



Removal of Ni (II) and Pb (II) ions from aqueous solutions by grapefruit (*Citrus paradisi*) Mesocarp Biomass

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ABSTRACT: The surface characteristics of *Citrus paradisi* (grapefruit mesocarp biomass) on the biosorption of Ni (II) and Pb (II) ions from aqueous solution were studied adopting a batch reactor technique. The dried grapefruit mesocarp biomass was characterized using phytochemical screening and Fourier Transform Infra – Red (FTIR) Spectroscopy. The results of the characterization revealed the presence of alkaloids, tannins, saponins, cyanogenic glycosides. Furthermore, the FTIR spectrum pattern of the biomass showed broad and sharp absorption peaks indicating the existence of functional groups like – OH, C=O, C-H, C-O, N-H, etc. The biosorption process was found to be pH, time and concentration dependent. The rate of biosorption was higher in Ni (II) ion than Pb (II) ion. The result of the equilibrium modeling showed that the biosorption process fitted well with the Freundlich isotherm equation indicating a multilayer biosorption. The mechanism of the biosorption process followed pseudo – second – order kinetic model equation with correlation coefficient (R^2) of 0.999 for Ni (II) ion and 0.991 for Pb (II) ion respectively. Thermodynamic parameters determined showed that the biosorption of Ni (II) and Pb (II) ions on the surface of the biomass was an exothermic and spontaneous process. The rate of biosorption was found to decrease with increasing temperature. The results showed that the dried grapefruit mesocarp biomass was efficient and effective in the biosorption of Ni (II) and Pb (II) ions and is recommended to be applied in wastewaters. © JASEM

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INTRODUCTION

The degradation of natural waters with several heavy metal contaminants, have been found to be emanating mostly from mining waste and industrial discharges (Baig *et al.*, 1999). These toxic materials cause problems to the entire ecosystem. Although some heavy metals are necessary for the growth of plants, aquatic lives and humans, after certain concentration, it becomes lethal to plants, microorganisms and humans.

Heavy metal pollution has become a global issue owing to the fact that it threatens human health and the ecosystem. Their presence over permissible levels in drinking water may cause adverse effects on human biochemical dynamics (Dahiya *et al.*, 2008). These metals may come from different sources such as electroplating, textile, smelting, mining, glass and ceramic industries as well as storage batteries, metal finishing, petroleum, fertilizer, pulp and paper industries (Aksu, 2001). Heavy metals are not biodegradable and tend to accumulate in living organisms (Koby, 2005). Water pollution due to

heavy metals contamination is an issue of great environmental concern (Vasudaran *et al.*, 2003).

In Nigeria today, greater percentage of its citizenry depend on treated sachet and bottled water as the major source of drinking water. Therefore, there are a lot of health related challenges coming out due the consumption of contaminated water. The effect of heavy metals on man cannot be neglected because exposure to these contaminants even at low concentration in the environment can cause severe dysfunction in the renal, reproductive and central nervous systems (Manaham, 2004).

Lead is a major harmful pollutant to the biosphere, and even trace amount of it pose a detrimental risk to human health. In the recent times, the Northern part of Nigeria has recorded over 400 deaths due to lead poisoning. Nickel on its own also has toxic effect on human, animals and plants. As a result of the increasing environmental concern for these contaminants, there has been serious interest in the removal of heavy metals from contaminated soils and waste waters. A number of technologies have been developed over the years to

remove toxic metals from water. The most important of these techniques include chemical precipitations, electro – flotation, ion – exchange, reverse osmosis and adsorption on activated carbon (Gaikward, 2004). These methods of water treatment are expensive and sometimes ineffective especially when metals are present in solution at very low concentration except for adsorption technique (Baig *et al.*, 1999).

An emerging field of interest is employing natural, agricultural and agricultural by – products as biosorbents for the removal of heavy metals from aqueous solution. Removal rates of 80% or higher can be expected with biosorption process. Biosorption is also able to achieve this removal in hours and sometimes even minutes; thereby potentially reducing or eliminating the high cost associated with other technologies (Mack *et al.*, 2007). Many agricultural wastes that are available at low cost have been reported to be capable of removing substantial amounts of metal ions from aqueous solutions (Igwe *et al.*, 2005; Gardea – Torresdey *et al.*, 2005). The exchange properties of these agricultural wastes can be attributed to the presence of carboxylic, phenolic, hydroxylic, cyano groups, etc (Babarinde *et al.*, 2013). These functional groups attract and sequester metal ions.

