-second-order which represented [28] by equation (13):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad (13)$$

k_2 (g/(mg min) is the pseudo second- order rate constant, k_2, and qe, cal values attained through pseudo second- order linear equations have been represented in (Table 4). Adsorption of lead(II) ions from aqua solution of different doses 0.2,0.5,0.7, 1.0 ,1.5 and 2.0 g of different biomasses were comparatively fitting well by means of the pseudo-second-order kinetics model. It was showed that, correlation coefficient of (R^2), computed from the curve slopes (Figure 12) was 0.999 which indicate that indicates chemisorption occurred between Pb(II) and banana and pomegranate peel and entails valence influences via contribution or swap of electrons among the sorbent and sorbate. Also (qe,cal) values calculated through kinetic model of pseudo-second-order decreases along with increasing adsorbent dose

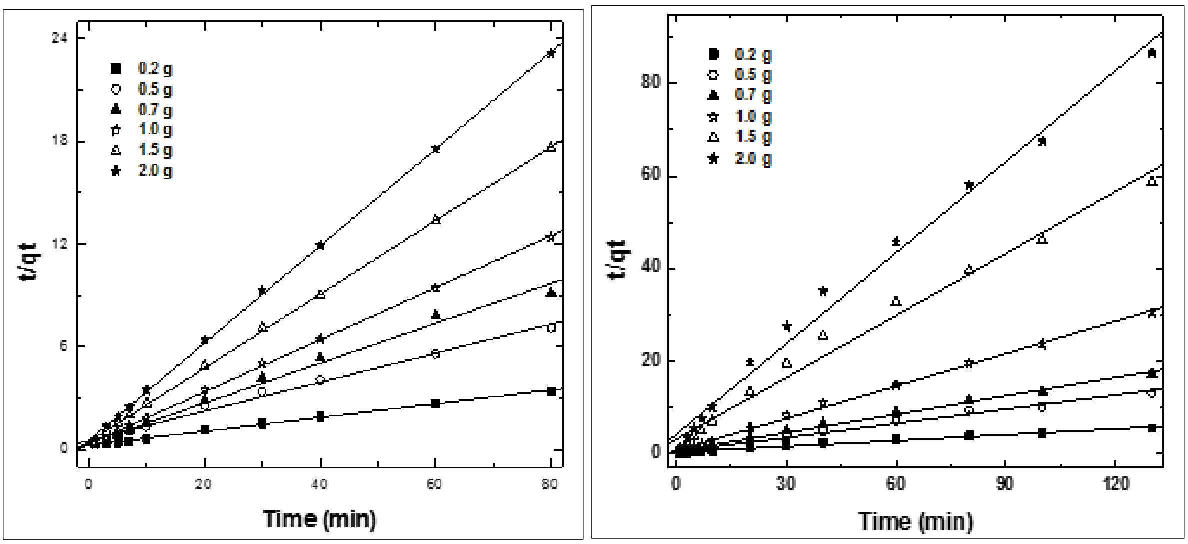

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Figure 12. Pseudo second order linear fit for the adsorption of for Pb(II) ions onto a) banana and peel (T=293K, 250rpm and maximum *p*H for each adsorbent)

