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(Research Article)

Modified agricultural waste adsorbent for zinc ions removal from aqueous solution: Equilibrium, kinetics, and thermodynamics investigation

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Abstract

The current research signifies potential bio sorbent (banana and Pomegranate peel) With a view for zinc ions adsorption as of aqueous solution. Mass, zinc ion concentration, pH, time, and temperature parameters were examined. The highly beneficial requirements for zinc ion adsorption are 10 ppm as preliminary concentration, 0.21 g as pomegranate and banana rinds dosage and 5.5, 5.23 as pH for banana and Pomegranate rind. Elimination results follow the Langmuir replica with qmax of 25.64 mg/g for banana and 41.66 mg/g for Pomegranate rind. The elimination process kinetic was equipped well via second -order equivalence. It was examined that the zinc ion adsorption procedure on both bio sorbents is instinctive procedure, endothermal for banana and pomegranate rind. A distinctive enhancement in the adsorptive shell was observed once the adsorption procedure that revealed through scanning electron microscope.

Keywords: Zinc Ions; Banana Peel; Pomegranate Peel; Second -Order Equation

1. Introduction

Water has been one of the essential prerequisites of human development. Although water covers more than 70% of the world's shell, less than 1% is accessible for human being conservation [1].

Waste water contamination originated from several metal ions which obtained via different manufacturing waste matters is a worldwide trouble that has obtained international consideration [1]The waste matter water of several industries, for instance mining [2],metal smelting [3], tanneries[4] and batteries [5] and so on, includes poisonous metal particles that the non-ferrous metal founding manufacturing as one of the elevated contamination productions has involved broad awareness due to numerous heavy metal infectivity mishaps. Release of such poisonous heavy metal can gravely control the surroundings since they may not be debased, other than buildup via the food chain resulting in significant environmental subjects and health issues.

One of the most important heavy metals is zinc, that is a significant metal for humans, plants, and animals. Zinc contributes to the peptides and nucleic acids metabolism, motivates various enzymes activity, and organizes the immunological system work. zinc deficit and zinc overdose difference is extremely little. Zinc insufficiency may cause troubles with skin, thymus, reproductive system and brain, Zinc dosage above 100 mg/day may cause gastrointestinal tract brain, respiratory tract, and prostate dysfunctions. Extensive zinc procedure in materials manufacture, cosmetics, paints, anti-corrosive coatings, and batteries, in addition to its occurrence in the excavation waters permits the element to mount up in the surroundings and does zinc elimination from effluent significant subject [1,6,7]

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Recently, several adsorption procedures, like biosorption, customized media adsorption, manufacturing desecrates adsorption, and so on, have materialized as possible substitute techniques that, owing to little charge and relaxed-to-acquire natural world, the manufacturing squanders so absorbents partake for poisonous contaminants elimination as of dissipate water, especially for dyes. In the meantime, some organically obtainable adsorbents like chicken quills and wheat berry straw have also been utilized for hazardous dye exclusion. However, it was seldom that the above absorbents were used heavy metal ions adsorption.

The zinc concentration in ordinary squanders is quite little, that creates bio-sorption an appropriate elimination technique. Bio-sorption is comparatively contemptible and rapid division procedure. A group of natural materials may be utilized: eukaryotic organisms, microbes, caffeine compound, fungi, kernel explosives, wood dust, rice hulls [8,9]. The physical -chemical procedures, are non-useful and not feasible to achieve in financial opinion, the necessitate stern removal characteristic in surface water bodies the highest adequate zinc concentration in consumption water is 5.0 mg/l as WHO recommended. Consequently, lately, Zn^{2+} ions elimination via means of natural textiles has been inexpensively suitable techniques [10,11]

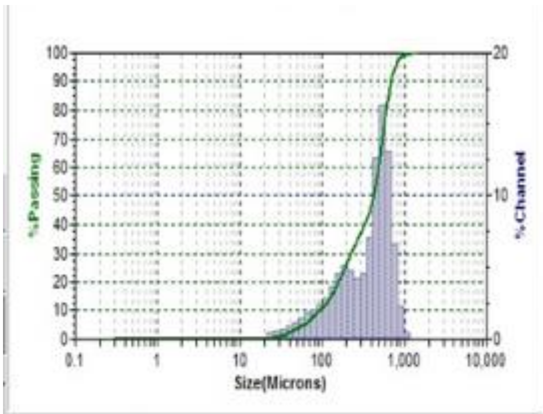
The progress of novel chemicals is mainly demanding, as they would require preserving the good eminence beneath a diversity of situations, even as being ecologically adequate. There is mounting anxiety concerning the electrochemical reactions to toxicity - additives all through in the manufacturing. Every poisonous consequence not only influences living organisms but is also toxic to the earth. Consequently, over recent years, the conventional approach concerning electrochemical - additives have regularly changed, due to the rising awareness and thought of the world in the direction of ecological problems, towards caring for the surroundings, the dangerous results of the using of chemicals on the conservation equilibrium. It is supposed that contaminated substances as broadly used inside manufacturing procedures should be restored via novel ecologically friendly ones [12,13]

Therefore, in this study a kind of banana and Pomegranate peel possibility in nano size, owing to great surface, elevated porosity, and minor charge and an efficient sorbent for Zn^{2+}ion removal. Several parameters, for instance primary zinc ions concentration, procedure time, adsorbent mass and solution pH were examined. The Freundlich and Langmuir isotherm was applied for equilibrium sorption also kinetic studies were represented.

