

Sequestration of Pb(II), Cd(II) and Ni(II) Ions from Aqueous Solution Using EDTA Modified *Citrus sinensis* Mesocarp

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Abstract: The potential of *Citrus sinensis* mesocarp as an adsorbent to remove Pb(II), Cd(II) and Ni(II) ions from aqueous solution was explored. The residual concentrations were determined using atomic absorption spectrophotometer (AAS). The effect of contact time, pH, initial metal ion concentration and temperature were studied. The study showed that the equilibrium contact time for the biosorption process was 100 minutes for all three metals and the maximum adsorption for Ni(II), Cd(II) and Pb(II) ions occurred at pH of 5, 6 and 7 respectively. The percentage removal of the metal ions increased with increase in temperature and initial metal ion concentration. The kinetics study of the biosorption process exhibited pseudo-second order kinetic models and the equilibrium data fitted well to Langmuir isotherms. The thermodynamic study revealed that the reaction was not spontaneous as Gibbs free energy (ΔG°) and standard entropy (ΔS°) values were negative for all the metal ions, but it was feasible and endothermic in nature as standard enthalpy (ΔH°) was positive. This study has demonstrated that *Citrus sinensis* mesocarp could be efficiently and effectively used to remove the metal ions from aqueous solution

Key words: Equilibrium • Biosorption • Aqueous solution • *Citrus sinensis* • Mesocarp

INTRODUCTION

The treatment of polluted industrial wastewater remains a topic of global concern in the management of water resources. Water pollution by potentially toxic elements (PTE) as a consequence of rapid industrialization as well as technological advancement continues to rise on daily basis. This may be due to lack of adequate legislation. PTE's are stable and known to be tenacious environmental contaminants, Since they are not biodegradable and cannot be destroyed, their release into immediate environment pose a significant threat because of their acute toxicity [1].

Several episodes due to metal contamination in aquatic environment have recently increased the awareness about their toxicity. The recent lead poisoning in Zamfara State, North Western, Nigeria which led to loss of lives [2] and "Itai-Itai" disease (a disease characterised

by excruciating pain in the bone) in Japan due to cadmium toxicity could attest to the detrimental effect of these metals [3].

Numerous physico-chemical methods such as: Liquid-liquid extraction, precipitation, floatation, ion exchange, reverse osmosis, resin chelation, membrane related process, coagulation, solid-liquid extraction and electrochemical technique have been developed over the years for the removal of potentially toxic elements from industrial wastewater [4, 5, 6, 7]. These methods have certain limitations such as high capital and operational costs, incomplete metal removal, generation of toxic sludge and high reagent and energy requirements.

A new emerging method of treating contaminated water considered in this study is biosorption. This process provides an attractive alternative treatment, due to the availability, affordability and eco-friendliness of the adsorbent materials [8, 9]. Quite a large numbers of

agricultural wastes have been used as adsorbent to remove potentially toxic elements from aqueous solution in the literature among them were Maize leaf [10], Pomegranate peel [11], *Chrysophyllum albidium* shell [12], Mangrove barks (*Rhizophora apiculata*) [13], Mango biomass [14], *Blighia sapida* pod [15], Banana (*Musa acuminata*) leaves [16].

Recently, Nigeria has witnessed tremendous increase in annual production of Orange (*Citrus sinensis*) due to its nutritional value and richness in vitamin C. The consumption rate by the populace continues to increase on daily basis as a consequence of benefits derived from it. Large volumes of its wastes are being generated and as such constitute environmental nuisance due to lack of proper waste disposal system. A critical review of the literature showed that there is little or no information as regards the suitability of using EDTA modified *Citrus sinensis* mesocarp to sequester Pb(II), Cd(II) and Ni(II) ions from aqueous solution. It is on this basis that this research was conducted so as to develop an adsorbent from Orange mesocarp for the removal of selected potentially toxic elements from aqueous solution.