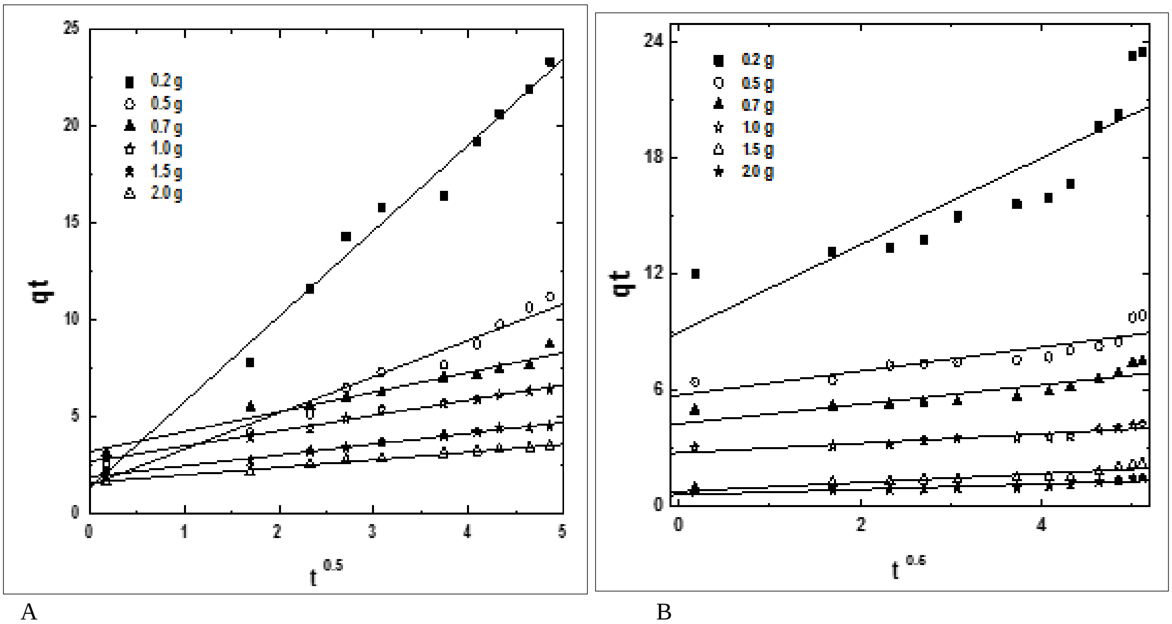


Figure 13. Intra particle diffusion fit for Pb(II) ions adsorption onto a) banana and b) Pomegranate peel (T=293 K, 250rpm and maximum *p*H for each adsorbent)

Table 3. Kinetic parameters (pseudo –first order) Pb (II)ions adsorption onto different biosorbents at several doses, (C_O= 50 mg/L, 250 rpm and 298K)

Adsorbent	Parameters	Pseudo-first order					
		0.2g	**0.5g**	**0.7g**	**1.0g**	**1.5g**	**2.0 g**
	q_e(Exp) (mg/g)	23.33	11.23	8.75	6.44	4.54	3.46
Banana peel	q_e(Cal) (mg/g)	15.15	7.53	3.56	2.36	1.87	1.30
	k_1(min^{-1})	0.4163	0.0422	0.0236	0.0573	0.062	0.0597
	R^2	0.97	0.98	0.91	0.985	0.985	0.98
Pomegranate peel	q_e(Exp) (mg/g)	23.50	9.92	7.51	4.26	2.22	1.50
	q_e(Cal) (mg/g)	13.73	3.63	2.94	1.23	1.20	0.81
	k_1(min^{-1})	0.028	0.023	0.027	0.029	0.025	0.029
	R^2	0.88	0.84	0.92	0.96	0.94	0.94

Table 4. Comparison of kinetic parameters (second order) for Pb (II)ions adsorption onto different biosorbents at different masses, (C_O= 50 mg/L, 250 rpm and 298K)

Adsorbent	Parameters	Second order					
		0.2g	**0.5g**	**0.7g**	**1.0g**	**1.5g**	**2.0 g**
	q_e(Cal) (mg/g)	24.93	11.80	8.62	6.58	4.65	3.53
Banana peel	10^{3} $\mathbf{k2}$ (g/mg.min)	5.54	12.69	33.06	65.99	99.36	141.28
	R^2	0.999	0.999	0.999	0.999	0.999	0.999

Pomegranate peel	q_e(Cal) (mg/g)	23.81	9.80	7.69	4.29	2.24	1.52
	10^3 **k2** (g/mg.min)	5.65	23.77	30.19	85.03	63.87	104.55
	R^2	0.993	0.994	0.997	0.997	0.992	0.995

The model of Weber and Morris (intra-particle diffusion procedure) was examined by means of [29, 30]:

$$Q_t = k_p\, t^{0.5} + C \tag{14}$$

In relation to this pattern, plotting of qt versus $t^{1/2}$ (Figure 13 and Table 5).

Table 5. Kinetic parameters (Intra particle diffusion) Pb (II)ions adsorption onto different biosorbents at several masses, (C_O= 50 mg/L, 250 rpm and 298K)

Adsorbent	**parameters**	**Intra particle diffusion**					
		0.2g	**0.5g**	**0.7g**	**1.0g**	**1.5g**	**2.0 g**
	k_i(mg/g.min$^{0.5}$)	4.42	1.87	1.02	0.79	0.559	0.393
Banana peel	*C*	1.35	1.47	3.22	2.71	1.925	1.62
	R^2	0.997	0.979	0.979	0.995	0.996	0.996
Pomegranate peel	k_i(mg/g.min$^{0.5}$)	2.24	0.62	0.50	0.25	0.23	0.14
	C	9.04	5.79	4.30	2.80	0.81	0.63
	R^2	0.87	0.87	0.876	0.926	0.916	0.885

3.9. Surface description

3.9.1. Scanning electron microscope

The SEM micrographs of nano size (banana and Pomegranate peel) before & after adsorption of lead (II) ions are represented in Figure 14a-d. The SEM images show that peels surface is asymmetrical shape, uneven and several breaks represented also bio-sorbent surface includes great amount of holes , diffused and generally loosened structural morphology (Figure 14a, c) .While once adsorption occurred ,the bio-sorbent surface shows normal, even and compacted to a great extent (Figure 14b, d) which designate the great attraction between bio sorbent and lead (II) ions. It is observed that Figure 14d represent the more smooth, even, regular surface after adsorption which reflect that nano size pomegranate peel adsorb relatively higher lead metal ions than banana peel and also confirmed that the higher value of q_{max} obtained for pomegranate nano peel.