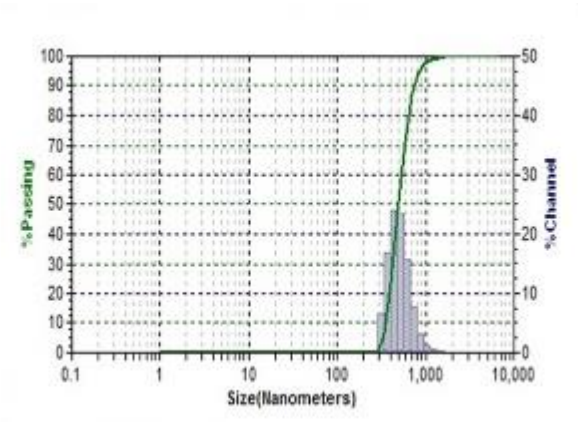
2. Method and Material

2.1. Adsorptive materials and its preparation

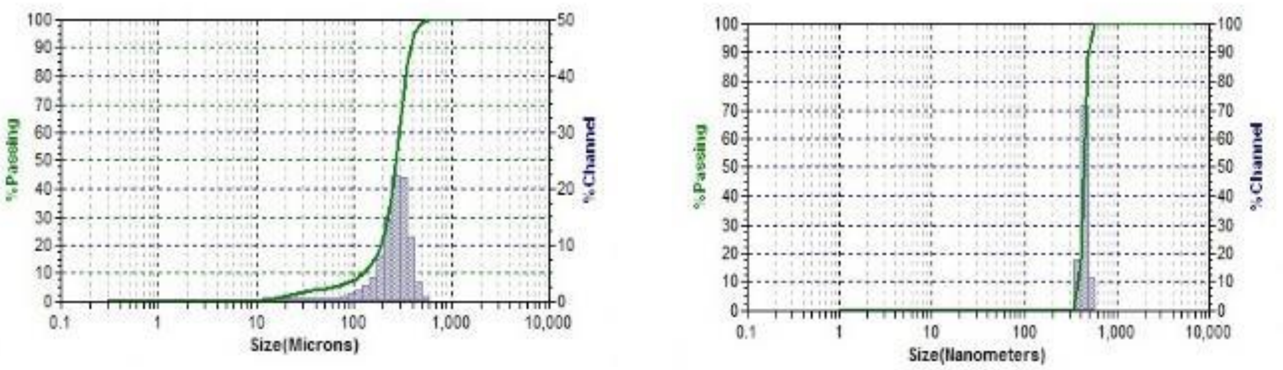
The adsorbent material banana and Pomegranate rind was compiled as juices stores waste. The numerous strips were cleaned using valve water then deionized water, then filtered and ultimately dried out at 80°C for 48 h. The numerous rinds were crushed and sifted (wire sizing 200,150 and 75 µm) (strainer style), the lowest fragment size (< 75 µm) was grinded utilizing Microcrack, S3500Alright Ball miller apparatus which were organized the nano size of all specimens afterward ball crushing utilizing 25 g sample,1250 g Zircon balls and elevated energy system, used HDDM program, the chiller with 13C, the control was 4000 m Amps and the sphere mill for 6 h for each specimen.(fig.1)



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



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



Average size (279.15µm) (peak diameter,270.5), Pomegranate rind

Before milling

Average size (448.8 nm) (peak diameter, 442), Pomegranate rind

After milling

Figure 1 DLS result for adsorbent samples before and after grinding

2.2. Surface investigation

Scanning electron microscope, JEOL (Inspect S50, FEI, Therma Fisher scientific.).DLS dimensions,ball miller requires particle size prior to and after grinding as displayed in Fig.1.

2.3. Adsorbate preparation

Analytical grade chemicals were used. Zn^{2+} standard solution (1000 ppm) was made via zinc nitrate (Merck) dissolution in demineralized water (measured resistivity > 18 mΩ.cm). Test solutions were prepared through dilution using de-ionized water, 0.1M H NO_3 and 0.1M NaOH solution was employed for pH change (Mettler Toledo.). Inductively Coupled Plasma Atomic Emission Spectroscopy (**ICP**-AES) was used for Zn^{2+} ion fortitude. The water bath was used for controlling temperature.

2.4. Adsorption procedures

Batch adsorption trials were performed, zinc nitrate solution with the banana or pomegranate peel were arranged in glass container and stirred up using thermostatic magnetic stirrer (250 rpm) for 60 minutes. The suspensions were centrifuged (Centrifuge. Thermo Scientific, Heraeus Megafuge 40R, model MEGAFU) at 10000 rpm and the concentration of supernatant solution was determined via (ICP).

2.5. Practical adsorption procedure.

- **pH :** The initial $Zn(NO_3)_2$ solution pH varied from 1.2 to 7.2 which adjusted by 0.1M HNO_3 and 0.1M NaOH at 293 K, 250 rpm and 60 minutes as contact time.
- **Contact time effect:** at optimum pH, 50 mg/L $Zn(NO_3)_2$, adsorbent mass 0.2 g /50 ml $Zn(NO_3)_2$ at 293 K. The disturbance rate (250 rpm) was stayed constant for every trial to guarantee equal combination, then samples were done after 1,3,5,7,10,20,,40 and 60 min.
- **Adsorbent mass effect:** several mass ranges (0.2g - 2g) of bio sorbents were located in a 100 ml glass container including 50 ml of 50 ppm $Zn(NO_3)_2$ at 293 K
- **Adsorbate concentration effect:** 50 ml of $Zn(NO_3)_2$ solutions was stirred with 0.2g of bio sorbents for 60 minutes at 250rpm, 293 K. 10, 20, 30, 40 and 50 mg/L as several adsorbate concentration.
- **Temperature effect:** 50 ml of 50mg/L of $Zn(NO_3)_2$ solution stirred (250rpm)with 0.2g of bio sorbents for 60 minutes with several temperature (293, 303, 313, 323K). solution pH is controlled.

2.6. Results investigation

Zn $^{2+}$ % removal results were determined according to the subsequent equation:

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

C_o(mg/L) is the original concentration for Zn^{2+} ion and C_t(mg/L) is the concentration for Zn^{2+} ion at time t. The adsorption capability, metal ions quantity adsorbed per adsorbent unit mass, was estimated via the subsequent equivalences:

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

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

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

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

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

2.7. Kinetic and Adsorption isotherm modeling

Pseudo first order, pseudo second order and intra particle diffusion were applied. Also, Langmuir, Freundlich and Dubinin-Radushkevich (D-R) were investigated in a series of solutions containing several Zn^{2+} original concentration.

3. Result and discussion

3.1. Influence of time

Contact time influence on the Zn^{2+} adsorption is indicated in Fig. 2. The testing was carried out through 50 mg/l Zn^{2+} solution containing 0.2 g of nano size banana or pomegranate peel at pH 4.4 and 20°C. Zn^{2+} Removal percentage regularly raises via contact time amplify pending the equilibrium was accomplished. After that, once the contact time was auxiliary raised, there was no more change in the removal percentage. The consequences make conclude that most favorable contact time to reach equilibrium for nano size banana and pomegranate rind for zinc ions adsorption is 40 min [14]

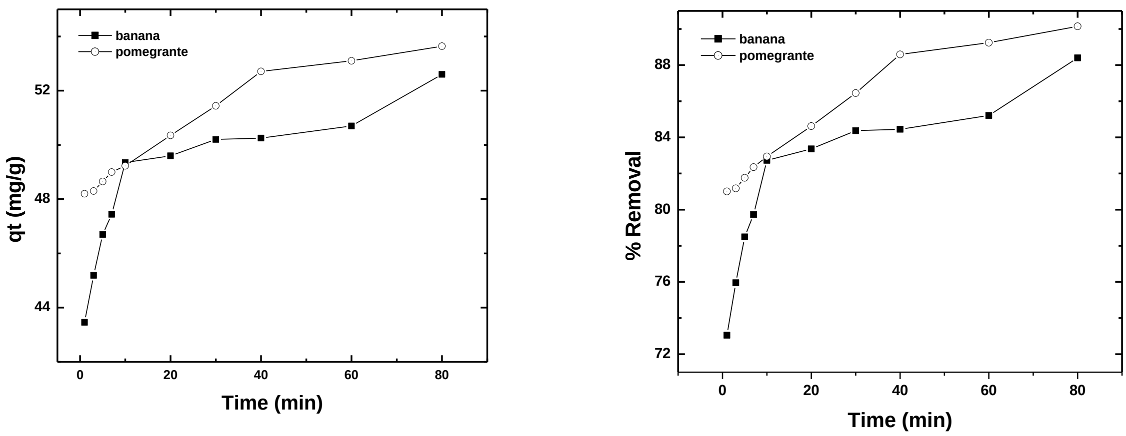


Figure 2 (a)qt (b) %removal- Time dependence of Zn^{2+} ions adsorption onto banana and pomegranate peel.

3.2. pH effect

heavy metals removal by adsorbent is pH dependent. So, adsorption of Zn^{2+}ions on to banana and pomegranate rinds surface was investigated at several pH values. The pH choice was selected as 1.3 –7.6 to keep away from metal hydroxides formation, that has been inspected to form at pH > 7.6. Fig. 3 represents zinc ions amount eliminated from zinc nitrate as is pH dependent at Zn^{2+} ions removal amount from solution augments speedily from pH 1.3 to pH 5. At pH 5, 52.5 % of zinc ion was removed via banana peel, while 55.7 % of zinc ion was removed via pomegranate peel. After pH 5, there is a drop in % removal of zinc ions.