Grapefruit popularly known as ‘fruit from the paradisi’ (*Citrus X paradisi*) mesocarp residue possesses these chemical characteristics and it is inexpensive and environmentally friendly (Williamson, 1997).

Literature showed scanty information on the characterization and biosorptive properties of the grapefruit mesocarp. It was therefore explored in the present study as a biosorbent for the removal of heavy metals – nickel (II) and lead (II) ions from aqueous solution. The data generated was modeled using two isotherm equations namely; Langmuir and Freundlich isotherms adsorption model equations respectively. The mechanism of the biosorption process and thermodynamic quantities was evaluated.

$$q_e = C_i - C_e/M \times V \quad [1].$$

Where C_i and C_e represent initial and equilibrium concentrations of metal ions in aqueous solution respectively in mg/L, q_e is the amount of metal ion biosorbed per gram of biosorbent, M is the mass of the biosorbent in grams and V is volume of the solution in L.

On the other hand, the adsorption percentage of metal ions was calculated using the expression in equation [2] below:

MATERIALS AND METHODS

Characterization: Functional group elucidation was done on the grapefruit mesocarp biomass using Fourier Transform Infrared (FTIR) Spectrophotometer. Phytochemical screening for tannins was carried out using the method described by Evans and Trease, (2009) while glycosides, alkaloids by Sofowora, (1993) and saponins by Harborne, (1973).

Biomass preparation: Grapefruits were harvested from the farm of Mr. Ekechukwu of Elekenaowasi Obohia in Imo State. It was washed with deionized water and peeled to obtain the mesocarp. The mesocarp was air – dried, ground and sieved using 250 μm mesh size sieve. The grapefruit mesocarp was used without any chemical treatment for the sorption studies.

Preparation of the biosorbates: All the chemicals used in this study were of analytical grade. A stock solution of lead (II) and nickel (II) ions of concentration 1000 mg/L was prepared by dissolving 1.6 g of $\text{Pb}(\text{NO}_3)_2$ and 4.24 g of $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ in 1 dm^3 of distilled water. Serial dilution of the stock solution was carried out to obtain working concentrations of Pb (II) and Ni (II) ions.

Batch biosorption study: The biosorption study was determined by batch experiments. The biosorption studies were conducted at room temperature to determine the effect of pH, contact time, initial metal ion concentration, and the effect of temperature (using thermo – stated water bath). The residual metal ion concentrations of the filtrate of each metal solution were analyzed using Buck Scientific Model 210 VGP Atomic Absorption Spectrometer (AAS). All experiments were conducted for a period of 60 mins except for the contact time where the time was varied. The amount of the metal ion biosorbed per gram of the biomass is calculated using the expression in equation [1] below:

$$\text{Biosorption (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad [2].$$

Effect of pH on biosorption: The effect of pH on the biosorption of the metal ions was carried out within pH 2 – 12 for both Ni (II) and Pb (II) metal ions. This was done by adding 0.3 g of grapefruit mesocarp biomass with 50 ml of 50 mg/L metal ion solution in plastic bottles. The pH of each solution was adjusted by drop wise addition of 0.1 M HCl or 0.1 M NaOH. The plastic bottles containing the mixture were mounted on a shaker and shaken continuously for 60 mins at room temperature. The contents of the plastic bottles were filtrated through filter paper and the filtrate collected into various sample bottles for AAS analysis.

Effect of contact time on biosorption: The effect of contact time on the biosorption studies for Ni (II) and Pb (II) ions was monitored with a 50 ml of working concentration of 50 mg/L. The solution of each metal ion was transferred into a 150 ml plastic bottle, corked and labeled. An accurately weighed sample of 0.3 g of the biosorbent was added into each of the plastic bottles and shaken for time intervals of 10, 20, 30, 40, 50 and 60 mins, respectively. After each agitation time (contact time), the content of each bottle was filtered rapidly and filtrates collected into various sample bottles for AAS analysis.