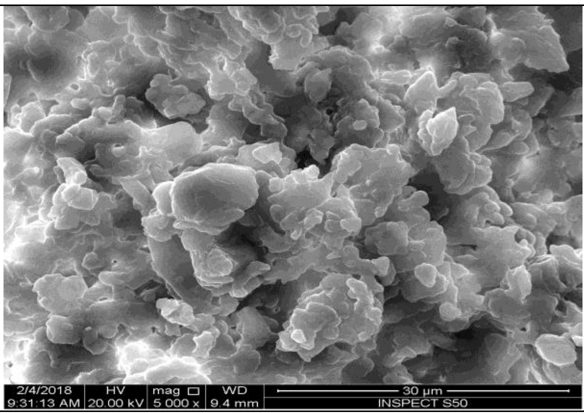


Figure 14a. Banana, Nano waste before adsorption

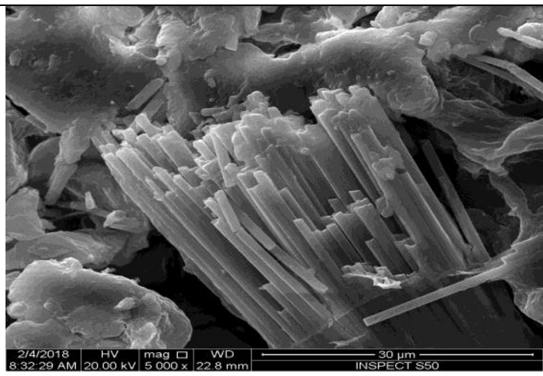


Figure 14b. Banana, Nano waste after adsorption of lead (II)

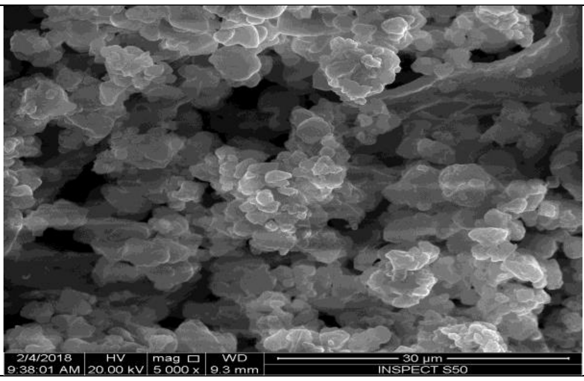


Figure 14c. Pomegranate, Nano waste before adsorption

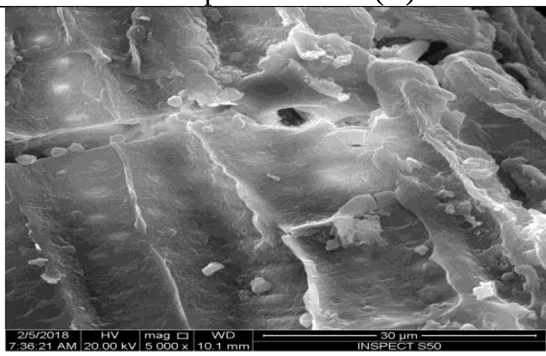


Figure 14d. Pomegranate, Nano waste after adsorption of lead (II)