$Zn^{2+}{}_{(aq)} + n\ H_2O = Zn\ (\ OH\ )_n + n\ H^+$

At lower pH values, banana and pomegranate peel surface are positively charged and there was of $[Zn(OH)_4]^{2-}$ complex formation [15] therefore, the complex that shaped will be absorbed via adsorbent surfaces. [OH-Zn] complexes have elevated resemblance for adsorption than the hydrous zinc ion, owing to an OH adduct formation of the metal ion that diminishes the adsorption free energy. Small sorption at lesser pH values might be ascribed to the hydrogen ions and metal ions competition for active sites. This indicates that, at elevated proton concentration, banana and pomegranate peel surface develop into more positively charged which leads to diminished metal ions and adsorbent attraction [16]. On the contrary, as the pH values amplifies, extra surface with negative charge becomes accessible, consequently assist superior metal elimination. The ability of banana and pomegranate peel to metal ion elimination enlarges at elevated pH values that might be featured to adsorbent components that supplies alkalinity in the scheme, growing the pH to powerfully alkaline ranges.

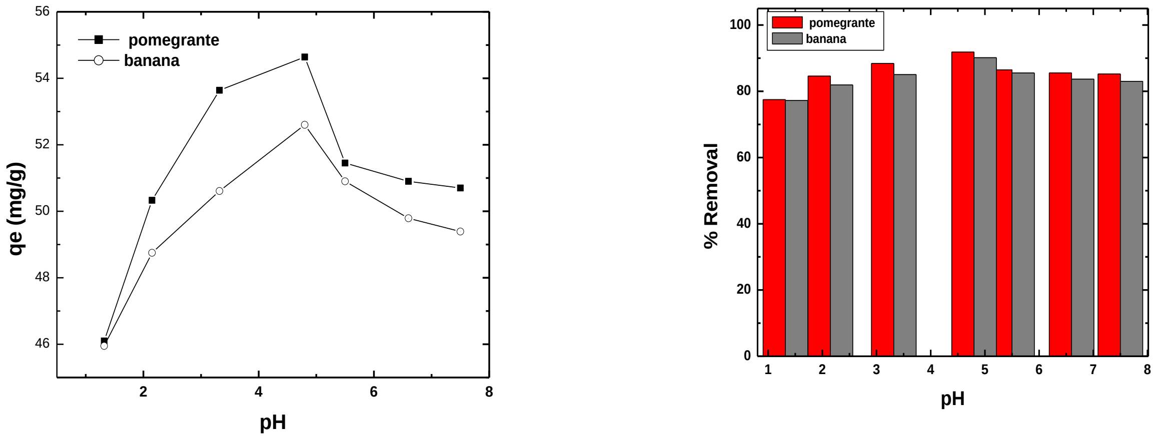


Figure 3 pH influence on (a) the adsorption equilibrium capacity and (b) % elimination of Zn^{2+} ions on banana and pomegranate peel.

3.3. Dose influence

The investigation results via changeable adsorbent dosage are demonstrated in Fig. 4. By increasing the adsorbent dosage (0.2 - 2 g), the zinc metal adsorption amount amplified as nano size banana peel mass increase but for pomegranate peel, the optimum dosage recorded at 0.7 g. As the active sites number in the solution enlarges, greater metal ions have accessibility to react with active sites resulting in increasing in zinc ion adsorption. Alternatively, the adsorbed zinc amount for nano banana peel decreased from 29.25 mg/g to 3.72 mg/g and, for pomegranate peel decreased from 32.65 mg/g to 4.12 mg/g. This diminish in adsorbed zinc ion quantity is owing to augment active sites ratio to zinc ions that is reliable with Eq. (3). [17]

3.4. Initial concentration influence

Initial zinc ion concentration was regulated via the 10–50 ppm range. The adsorbed metal ions quantity for each banana and pomegranate peel unit mass (qe) regularly amplifies as the adsorbate initial concentration solution enlarges. Although the lower preliminary zinc ion concentration results in elevation, the percentage elimination as represented in Fig. 5. With little preliminary concentration of the solution, the metal ions number / adsorptive situates accessible ratio is little; accordingly, adsorption be contingent on the preliminary concentration. Consequently, every adsorbent unit mass is imperiled to a great metal ions quantity that regularly obstruct the sites. Therefore, qe value increase and adsorbed percentage reduction are monitored [18]. This result is consistent with current research using natural zeolite [19] and olive cake [20]; this is in addition to what has been found by Abdel Salam et al. [21] and Karthikeyan et al [22].

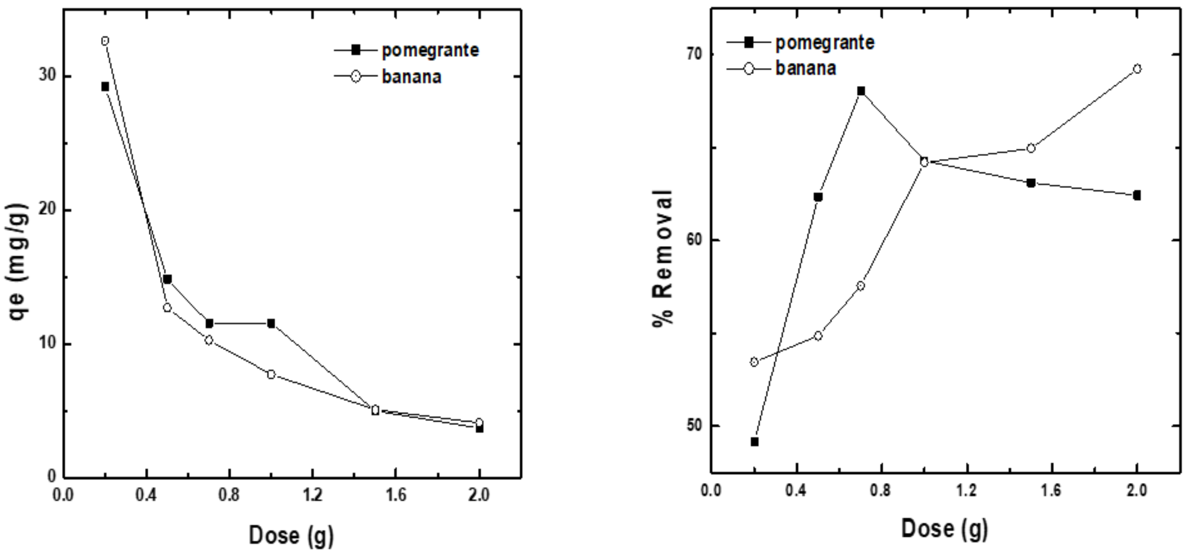


Figure 4 Effect of banana and pomegranate peel dose on (a) the adsorption equilibrium capacity and (b) % elimination of Zn^{2+} ions