Effect of initial concentration on biosorption: Batch biosorption study of metal ion was carried out using 50 ml of concentration range of 50 – 400 mg/L. This was done by adding 0.3 g of grapefruit mesocarp at pH 6. The plastic bottles containing the mixture were agitated on a shaker for 60 mins, the content of each bottle was filtered rapidly and filtrates collected into various sample bottles for AAS analysis.

Effect of temperature on biosorption: The batch biosorption process was studied at different temperatures within the range 30°C – 60°C using water bath with a regulator. This was done by adding 0.3 g of grapefruit mesocarp biomass with 50 ml of 50 mg/L of metal ion solution at pH 6. The plastic bottles were withdrawn at 60 mins from the water bath for each temperature. The contents of the plastic bottles were filtrated through filter paper and the residual metal ion concentration in solution was determined using AAS. The amount of metal ions biosorbed was calculated for each sample.

RESULTS AND DISCUSSION

Characterization: Phytochemical screening of the grapefruit mesocarp revealed the presence of tannin (0.25%), alkaloid (7.28%), saponin (23.10%) and cyanogenic glycoside (0.14 mg/kg).

The Fourier Transform Infra – Red Spectroscopy is employed to study the functional groups present in the dried mesocarp. The region of interest for determining the functional groups is the frequency region between 4000 – 1000 cm^{-1} . The spectrum generated is represented in Figure 1. The functional groups present on the mesocarp form the active sites on the biosorbent surface. The FTIR absorption bands representing various functional groups are presented in Table 1. Examination of the FTIR spectrum generated showed the presence of ionizable functional groups which are able to interact with the Pb (II) and Ni (II) ions (Pradhan and Singh, 2007; Bueno *et al.*, 2008; Sun *et al.*, 2008; Ertugay and Bayhan, 2008). Furthermore, the FTIR spectrum pattern of the biomass showed broad and sharp absorption peaks indicating the existence of functional groups like – OH, C=O, C-H, C-O, N-H, etc.

Bond	Wavenumber (cm ⁻¹)	Functional group
O-H Stretch	3450-3280	H – bonded alcohol
C-H Stretch	2926-2854	Alkanes
C=C Stretch	2223-2204	Alkynes
C=O stretch	1743.65	Saturated aliphatic esters (carbonyl group)
C=O	1710.86	Alpha, beta, unsaturated aldehydes, ketone (Carbonyl group)
N-H bend	1639-1616	Primary amines
N-O asymmetric stretch	1544-1517	Nitro compound
C-C stretch (in ring)	1440-1400	Aromatics
C-N stretch	1257.59	Aromatics amines
C-N stretch	1238-1031	Aliphatic amines
O-H bend	921.97	Carboxylic acid (carbonyl group)
C-Cl Stretch	831-761.88	Alkyl halides
C-Br stretch	617-532.35	Alkyl halides

Tab.1: FTIR spectrum characteristics of absorption bands of functional groups for grapefruit mesocarp biomass