MATERIALS AND METHODS

Sample Collection: The (*C. sinensis*) Mesocarps of orange were randomly collected from different locations within Minna, Niger state in the month of April, 2012. A composite sample was made from where the representative samples were chosen for sorption studies.

Sample Pre-Treatment: The mesocarps were properly rinsed with deionized water to remove sand and debris and then sun dried for two weeks and ground to fine powder using mortar and pestle. The sample was then defatted for 72 hours and later sieved through a 100 μm mesh size sieve. The sample was rinsed with deionized water to remove colouration and then modified with 1M EDTA. Modification process was carried out by adding 300 cm^3 of 1M solution of EDTA into the sample and stirred to form a homogenous mixture. It was left to stand for 6 hours and then rinsed with deionized water and sun dried.

Preparation of Aqueous Solution: The stock solution were prepared by dissolving 1.6, 2.76 and 4.02 g of analytical reagent of $\text{Pb}(\text{NO}_3)_2$; $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 1000 cm^3 volumetric flask and diluted with

deionized water to the mark. This gave a concentration of 1000 ppm. A concentration of 100 ppm was prepared from the 1000 ppm by measuring 10 cm^3 of solution into a 100 cm^3 volumetric flask and diluting it with deionized water to the mark. Various concentrations of working solutions; 5, 10, 20, 30, 40 and 50 ppm were also prepared by sequential dilution of the 100 ppm solution.

Batch Adsorption Experiment

Effect of pH: This was determined by dissolving 0.5 g of sample each in 30 cm^3 of the initial concentration of 5 mg/l metal ion solution in different conical flasks. The pH of each solution in the flasks was adjusted to values of 1, 2, 3, 4, 5, 6, 7 and 8 by adding 1M HNO_3 or 1M NaOH solutions. Then the mixture was agitated in a shaker for 45 minutes then filtered and the filtrate was analysed using Atomic Adsorption spectrophotometer (AAS) (Perkin Elmer; analyst 200) to determine its residual concentration.

Effect of Contact Time: 0.5 g of modified sample each was mixed with 30 cm^3 solution of the initial concentration of 5 mg/L in a corked conical flask. The mixture was shaken constantly in mechanical shaker for the time periods of 20, 40, 60, 80, 100 and 120 minutes at a speed of 300 rpm. At the end of each contact time, the mixture was filtered and the filtrate was analysed using Atomic Adsorption spectrophotometer (AAS) to determine its residual concentration.

Effect of Initial Metal Ion Concentration: 0.5 g of modified sample each was mixed with 30 cm^3 solution of initial concentration of 10, 20, 30, 40 and 50 mg/l. The mixtures were shaken constantly in a shaker at 300 rpm for 100 minutes for Ni (II), Cd (II), Pb (II) ions. After 100 minutes, the mixtures were filtered and analysed using Atomic Adsorption Spectrophotometer (AAS) to determine its residual concentration.

Effect of Temperature: This was determined by dissolving 0.5 g of sample in 30 cm^3 of the initial metal ion concentration of 10 mg/l in different beakers. The beakers were placed in a water bath and the temperature of each solution was adjusted to ranges of 20, 40, 60, 80 and 100°C by regulating the temperature of the water bath. The solutions were allowed to stand at each temperature range for 100 minutes then filtered and the filtrate analysed using Atomic Adsorption Spectrophotometer (AAS) to determine its residual concentration.

Data Analysis: The percentage removal of the metal ions from aqueous solution was evaluated using the following equation;

$$\% \text{ Rem} = (C_i - C_e) / C_i \times 100\%$$

where C_i is the initial metal ion concentration (mg/l) and C_e is the final metal ion concentration. The results are shown in the tables below.

The adsorptive capacity of heavy metal ions per unit of adsorbent was determined using the following equation;

$$q = V(C_i - C_e) / M$$

where q is the metal uptake, V is the volume of metal ion solution (cm^3), C_i is the initial metal ion concentration in solution (mg/l), C_e is the final metal ion concentration in solution and M is the dry weight of adsorbent (g). The results are shown in the tables below.