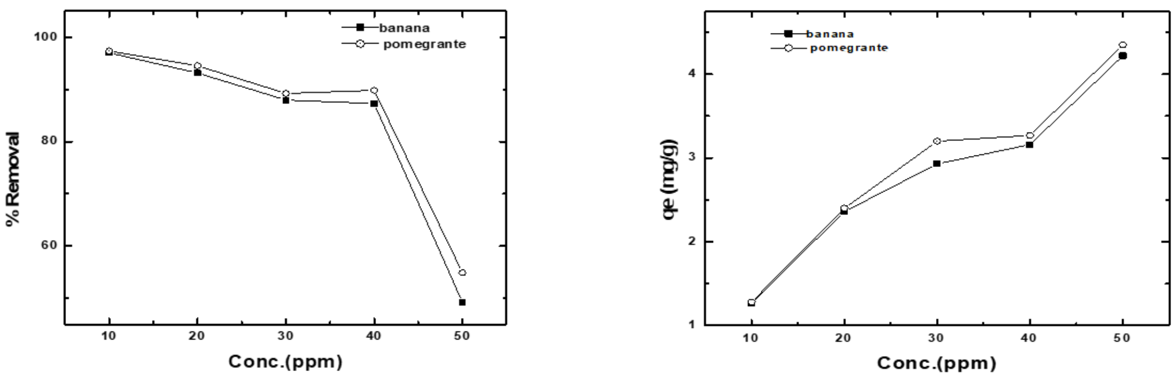


Figure 5 Preliminary concentration impact on a) elimination % and b) qe of zinc ions in banana and pomegranate rind

3.5. Temperature influence

To conclude whether the investigated adsorption reaction was endothermic or exothermic behavior, Zn^{2+} adsorption studies over nano size banana and pomegranate rinds were carried out between 20-50 ºC at 50 ppm,250 rpm, 0.2 g of adsorbent and maximum pH. It may be shown that the zinc ions adsorption enlarged as the temperature was augmented (Fig. 6). The figure represents that the elimination efficiency enlarges via growing the temperature, where the greatest adsorption is attained at 323 K. The increase of the elimination effectiveness by speeding up the temperature is owing to the subsequent explanations: first, the elevated temperature stimulates the metal ions for adsorption ornamental at the adsorbent coordinating site, and make the metal cation movement become faster; second, speeding up of some initially sluggish step and new activation sites creation on the adsorbent [23,24]

As represented in Figure 6, the enhancement in banana and pomegranate peel equilibrium adsorption capacity with temperature which reflects an endothermic nature of adsorption process. The amplify in adsorption via temperature may be ascribed to either augment active sites number that accessible for adsorption on the adsorbent or adsorbing species de-solvation and the diminish in boundary layer thickness which adjacent the adsorbent with temperature increase, so that the mass transference confrontation of adsorbent in the periphery layer diminishes. Since dispersion is endothermal in nature, higher adsorption will be noticed at an elevated temperature. Consequently, the ions dispersion rate in the exterior mass transportation procedure enlarges along with temperature. [18, 25,26]

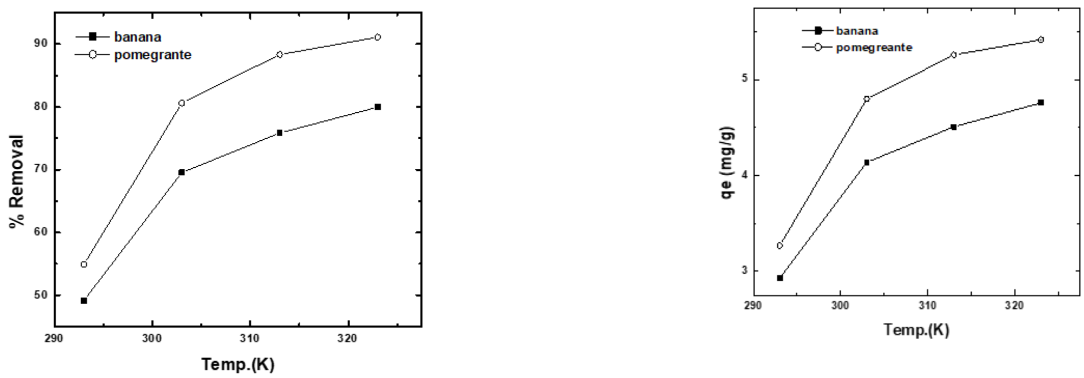


Figure 6 Temperature effect on (a)the adsorption equilibrium capacity and (b) % elimination of Zn^{2+} ions on banana and pomegranate peel

3.6. Thermodynamic parameters

The results attained from the sorption isotherms were utilized to estimate the thermodynamic parameter (Fig.7) such as Gibbs free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°), using the relationship below:

$\Delta G^o = \Delta H^o - T\,\Delta S^o$

$\mathrm{Ln}K_o = (\Delta S^o/R) - (\Delta H^o/T\,R)$

Where K_o is the distribution constant*(L/g)* (K_o= qe / C_e),R is the gas constant and T is the absolute temperature (K). Data are reviewed in Table 1 below: The positive values of enthalpy, ΔH, reflects that the zinc ions adsorption on to nano size banana and pomegranate peel is an endothermic in nature. The positive entropy , ΔS value recommends that mounting arbitrariness at the solid-liquid boundary through the adsorption of zinc ions on to nano size banana and pomegranate peel, and may also be a reflection of the affinity of the nano size banana and pomegranate peel for the zinc ions. The free energy values were negative at elevated temperature reflecting that the adsorption process nature is spontaneous and its practicability at elevated temperature [27-29]

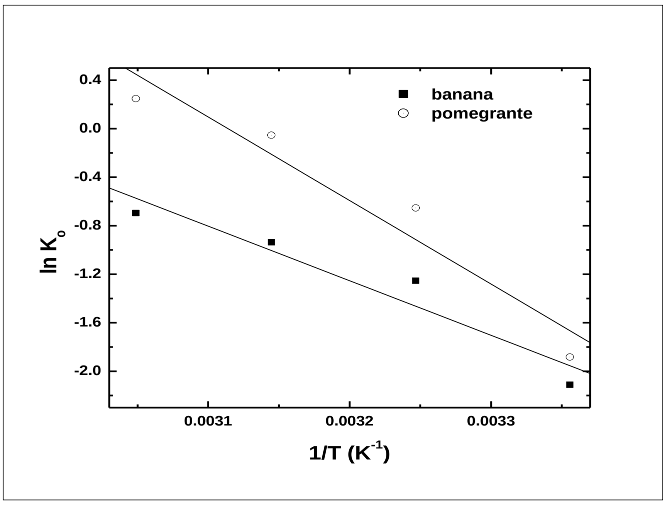


Figure 7 Temperature effect on the thermodynamic behaviour of Zn^{2+} ions adsorption onto banana and Pomegranate rinds

Table 1 Thermodynamic parameter for Zn^{2+} ions adsorption onto various bio sorbent

T (K)	*ΔG^O(kJ/mol)*	*Adsorbent*	*ΔH^O(kJ/mol)*	*ΔS^O(J/mol.K)*
293	5.39	**Banana peel**	37.40	109.24
303	4.30			
313	3.21			
323	2.11			
293	5.03	**Pomegranate peel**	57.26	178.25
303	3.25			
313	1.46			
323	-0.314			

3.7. Adsorption isotherms

The adsorption isotherms attained with the several adsorbent substances are shown in Figs. 8-10. The equilibrium data attained in the several adsorbent–zinc schemes supplied the Langmuir and Freundlich models. The Langmuir isotherm suits the subsequent equivalence.

$q_e = QkC_e / (1 + kC_e)$ (6)

where k = Langmuir's equivalence constant, related to the process enthalpy; Q= the adsorption capability to structure the individual layer. This isotherm is an instance of a constructive isotherm and is appropriate under the subsequent supposition: a homogeneous solid surface, there is no contact among the dissimilar adsorbed particles and adsorption in a solitary layer.