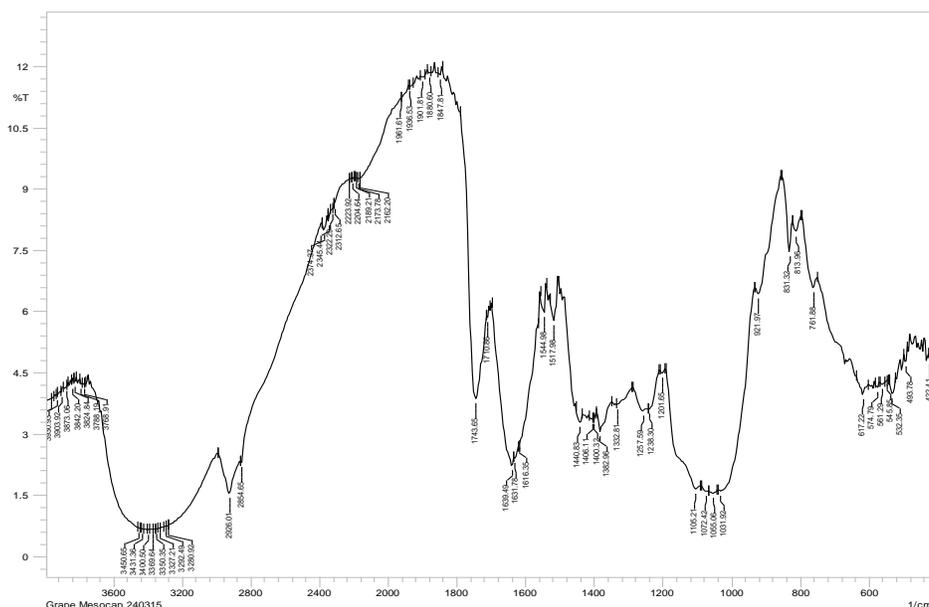


Fig.1: FTIR spectra of the dried grapefruit mesocarp

Kinetic dynamics: The kinetic dynamics of the biosorption of Ni (II) and Pb (II) ions by grapefruit biomass is presented in Figure 2. The result obtained showed that there was an initial fast uptake of the metal ions followed by a slow and constant uptake of the metal ions. This could be as a result of the precipitation of the active sites of the biomass at a given time. The optimum time of 40 mins was established contrary to the work done by Babarinde

et al., (2013) that reported the metal ions to have saturated at different contact times. The equilibrium biosorption capacity of Ni (II) ion was higher than the Pb (II) ion at the same optimum time. The differences in equilibrium biosorption capacity could be as a result of their ionic sizes. The lower the ionic size, the more it is biosorbed on the surface of the biomass. At the optimum time, 90% Ni (II) ion

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biosorption was achieved while 48% Pb (II) ion biosorption was equally achieved.

In order to propose the mechanism of biosorption of the metal ions by grapefruit biomass, several kinetic model equations were examined but only two of the models was applied due to the correlation coefficients (R^2) generated from the equilibrium time data. Pseudo – second – order and intraparticle diffusion kinetic model equations were applied. The linearized forms of the equations used are presented in Table 2.

Tab. 2: Kinetic model equations

Model	Equation	References
Pseudo – second - order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	Dela – Rosa <i>et al.</i> , 2008
Intra – particle diffusion	$\ln q_e = b \ln t + \ln k_c$	Sun <i>et al.</i> , 2008

Where k_2 is the equilibrium rate constant of pseudo – second – order biosorption process in g/mg/min, t is the time of biosorption in mins, q_e and q_t are the amounts of metal ions biosorbed at equilibrium and at a given time in mg/g, respectively, k_c is the intra – particle diffusion constant and b is the gradient of the linear plot.

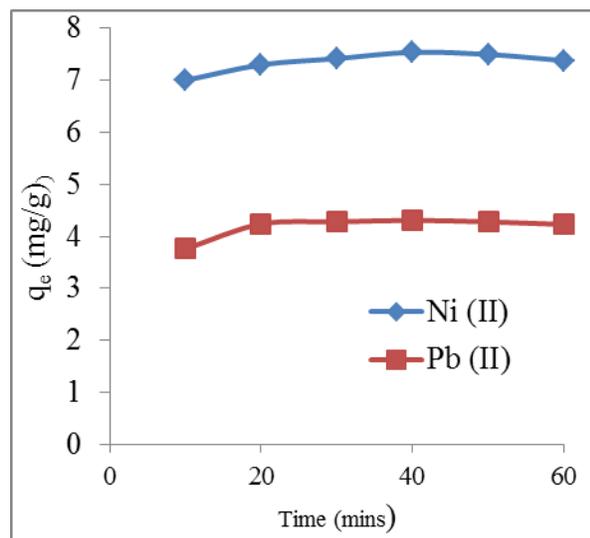


Fig. 2: Contact time biosorption isotherm using grapefruit mesocarp biomass at 298 K

The plots of $\frac{t}{q_t}$ versus t and $\ln q_e$ versus $\ln t$ are presented in Figures 3 – 4. The correlation coefficients (R^2) obtained for pseudo – second – order kinetic model equation was 0.999 and 0.971 for Ni (II) and Pb (II) ions while intra – particle diffusion model equation gave 0.586 and 0.755 for Ni (II) and Pb (II) ions respectively.

The results obtained showed that the pseudo – second – order kinetic model equation was the best model to explain the kinetic dynamics for the biosorption of Ni (II) and Pb (II) ions by grapefruit mesocarp biomass. This observation is in agreement with the work done by Babarinde *et al.*, (2012, 2013). The differences in the rate of biosorption may be accounted for in terms of their ionic size variations. The kinetic model equation parameters for pseudo – second - order are presented in Table 3 below.