Adsorption Isotherm: Two adsorption isotherms such as Langmuir and Temkin model were used to describe the sorption data.

Langmuir Isotherm: The Langmuir adsorption isotherm model was used to describe the sorption data and expressed as;

$$q_e = (q_m K_a C) / (1 + K_a C_e)$$

It could be linearized as follow to give;

$$1/q_e = 1/q_m + (1/K_a q_m) / C_e$$

where q_m and K_a are the Langmuir constants.

The isotherm coefficients were determined by plotting $1/q_e$ against $1/C_e$.

Temkin Isotherm: Temkin adsorption isotherm model was also used to describe the sorption data and expressed as;

$$q_e = \ln A + B \ln C_e$$

where q_e is the amount adsorbed at equilibrium and C is the equilibrium concentration.

The isotherm coefficients were determined by plotting q_e against C_e .

Adsorption Kinetics: The Pseudo-first order kinetics rate law is given as;

$$dq_t/dt = k_1 (q_e - q_t)$$

on integration, it gives

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

A plot of $\text{Log} (q_e - q_t)$ against time t , was made and values of k_1 and q_e were obtained from the slope and intercept respectively.

The pseudo-second order kinetics rate equation is given as;

$$dq_t/dt = k_2 (q_e - q_t)^2$$

Its integrated form is;

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

A plot of t/q_t against time t gives $1/q_e$ as slope and $1/k_2 q_e^2$ as intercept from which k_2 can be obtained.

Thermodynamics Determination: The thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were estimated using the relation below;

$$\begin{aligned} \Delta G^\circ &= -RT \ln K_c \\ \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \\ \ln K_c &= (\Delta S^\circ / R) - (\Delta H^\circ / RT) \end{aligned}$$

where R is the universal gas constant (8.314 J/mol.K), T is the temperature in Kelvin, K_c is the equilibrium constant.

The value of K_c was obtained from the relation below;

$$K_c = C_{ad} / C_e$$

where C_{ad} is the concentration of the metal ion adsorbed and C_e is the initial metal ion concentration.

A plot of ΔG against $T(K)$ gives ΔS as slope and ΔH as intercept.

RESULTS AND DISCUSSION

It was observed that at pH of 1, more of Pb ions were adsorbed than Cd and Ni at pH of 2, more of Cd and Pb ions were adsorbed than Ni ions, at pH of 3 and 4, more of Pb and Cd ions were adsorbed than Ni ions, at pH of 5, more of Cd and Pb ions were adsorbed than Ni ions, at pH of 6, more of Cd and Pb ions were adsorbed than Ni ions, at pH of 7, more of Pb and Cd ions were adsorbed

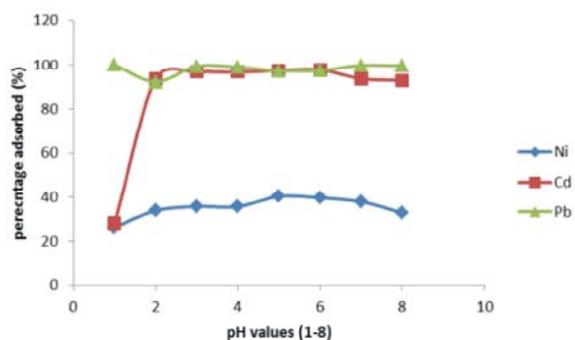


Fig. 1: Effect of variation of pH on biosorption of Ni(II), Cd(II) and Pb(II) ions by *Citrus sinensis* mesocarp.