Freundlich's isotherm take up the subsequent equivalence:

$q_e = K_F\ Ce^{1/n}$ (7)

where, K_F = a constant related to the adsorption capacity; n = an experiential constraint related to adsorption intensity, that differ with the adsorbent heterogeneity. For values ranged through $0.1 < 1/n < 1$, adsorption is sympathetic.

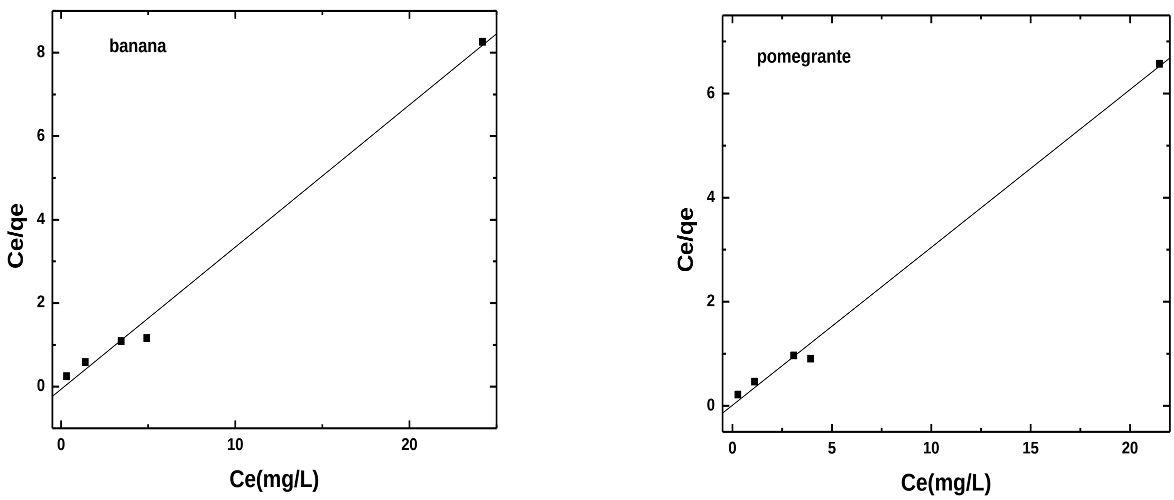


Figure 8 Langmuir adsorption isotherm for Zn^{2+} ions onto nano size banana and pomegranate rind

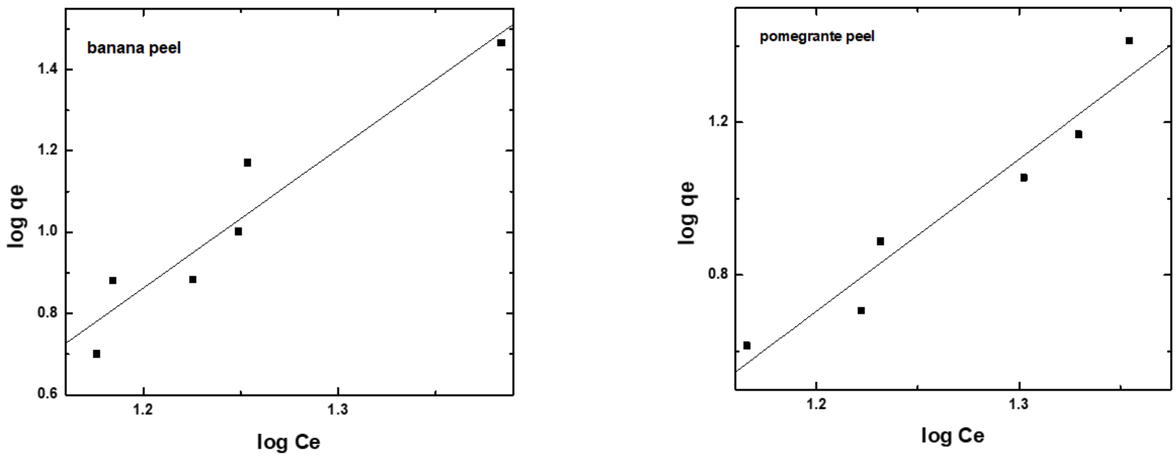


Figure 9 Freundlich adsorption isotherm for Zn^{2+} ions onto nano size banana and pomegranate rind

This model is suitable for dissimilar surfaces and forecasts an amplification in the ionic species concentration that adsorbed onto the solid surface when growing the solid species concentration in the liquefied form [30,31].

Table 2 Langmuir, Freundlich and Dubinin-Radushkevich(D-R) Parameters for the Zn^{2+} ions adsorption onto 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	*1/n*	K_f (L/g)	R^2	X_m *(mg/g)*	β(mol²/J²)	*E* *(kJ/mol)*	R^2
Banana peel	29.35	0.529	0.072 0.095 0.111 0.101 0.097 0.096	0.996	0.673	4.89 $\times 10^{-4}$	0.95	57.97	8.49×10^{-5}	0.013	0.98
Pomegranate peel	32.98	2.02	0.022 0.021 0.024 0.029 0.028 0.032	0.997	0.521	8.51 $\times 10^{-5}$	0.96	69.75	1.16×10^{-4}	0.015	0.95

The results are represented in Tables 2. The Langmuir model (Fig.8) matches the data well. The most excellent fittings gained with both models for banana and pomegranate peel. Regarding to the adsorption of zinc, the capacities gained diverse among 29.35 mg/g for the zinc–nano size banana peel system and 32.98 mg/g for zinc –nano size pomegranate peel

Separation factor (R_L) was computed to establish the constructive circumstance of adsorption, that is characterized via the subsequent equivalence.

$R_L = 1/(1 + kCe)$ (8)

The R_L values estimated for zinc ions are less than one, which demonstrates that the adsorption is constructive ($RL < 1$).

Freundlich isotherm with a great-value association factor (R^2) for nano size banana (R^2=0.996) and nano size pomegranate bio sorbent (R^2=0.997) (Fig.9). The greatest contest of equilibrium statistics with Freundlich isotherm designates that dissimilar bio-sorption carry outs a core point in Zn^{2+}elimination ions. The smaller value of 1/n attained (0.673, 0.521) illustrates enhanced sorption and configuration of a moderately stronger bond between nano size banana peel and Zn^{2+}ions. compared to pomegranate peel. [32,33]

with the intention of understanding the adsorption nature, equilibrium statistics was investigated via Dubinin–Radushkevich isotherm (Fig.10)

The linearized D.R. equivalence may be characterized as

$\ln qe = \ln qm - \beta \varepsilon^2$ (9)

The mean adsorption free energy (E) was computed from the constant K using the equation [33].

$E = 1 /(2\beta^{)-1/2}$ (10)

It is described as the free energy modification when 1mol metal ion is transported to the solid surface as of immensity in solution. The E value is extremely helpful in expecting the adsorption nature and if the value is less than 8 kJ/mol, so the adsorption is physical in nature and if it is between 8kJ/mol and 16 kJ/mol, then the adsorption performance is owing to ions exchange. The value in the current research was observed to be less than 8 kJ/mol which reflect that the physical nature of zinc ion adsorption on nano size banana and pomegranate peel [18]

3.8. Kinetic study

Kinetic adsorption might provide precious understanding into the reaction methods and sorption paths mechanisms. To elucidate the sorption kinetic of Zn^{2+} ion onto bio-sorbents was investigated by the two most normally used replicas, specifically, pseudo-first-order model and pseudo-second-order model. The fulfillment among investigational data and the model expecting values was shaped via the correlation coefficient (R^2).