Tab. 3: Pseudo – second – order parameters for the biosorption of Ni (II) and Pb (II) ions by grapefruit biomass

Metal ion	q_e (mg/g)	k_2 (g/mg/min)	R^2
Ni (II)	4.20	1.41	0.999
Pb (II)	0.80	- 0.42	0.971

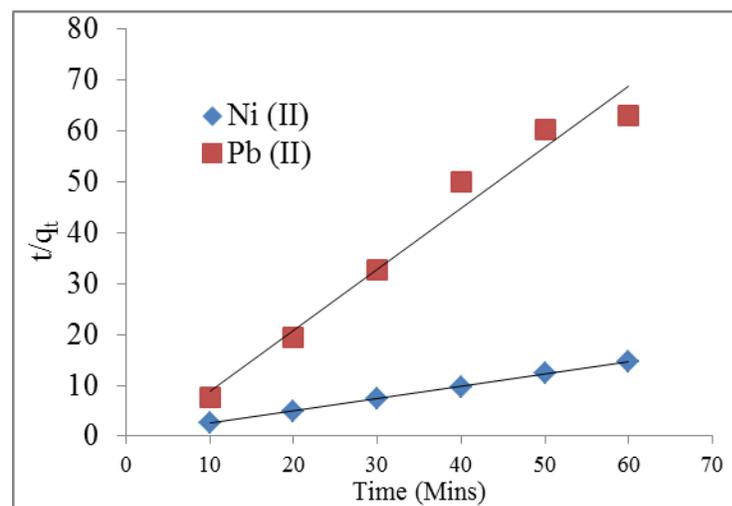


Fig. 3: Pseudo – second – order kinetic model plot for Pb (II) and Ni (II) ions biosorption

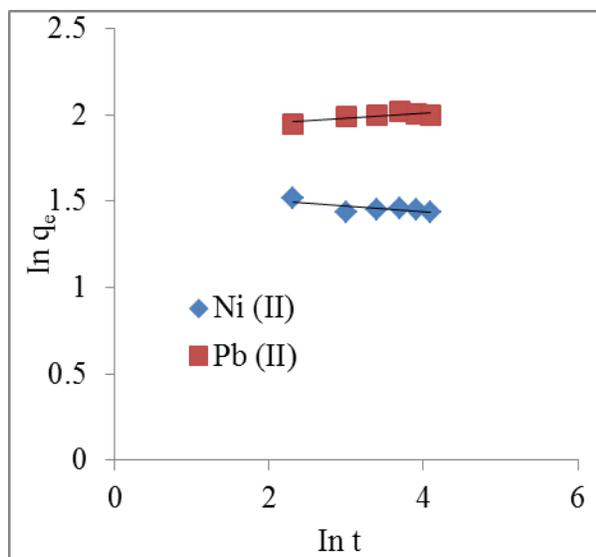


Fig. 4: Intraparticle diffusion kinetic model plot for Pb (II) and Ni (II) ions biosorption

pH dynamics: The biosorption of Ni (II) and Pb (II) ions by the grapefruit biomass was found to be pH dependent. The metal ions surface dynamics with respect to pH is presented in Figure 5. It was evident as reported by other researchers (Akar *et al.*, 2007; Babarinde *et al.*, 2013; Low and Lee, 2000) that at low pH, competition between the metal ion and the net positive charge on the biosorbent lower the rate of biosorption. However, as the pH increased i.e. from 2 – 6 for both metal ions, the rate of biosorption increased and the biosorption efficiency of 35% – 100% was achieved. This could be as a result of the deprotonation the metal binding sites on the surface of the biomass indicating a strong chemical interaction between metal ions and the functional groups on the biomass. At pH above 6, the biosorption of the metal ions by the biomass decreased. This could be as a result of saturation of the active sites of the biomass by the metal ions. At this point, precipitation of the lead (II) and nickel (II) hydroxides set in leading to constancy or in some cases a steep decrease in the rate of biosorption (Wang *et al.*, 2002).