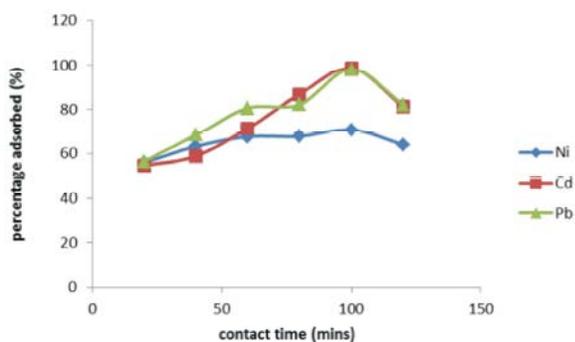


Fig. 2: Effect of variation of contact time on biosorption of Ni(II), Cd(II) and Pb(II) ions by *Citrus sinensis* mesocarp.

than Ni ions and at pH of 8, more of Pb and Cd ions were adsorbed than Ni ions. As pH increased from 3 to 4, the percentage removal of Pb, Cd and Ni ions remained the same.

From Figure 1, it was observed that at 20 minutes, more of Pb>Ni>Cd ions (56.4>55.8>54.6) was adsorbed, at 40 minutes more of Pb>Ni>Cd ions (68.4>63.2>58.8) was adsorbed, at 60 minutes more of Pb>Cd>Ni ions (80.6>71.4>67.6) was adsorbed, at 80 minutes more of Cd>Pb>Ni ions (86.8>82.2>67.8) was adsorbed, at 100 minutes more of Cd>Pb>Ni ions (98.4>98.0>70.8) was adsorbed and at 120 minutes more of Pb>Cd>Ni ions (82.0>81.2>64.0) was adsorbed.

Effect of pH: The pH of the solution has a significant impact on the uptake of toxic metals, since it determines the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate. The effect of pH on the biosorption of Pb(II), Cd(II) and Ni(II) ions by *Citrus sinensis* mesocarp shown in Figure 1. The minimum removal of the metal ions observed at low pH of 1-2 could be attributed to the protons competing with metal ions

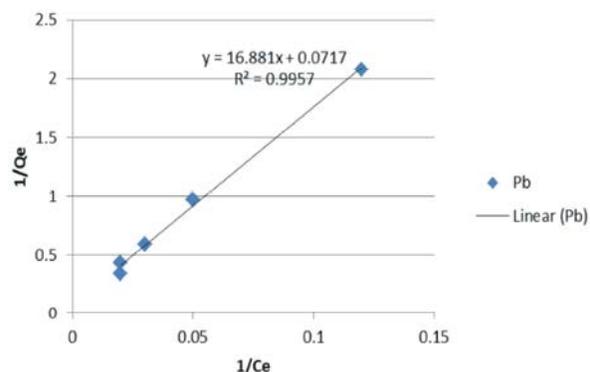


Fig. 1: Langmuir isotherm for the biosorption of Pb(II) ion by *Citrus sinensis* mesocarp.

for active sites. Meaning that there was a higher H⁺ concentration and so the adsorbent surface becomes more positively charged, thus reducing the attraction between adsorbent and metal ions. It was observed that the percentage removal of the metal ions increased with increase in pH value. But as pH increases, there is availability of more negatively charged surface thus reducing competition between proton and metal ions and facilitating greater metal uptake. Also, the improved removal levels of Pb(II) ion and other metal ions as result of EDTA modification may be ascribed to the chemical reaction of the metal ions with the EDTA on the mesocarp. More so, the highest adsorption for Ni(II) ions occurred at pH of 5 and as pH increased further, adsorption reduced. This is in line with what was reported by Rozaini *et al.* [13] who studied modified mangrove barks to optimize the removal of Ni and Cu ions. The highest adsorption for Cd(II) and Pb(II) ions occurred at pH of 6 and 7 respectively. Further increase in pH later led to decrease in adsorption. Similar result was obtained when effect of pH on sorption of Cd(II), Pb(II), Ni(II) and Cr(II) ions by unmodified African white star apple were studied by Onwu and Ogah, [12].