3.8.1. Pseudo-first-order model

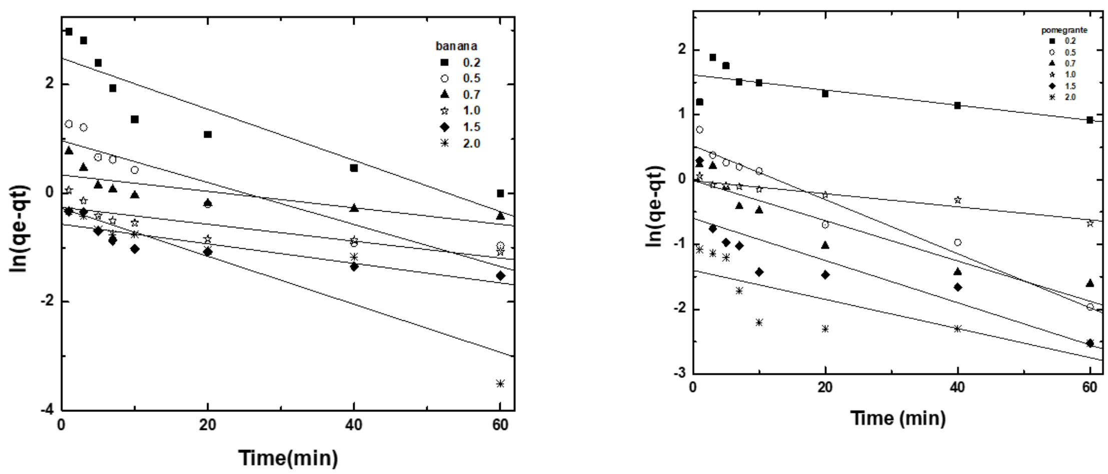


Figure 11 Pseudo first order fit for the adsorption of for Zn^{2+} ions onto banana and pomegranate peel.

The Lagergren pseudo-first order rate [33, 34] is based on solid capacity and represented as follows.

$\text{Log}(qe-qt) = \log qe - k_1/ 2.303\ t$ (11)

where qe k_1 is the sorption constant. It is the extremely recognized form of the pseudo-first-order kinetic model. The value of k_1 at different masses was concluded from the schemes of log (qe-qt) versus t (Fig. 11) for Zn^{2+} ions deletion. Constant k_1 and association factor (R_2) had been calculated and represented in Table 3. The association factor (R_2) estimates found were relatively little. It revealed that the pseudo-first order rate particularly bad relationship coefficient (R_2) for best fits statistics.

3.8.2. Pseudo-second-order model

For the pseudo-second-order model, the kinetic statistics were investigated using a prescription, that could articulate as a follow [35]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (12)$$

where k_2 (g/(mg.min)) is the pseudo-second-order rate constant; t (min) is the sorption time; qe (mg/g) is the equilibrium Zn^{2+} ion sorption ability of bio sorbent, and qt (mg/g) is the sorption ability at a time t. The k_2 and qe could be acquired from the slope (1/qe) and intercept ($1/ k_2.qe^2$)) of the linear curveof t/qt versus t (Fig. 12). The k_2 and qe, which is calculated from the model, are revealed in Table 4. It might be represented that the sorption of Zn^{2+} ion adheres to the pseudo-second-order rate style, with an association factor (R^2) of 0.999 for all bio-sorbent. These outcomes indicate that Zn^{2+} elimination on bio-sorbent respects pseudo-second-order mechanism, and the sorption reaction is typically controlled via chemi-sorption.

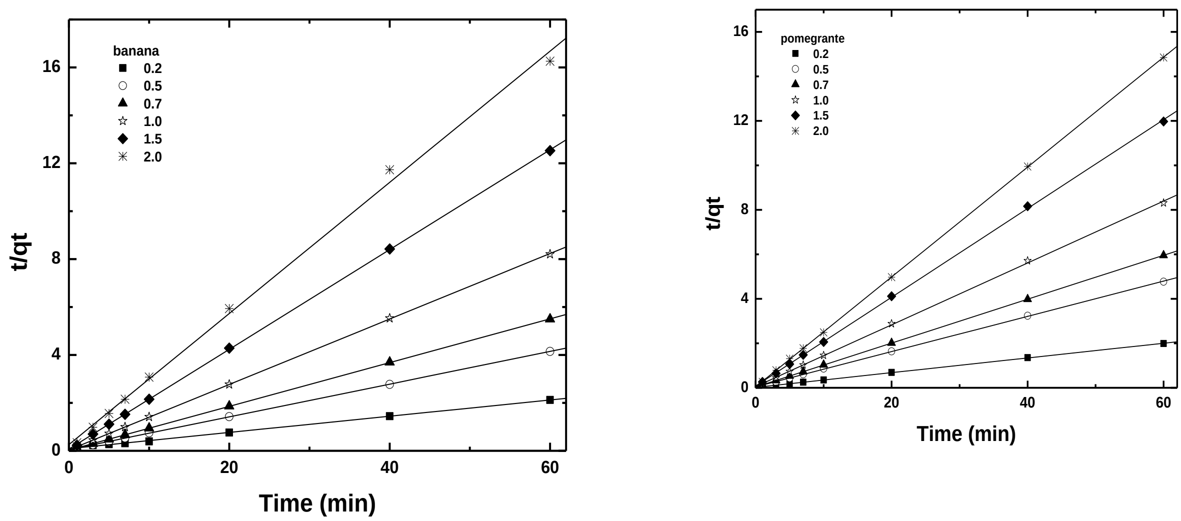


Figure 12 Pseudo second order fit for the adsorption of Zn^{2+} ions onto banana and pomegranate peel.

3.8.3. The intra-particle diffusion model

The intra-particle diffusion procedure was investigated using the Weber and Morris model [36]

$$q_t = k_p t^{0.5} + C \quad (13)$$

The linear schemes of qt against $t^{0.5}$ for banana and pomegranate peel are shown in Fig. 12. If the curve is a line that throws by the origin, then the intra particle dispersion is the sole rate- adjusting step. It may be simply monitored that in both banana and pomegranate peel the consequence is not a straight away line and that it also doesn't pass by the origin. This reflects that other mechanisms along sides distribution from the solid / liquid boundary are happening. In this investigation, the figures are shown as a plot with three linear parts. They signify the metal sorption stages by sorbents. The first part, with a greater slope, represents the quick zinc ions perception on the external surface of biomass (dispersion from solution bulk). Then observes the regular sorption phase, in which the zinc ions go through the bio-sorbent holes. As the holes become swarmed with sorbate, the distribution rate reduces and is the ratemonitoring step. This might be characteristic to distribution into the meso-pores. In the final region (region III), the intra-particle diffusion into micropores represents a significant symmetry between the zinc ions in the solution and on the sorbent, surface is being achieved. [37]