Concentration dynamics: The initial concentration isotherm for the metal ions studied is presented in Figure 6. The biosorption of the metal ions showed a concentration dependency. The rate of biosorption increases as the concentration of the metal ions increase from 50 – 300 mg/L. It was observed that the metal ions uptake decreased above 300 mg/L. This could be as a result of the concentration gradient established by these metal ions. The result further revealed that Ni (II) ion biosorbed more than Pb (II)

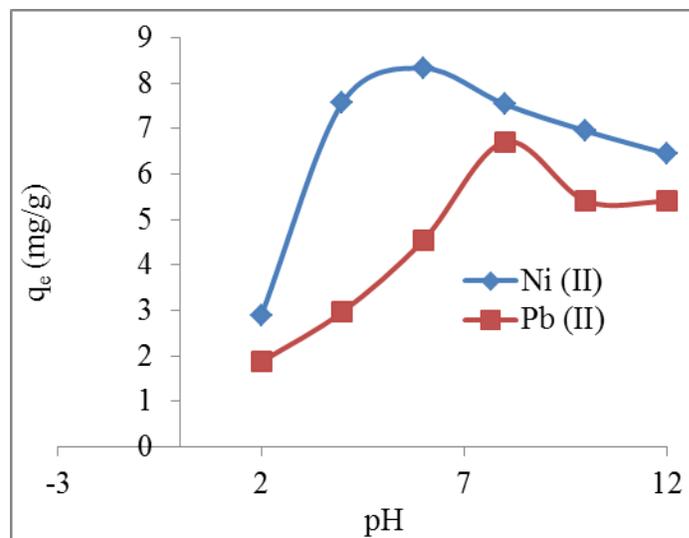


Fig. 5: pH biosorption isotherm using grapefruit mesocarp biomass at 298 K

ion at the same condition. The differences in the rate of biosorption could be due to variations in the ionic sizes as stated before. This observation is similar to the works done by Tsai and Chen, (2010).

To further propose the type of biosorption that took place, Langmuir and Freundlich isotherm equations were employed. The linearized forms of the equation were used for the plots.

For Freundlich, the equations [3] and [4] below were applied:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad [3].$$

For Langmuir, the equation below was applied:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{mo}} + \frac{1}{q_{mo}} C_e \quad [4].$$

Where q_e represents equilibrium amount biosorbed in mg/g, C_e is the equilibrium concentration in mg/L, K_F and K_L are Freundlich and Langmuir constants, $\frac{1}{n}$ is also a constant and q_{mo} represents the monolayer capacity in mg/g.

The plots of Freundlich and Langmuir are presented in Figures 7 – 8. The results showed that the correlation coefficient (R^2) obtained for Freundlich isotherm equation was higher than the Langmuir model equation. This is an indication of a multilayer biosorption existing between the metal ions and the functional groups embedded at the surface of the biom. This observation is contrary to the results of other biomass used which reported a monolayer biosorption (Ibezim – Ezeani *et al.*, 2010; Okoro and Abii, 2011). The Freundlich and Langmuir parameters are presented in Table 4.

Tab. 4: Freundlich and Langmuir parameters at 298 K

Model	Ni (II) ion	Pb (II) ion
Langmuir		
q_e (mg/g)	31.00	28.50
K_L (L/mg)	- 0.65	- 0.02
q_{mo} (mg/g)	1.10	- 7.94
R^2	0.83	0.022
Freundlich		
K_F (L/g)	0.34	0.84
n	3.53	5.81
R^2	0.91	0.67

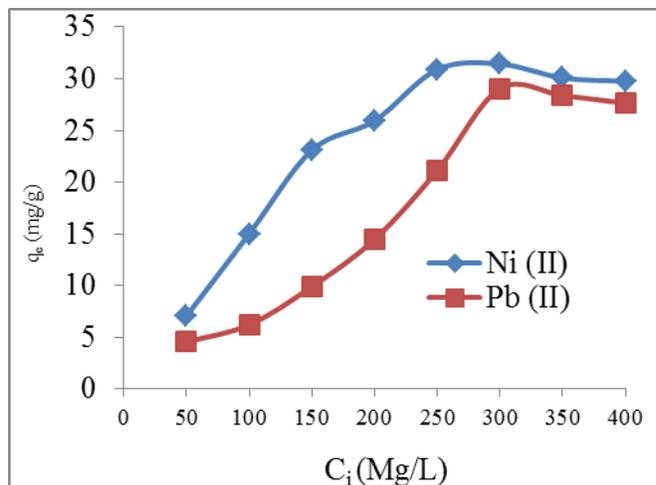


Fig. 6: Initial concentration biosorption isotherm using grapefruit mesocarp biomass at 298 K