Effect of Contact Time: The result of the effect of contact time on the biosorption of Pb(II), Cd(II) and Ni(II) ions by *Citrus sinensis* mesocarp is shown in Figure 2. For an initial metal ion concentration 5 ppm, there was progressive increase in the percentage of Pb(II), Cd(II) and Ni(II) ions removed as contact time increased from 20 to 100 minutes, this may be attributed to the availability of active sites. But as time increased further to 120 minutes, there was decrease in the percentage removed, this implies that equilibrium was attained at 100 minutes and the adsorption sites became saturated to maximum

Table 1: The effect of variation of metal ion concentration on adsorption of Pb(II), Cd(II) and Ni(II) ions

Concentration	Amount of metal ions adsorbed (mg/30cm ³)		
	Pb(II)	Cd(II)	Ni(II)
10	9.54	9.26	9.07
20	19.57	19.33	19.08
30	31.08	30.03	27.57
40	39.45	36.35	35.35
50	46.67	47.06	45.22

adsorptive capacity, further increase in time resulted into desorption. The percentage removal at equilibrium time of 100 minutes for Pb(II), Cd(II) and Ni(II) ions were 98.0%, 98.4% and 70.8% respectively. This study showed that *Citrus sinensis* mesocarp was more efficient for the adsorption of Cd(II) and Pb(II) ions than Ni(II) ions. This observation is similar to what was reported by Shukla and Pai, [17].

Effect of Initial Metal Ion Concentration: The result of the effect of initial metal ion concentration on the biosorption of Pb(II), Cd(II) and Ni(II) ions by *Citrus sinensis* mesocarp showed in Table 1 revealed that the biosorption was biphasic, first the initial fast phase occurs at lower concentrations when the surface area of the adsorbent was higher than that of the metal ions present in solution. Subsequently slow phase occurs at higher concentrations due to the need of metal ions to diffuse into the biomass surface by intraparticulate diffusion as reported by Liu *et al.* [18] and Babarinde *et al.* [16]. It was observed that as the metal ions concentration increases, the percentage removal by the substrates also increases. This increase could be explained in terms of higher availability of metal ion for sorption at higher concentration [19]. This finding corroborated the views expressed by several researchers Okieimen and Onyenkpa, [20], Asubiojo and Ajelabi, [21], Babarinde *et al.* [22], Choi *et al.* [23] and Elaigwu *et al.* [24].

Adsorption Isotherms: The experimental data obtained for the effect of initial metal ion concentration on the biosorption of Pb(II), Cd(II) and Ni(II) ions was applied to Langmuir and Temkin adsorption isotherm models as shown in Figure 2-6. The results for the Langmuir and Temkin isotherm constants were displayed in Table 2 and 3. The correlation coefficient for Pb(II), Cd(II) and Ni(II) for Langmuir model was higher than Temkin model, also the R_L values were in the range of 0-1 so the biosorption process was favourable for all the metals. Based on the

Table 2: Langmuir isotherm constants for the biosorption of Pb(II), Cd(II) and Ni(II) ions by *Citrus sinensis* mesocarp.

Metal ion	K_L (mg/l)	R^2	q_{max} (mg/g)	R_L
Pb(II)	4.24×10^{-3}	0.9957	13.94	0.702
Cd(II)	2.32×10^{-3}	0.9955	25.77	0.977
Ni(II)	1.74×10^{-3}	0.9957	33.44	0.982

Table 3: Temkin isotherm constants for the biosorption of Pb(II), Cd(II) and Ni(II) ions by *Citrus sinensis* mesocarp.

Metal ion	A	B	R^2
Pb(II)	3.6799	-2.4379	0.9375
Cd(II)	4.1849	-2.8641	0.9447
Ni(II)	4.102	-2.7993	0.9436

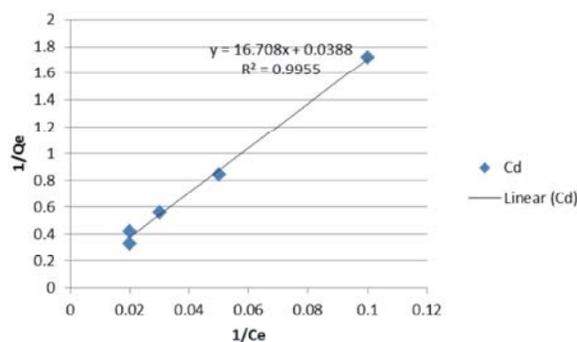


Fig. 2: Langmuir isotherm for the biosorption of Cd(II) ion by *Citrus sinensis* mesocarp.