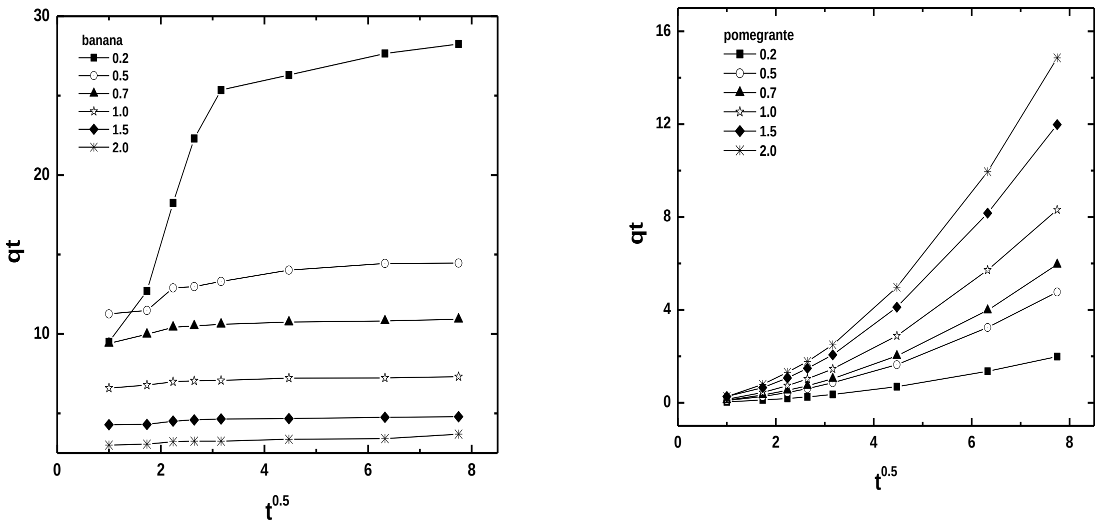


Figure 13 Intra particle diffusion fit for the adsorption of Zn^{2+} ions onto banana and pomegranate peel.

Table 3 Pseudo –first order parameters for the adsorption of zinc ions onto different bio sorbents at different doses.

Adsorbent	**Parameters**	**Pseudo-first order**					
		0.2g	**0.5g**	**0.7g**	**1.0g**	**1.5g**	**2.0 g**
	q_e(Exp) (mg/g)	29.25	14.84	11.57	7.65	5.01	3.72
Banana peel	q_e(Cal) (mg/g)	12.05	2.63	1.40	0.773	0.565	0.758
	k_1(min^{-1})	0.047	0.038	0.015	0.016	0.018	0.044
	R^2	0.91	0.93	0.80	0.85	0.87	0.92
Pomegranate peel	q_e(Exp) (mg/g)	32.65	12.72	10.28	7.73	5.09	4.12
	q_e(Cal) (mg/g)	5.02	1.69	0.99	0.98	0.55	0.246
	k_1(min^{-1})	0.0116	0.041	0.031	0.0101	0.032	0.022
	R^2	0.76	0.97	0.92	0.96	0.84	0.79

Table 4 Second order parameters for the adsorption of zinc ions onto different bio sorbents at different doses.

Adsorbent	**Parameters**	**Second order**					
		0.2g	**0.5g**	**0.7g**	**1.0g**	**1.5g**	**2.0 g**
	q_e(Cal) (mg/g)	29.58	14.64	10.95	7.32	4.81	3.66
Banana peel	$10^{3}k_2$ (g/mg.min)	12.87	92.57	317.23	533.22	625.50	287.12
	R^2	0.999	0.999	0.999	0.999	0.999	0.999

Pomegranate peel	q_e(Cal) (mg/g)	30.23	12.63	10.13	7.19	5.01	4.05
	$10\ ^{3}k_2$ (g/mg.min)	57.47	140.24	280.83	376.41	499.37	1429
	R^2	0.999	0.999	0.999	0.999	0.999	0.999

4. Surface characterization (Scanning electron microscope)

The SEM micrographs of bio sorbent (banana and pomegranate peel) prior to and next to zinc ions adsorption are displayed in fig.14 (a)-(d). It is obvious from SEM figures that bio- sorbent is uneven form, coarse and more breaks represented and the surface comprises a countless number of hovels, mellow and commonly undid structural geomorphology (fig.14.aandc).Subsequent to adsorption, the surface shows regular, smoother and compact to a great extent (fig.14.bandd) which indicate the high affinity between bio sorbent and zinc ions.