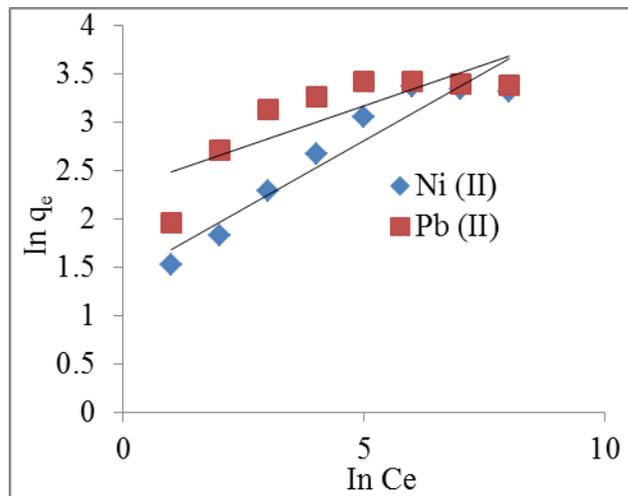


Fig. 7: Freundlich isotherm model plot for Pb (II) and Ni (II) ions biosorption

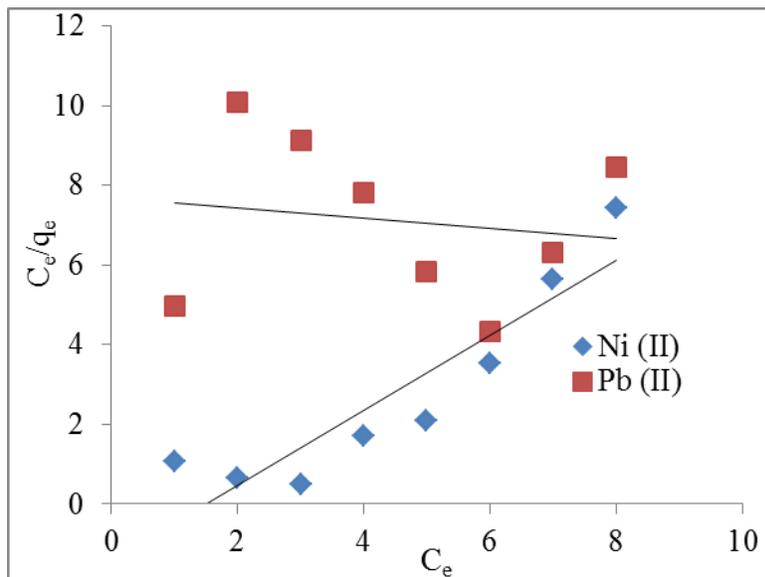


Fig. 8: Langmuir isotherm model plot for Pb (II) and Ni (II) ions biosorption

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Temperature dynamics: The variation in temperature on the biosorption of Pb (II) and Ni (II) ions is presented in Figure 9. The temperature dynamics showed that the rate of biosorption increased up to 40°C. Above this temperature, biosorption capacity decreased. This observation supports the conclusion that the biosorption process followed Freundlich isotherm model equation.

The thermodynamic parameters, the standard free energy of biosorption (ΔG^0), the standard heat of biosorption (ΔH^0), and the standard entropy of biosorption (ΔS^0) give an insight into the mechanism of biosorption process. From the Van't Hoff's equation, ΔH^0 was determined by a linear regression between $\ln K_F$ and $\frac{1}{T}$ (Zhao and Mu, 1999) as represented in Figure 10. The ΔG^0 and ΔS^0 was evaluated by using the equations [5] – [7] below:

$$\ln K_F = \frac{-\Delta H^0}{RT} + C \quad [5]. \quad \Delta G^0 = -RT \ln K_F \quad [6].$$

$$\Delta G^0 = \Delta H^0 + T\Delta S^0 \quad [7].$$

The thermodynamic parameters obtained are listed in Table 5. The thermodynamic evaluations showed that the high values of the enthalpy changes support the fact that the biosorption of Ni (II) and Pb (II) ions obeyed Freundlich biosorption isotherm model having $\Delta H^0 > 40$ kJ/mol (Rauf and Tahir, 2000). The high values of entropy changes suggest that the rate of disorderliness was high in the biosorption process and it further revealed that the rate of biosorption decreased as the temperature increased. The degree of disorderliness was higher in Ni (II) ion than Pb (II) ion. In addition, the values of the free energy change for both metal ions showed that the biosorption process was spontaneous (i.e. – 0.83 to – 4.52). The result further revealed that the values of the free energy changes decrease as the temperature increases. This observation further buttressed the fact that the rate of biosorption of these metal ions do not increase with temperature. This further supports that the biosorption process is endothermic having positive values of enthalpy changes.