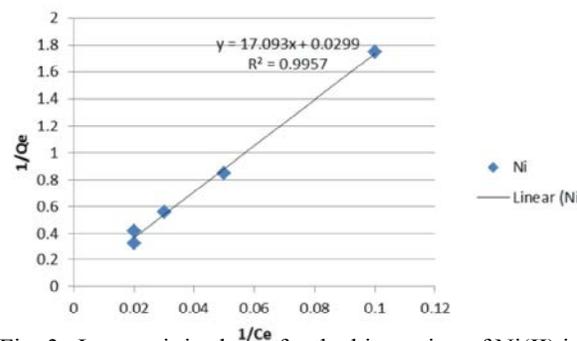


Fig. 3: Langmuir isotherm for the biosorption of Ni(II) ion by *Citrus sinensis* mesocarp.

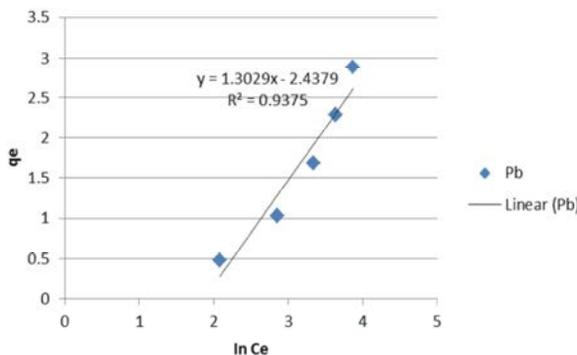


Fig. 4: Temkin isotherm for the biosorption of Pb(II) ion by *Citrus sinensis* mesocarp.

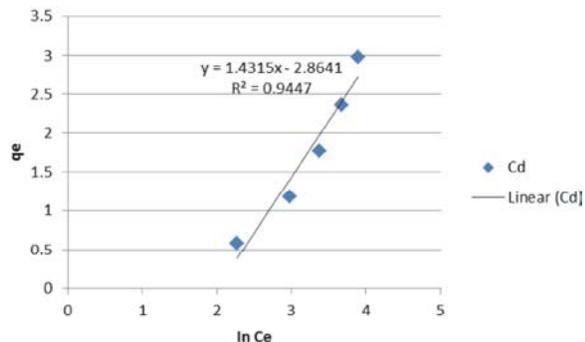


Fig. 5: Temkin isotherm for the biosorption of Cd(II) ion by *Citrus sinensis* mesocarp.

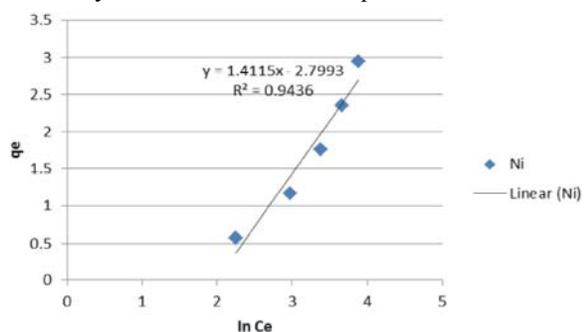


Fig. 6: Temkin isotherm for the biosorption of Ni(II) ion by *Citrus sinensis* mesocarp.

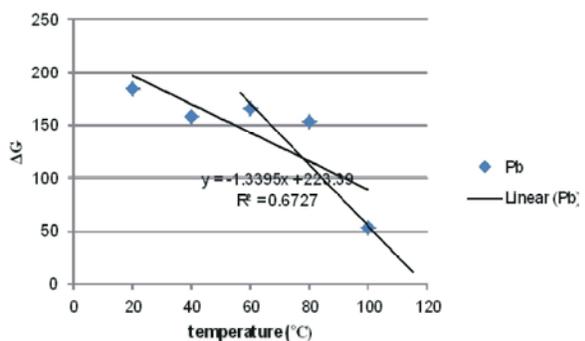


Fig. 7: Thermodynamics model for biosorption of Pb(II) ions by *Citrus sinensis* mesocarp.