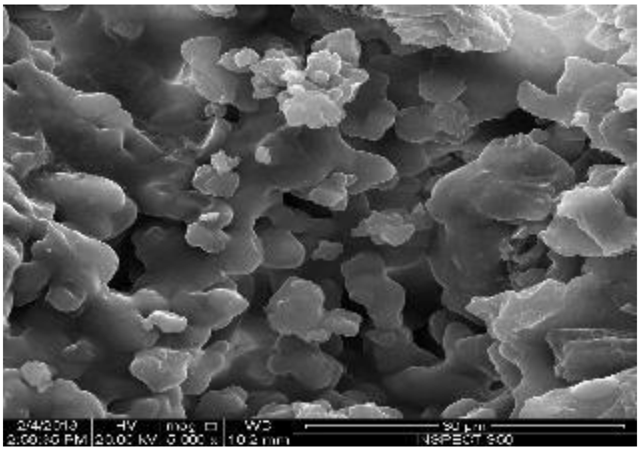


Figure 14a Banana, before adsorption

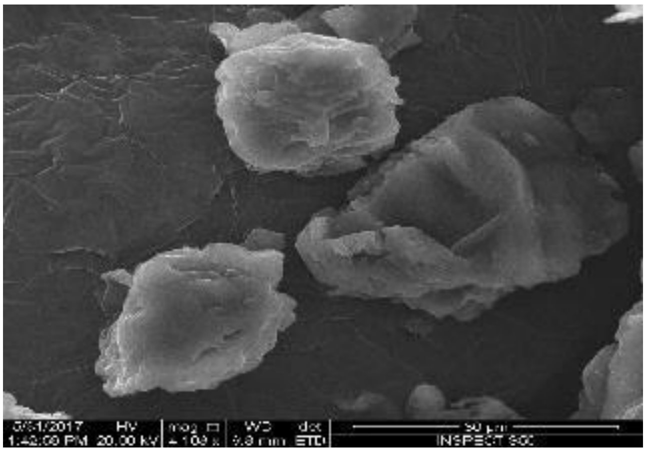


Figure 14b Banana, after adsorption

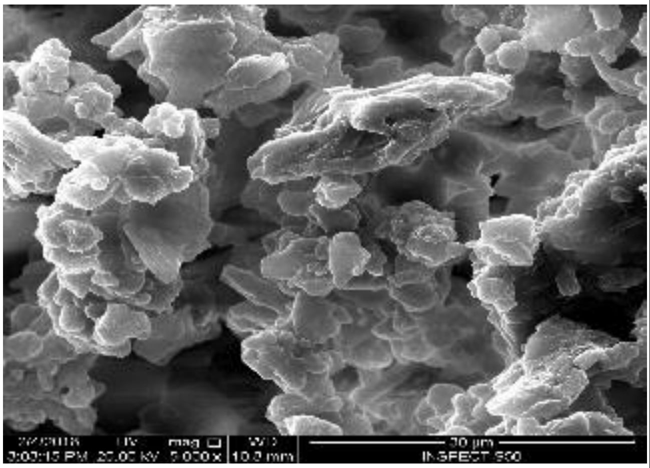


Figure 14 Pomegranate, before adsorption

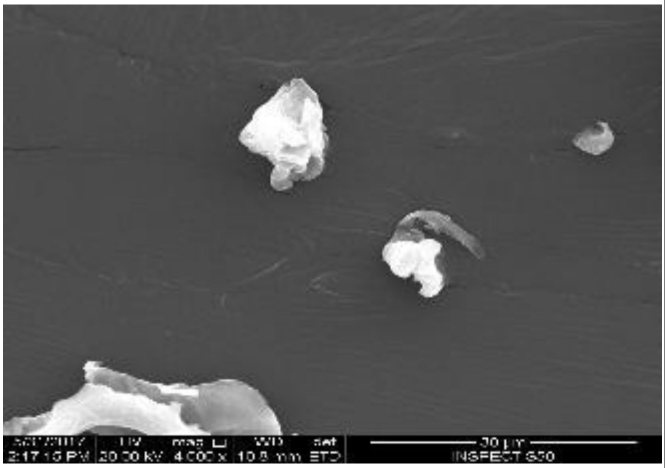


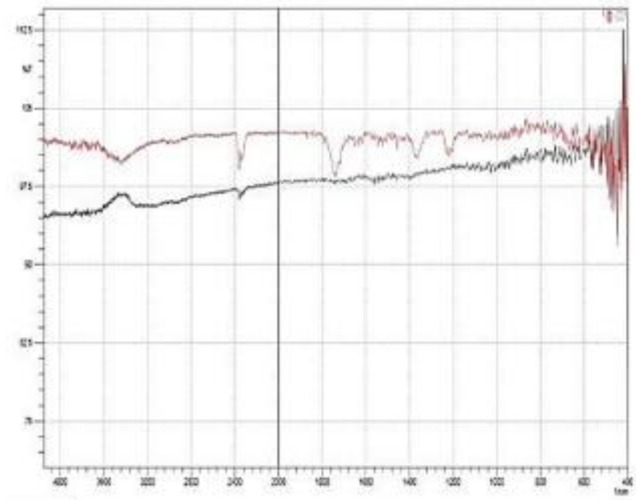
Figure 14 d Pomegranate, after adsorption

The FT-IR banana and pomegranate peel spectra before and after adsorption of zinc ions were shown in Table 5 and fig 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

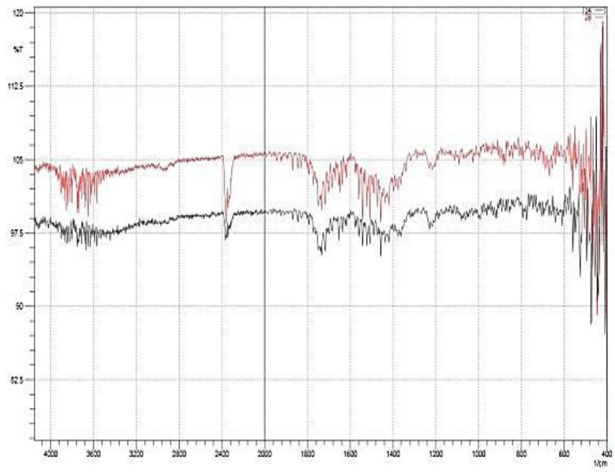
Table 5 FTIR Peak values of different nano size biosorbent

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

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 and1190 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 5)** confirmed the adsorption of zinc ions on nano-size banana and pomegranate peel [38].



Banana



Pomegranate peel

Figure 15 Spectrum of FTIR analysis from nanosized bio-sorbent before and after adsorption, with Zn^{2+} ions.

4.1. Gas Chromatography–Mass Spectrometry (GC–MS) analysis (analytical method):

Table 6 Some of chemical components identified in plant extract by GC–MS.

NO	Identified Compound	Molecular formula	Molecular weight	RT	% Compositions
banana peel (Musa sapientum peel)					
1	Pyrogallol	$C_6H_6O_3$	126.11	12.371	22.24
2	Cis-9-Hexadecenal	$C_{16}H_{30}O$	238.4	20.464	21.20
3	Pentadecanoic acid	$C_{15}H_{30}O_2$	242.397	18.735	18.81
4	Benzoic acid	$C_7H_6O_2$	122.12	8.139	16.04

5	Octadecanoic acid	$C_{18}H_{36}O_2$	284.48	20.703	6.18
6	Cis-9-Hexadecenoic acid	$C_{16}H_{30}O_2$	254.414	18.606	4.40
7	9-Tricosene	$C_{23}H_{46}$	322.621	20.995	2.10
8	Tetra decenoic acid	$C_{14}H_{26}O_2$	226.35	16.444	1.10
9	Ethanimidic acid	C_4H_9NO	87.12	3.124	0.89
10	1,2-Benzenedicarboxylic acid	$C_8H_6O_4$	166.13	23.797	0.96
*Pomegranate peel (*Punica granatum)					
1	2-Furancarboxaldehyde,5-(hydroxymethyl)	$C_6H_6O_3$	126.03	13.14	39.71
2	5,5-oxy-dimethylene-bis (2-furaldehyde)	$C_{12}H_{10}O_5$	234.05	23.31	11.77
3	2-Furancarboxaldehyde	$C_5H_4O_2$	96.02	3.98	9.38
4	2,5-Furandione,3-methyl-	$C_5H_4O_3$	112.02	6.46	6.66
5	Propanedioic acid ethyl-, diethyl ester	$C_9H_{16}O_4$	188.10	17.63	5.97
6	4H-pyran-4-one, 2,3-dihydro-3,5-dihydroxy16- methyl	$C_6H_8O_4$	144.04	10.6	5.58
7	2-Furancarboylic acid, methyl ester	$C_6H_6O_3$	126.03	9.11	3.59
8	1H-Indol-3-acetic acid,2-methyl	$C_{11}H_{11}NO_2$	189.08	16.15	1.69
9	9-Octadecanoic acid, methyl ester	$C_{19}H_{36}O_2$	296.27	24.26	1.64
10	9-Octadecanoic acid	$C_{10}H_{20}O_2$	172.24	24.74	1.50

The organic compounds found in banana peel (Musa sapientum peel)and *Pomegranate peel (*Punica granatum) were identified through GC–MS analysis. The molecular formula, molecular weight, retention time (RT), % compositions and probability percentage are presented in **Table 6.**

5. Conclusion

- The equilibrium adsorption is almost attained in 40 minutes.
- Zinc ion adsorption is pH-dependent since the adsorption capacity enhances via raising the pH value of the solution. Optimal pH recorded for banana and pomegranate rind is approximately 5.4
- The adsorption of Zn^{2+} by nano sized bio sorbent increases with growth in adsorbent mass due to increasing adsorption spot amount.
- The equilibrium data provided excellently in a Langmuir and Freundlich isotherm comparations.
- The results indicate that the adsorption kinetic sticks to the pseudo-second-order rate along with intra-particle dispersion as one of the rates regulating stages.
- The thermodynamic constraints of zinc adsorption reveal that the adsorption procedure endothermic, spontaneous, and accompanied by disordering at solid/solution interface.
- Surface geomorphology of nano sized bio sorbent was characterized by SEM which confirmed the experimental result.
- Since the adsorption, data are encouraging and considering that the nano sized bio sorbent have the subsidies of be really cost-efficient and easy to be prepared, thus, it may be recommended for the heavy metals elimination.
- It is possible to reuse banana and pomegranate rinds in another sorption process, which is considerable significance for financial development.

Compliance with ethical standards

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Disclosure of conflict of interest

Interesting about water treatment and removal of heavy metals using environmentally friendly materials also low cost materials

Availability of data and materials

The [table data, figures, FTIR and SEM data] data used to support the findings of this study are included within the article

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