Tab. 5: Thermodynamic parameters for biosorption of Ni (II) and Pb (II) ions

Metal ion	ΔH^0 (kJ/mol)	ΔS^0 (J/mol) @ 303 K	313 K	323 K	333 K	ΔG^0 KJ/mol @ 303 K	313 K	323 K	333 K	R ²
Ni (II)	+ 95	+ 316	+ 311	+ 305	+ 298	- 0.83	- 2.38	- 3.44	- 4.34	0.996
Pb (II)	+ 79	+ 268	+ 262	+ 256	+ 251	- 2.10	- 2.96	- 3.79	- 4.52	0.991

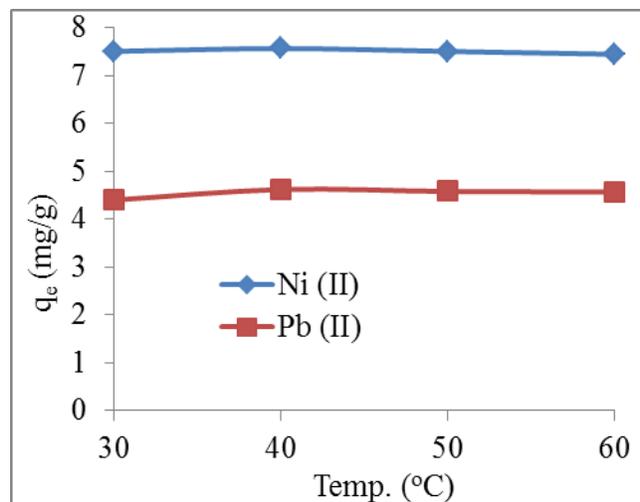


Fig. 9: Temperature biosorption isotherm using grapefruit mesocarp biomass

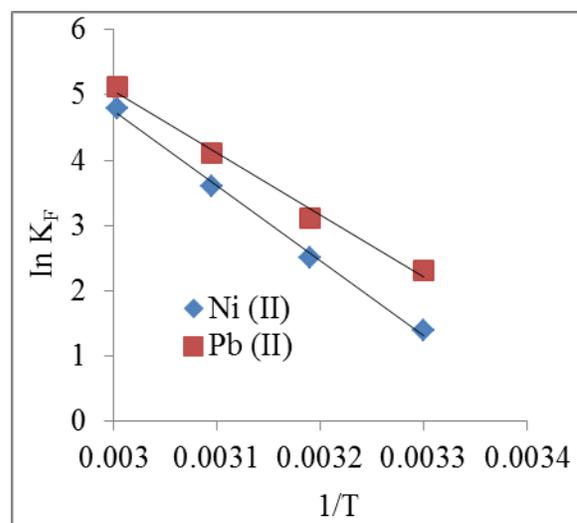


Fig. 10: Thermodynamic plot for Pb (II) and Ni (II) ions biosorption

Conclusion: The phytochemical screening of the dried biomass revealed the presence of saponins, alkaloids, tannins and cyanogenic glycoside. The FTIR spectrum pattern of the biomass showed broad and sharp absorption peaks indicating the existence of functional groups like – OH, C=O, C-H, C-O,

N-H, etc. The biosorption process was found to be pH, concentration and time dependent at 298 K with Ni (II) ion having higher biosorption capacity than Pb (II) ion. The biosorption process revealed a multilayer biosorption. The mechanism of the biosorption process followed a pseudo – second –

order kinetic model. Thermodynamic evaluations showed that the biosorption process was spontaneous and endothermic. The rate of disorderliness was found to decrease with increase in temperature. *Citrus paradisi* was found to be efficient and effective for the biosorption of Ni (II) and Pb (II) ions from aqueous solution.

Competing interest: The authors declare that there is no conflict of interests regarding the publication of this paper.

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