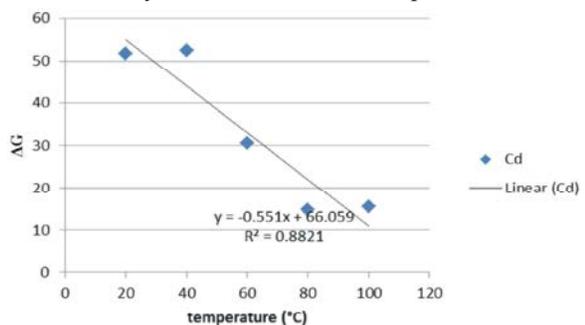


Fig. 8: Thermodynamics model for biosorption of Cd(II) ions by *Citrus sinensis* mesocarp.

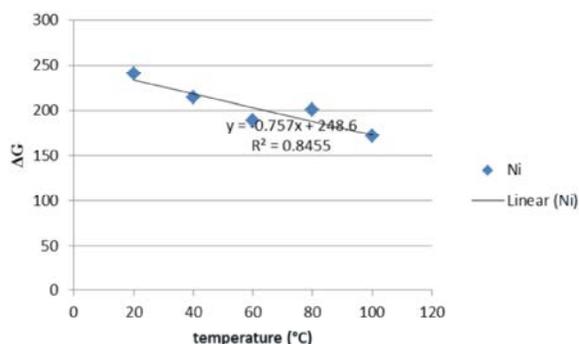


Fig. 9: Thermodynamics model for biosorption of Ni(II) ions by *Citrus sinensis* mesocarp.

obtained correlation coefficient (R^2), the experimental data was better fitted to Langmuir isotherm model. This means that the biosorption of the metal ions was chemisorption with monolayer coverage. Also, the homogenous energetic distribution of active sites was accompanied by interactions between biosorbed molecules. This is in line with the observation made by Bueno *et al.* [25].

Effect of Temperature: The effect of temperature on the adsorption of Pb(II), Cd(II) and Ni(II) ions by *Citrus sinensis* mesocarp was studied and the result showed that the percentage removal of Pb(II), Cd(II) and Ni(II) ions increased with increase in temperature from 20°C to 100°C. And at the maximum temperature of 100°C, biosorption of the metal ions was in the order of Cd(II)>Pb(II)>Ni(II) ions. This was because high temperature reduces the thickness of the outer surface of the adsorbent and increases the number of pores present and as a result, the metals ion adsorbed easily unto the surface of the adsorbent. This corroborated with the statement of Aksu and Tezer [26] that, the rate of biosorption of reactive dyes on the green algae *Chlorella vulgaris* increased with increasing temperature.

Thermodynamic Studies: Thermodynamic parameters such as standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated from the temperature data obtained from the biosorption of Pb(II), Cd(II) and Ni(II) ions on *Citrus sinensis* mesocarp. The values of the different parameters were presented in Tables 3 and 4. The positive value of ΔG° for the biosorption of Pb(II), Cd(II) and Ni(II) ions showed that the reaction was not spontaneous but feasible. The positive value of ΔH° indicated that the biosorption was endothermic in nature. Also, the positive value of ΔH° indicates the presence of

Table 4: Thermodynamic parameters for the biosorption of Pb(II), Cd(II) and Ni(II) ions by *Citrus sinensis* mesocarp.