3.9.2. Fourier transform-infrared spectroscopic analysis (FT-IR)

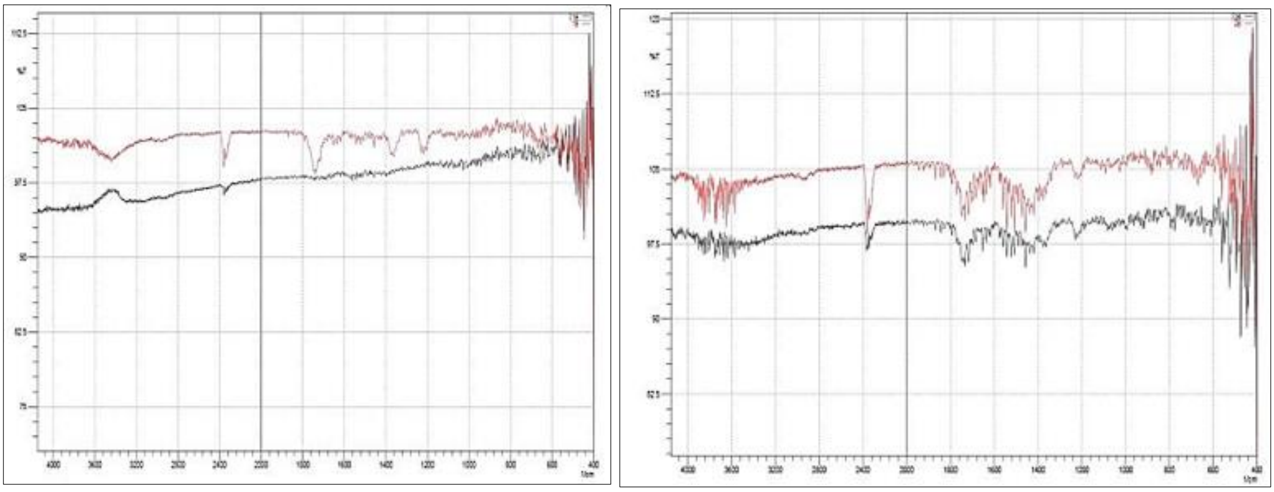
The literature survey reveals that information on GC-MS analysis of banana peel which indicate vitamin E presence, 1, 2 Benzenedicarboxylic acid, mono 2-ethylhexylester, β- tocopherol and estragole. While pomegranate peel contains phenolics, flavonoids, Proanthocyanidins compounds [31, 32].

The FT-IR banana and pomegranate peel spectra before & after adsorption of Pb(II) ions were shown in Table 6 and Figure 15. Clear band observed at 3625-3280 and 3680-3500 cm^{-1} designate the opportunity hydroxyl linkage presence, however abroad band at 3500 cm^{-1} recommend the prospect of water hydration in the adsorbent. The bands are owing to loose or feebly hydrogen welded water molecule to the oxygen surface of tetrahedral casing water molecules, water-water hydrogen bond.

The band at 1263 and cm^{-1} is related to C-O which became 1230 cm^{-1} after adsorption. The absorption band at 1027 and 1015 cm^{-1} can be identified as C-O-C which converted into 1050 and 1190 after adsorption. The C-H at 975, 780 and 800, 772 show the presence of benzene ring which shifted to 800,755 and 870,750 after adsorption. The noticed shift in the bands before and after adsorption (Table 6) confirmed the adsorption of Pb(II) ions on nano-size banana and pomegranate peel.

Table 6. FTIR Peak values of different nano size biosorbent

Group	Banana before	Banana after	Pomegranate before	Pomegranate after
OH	3625-3280(w)	3680-3449(s)	3680-3500	3750-3527
=C-H	3070, 3030	3050,3030(w)	3050,3030(w)	3050,3030(w)
C-H st	2900,2895(w)	2935,2850	2900,2895(w)	2900,2825
C=O	1740(w)	1740(s)	1725	1748
Ph-CO-	1650 (vw)	1650(s)	1629	1628
C-O	1263, 1180	1230	1230	1225
C-O-C	1027	1050	1015	1190
C-H bn	975, 780	800,755	800, 772	870,750



Banana Pomegranate peel

Figure 15. Spectrum of FTIR analysis from nanosized bio-sorbentbefore and after adsorption, with Pb(II) ions

4. Conclusions

The equilibrium adsorption is practically achieved in 60 min.

The removal lead metal ions was a function of *p*H as the adsorption capability improves with growing the solution *p*H value.

Investigational data indicated that the most excellent adsorption *p*H was 5.5 and 5.23 for nano sized banana and pomegranate respectively.

The adsorption of Pb(II) by both nono sized bio-sorbent is adsorbent dosage dependent. Raise in adsorbent dose indicates an growth in Pb(II) adsorption owing to the amplified adsorption sites number.

The equilibrium statistics supplied very well in a Langmuir and Freundlich isotherm comparations.

The kinetic analysis of Pb (II)onto biosorbent was accomplished based on pseudo-first-order, pseudo-second-order, and intra-particle diffusion equations. The statistics suggest that the adsorption kinetic adhere to the pseudo-second-order with intra-particle diffusion as one of the rate determining steps.

As the adsorption, results are hopeful and bio-sorbent has the benefits of being cost-effective and simple to be prepared, thus, it can be suggested for the toxic metals removal from aqueous solutions.

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