Metal ion	ΔS° (J/mol/K)	ΔH° (Kj/mol)	R ²	ΔG° (Kj/K)
Pb(II)	-1.3395	223.39	0.6727	631.9
Cd(II)	-0.551	66.05	0.8821	234.1
Ni(II)	-0.757	248.6	0.8455	479.4

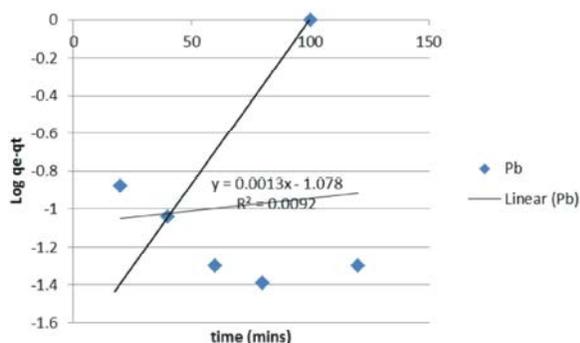


Fig. 10: Pseudo-First order for biosorption of Pb(II) ions by *Citrus sinensis* mesocarp.

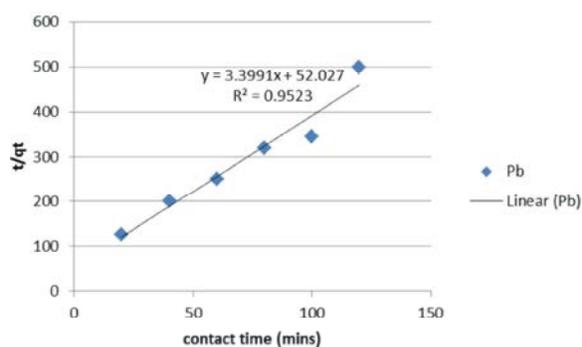


Fig. 13: Pseudo-Second order for biosorption of Pb(II) ions by *Citrus sinensis* mesocarp.

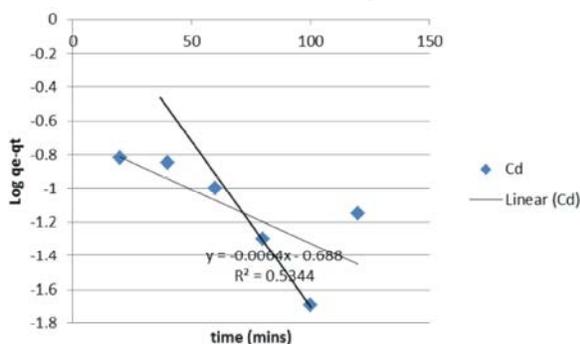


Fig. 11: Pseudo-First order for biosorption of Cd(II) ions by *Citrus sinensis* mesocarp.

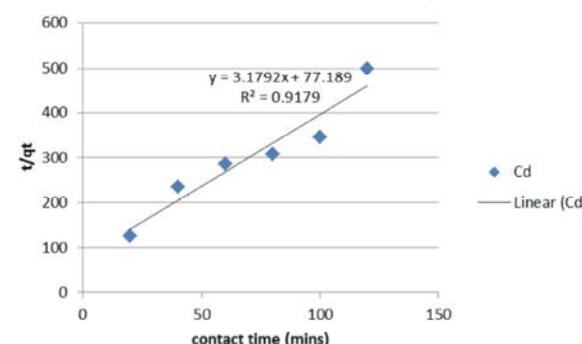


Fig. 14: Pseudo-Second order for biosorption of Cd(II) ions by *Citrus sinensis* mesocarp.

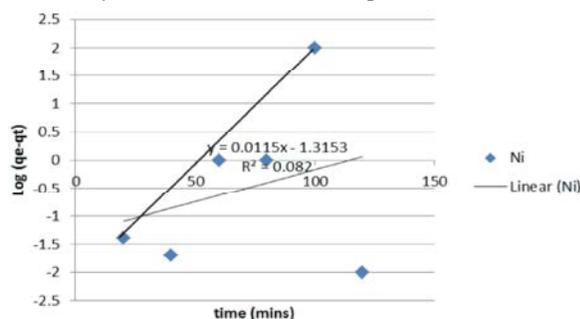


Fig. 12: Pseudo-First order for biosorption of Ni(II) ions by *Citrus sinensis* mesocarp.

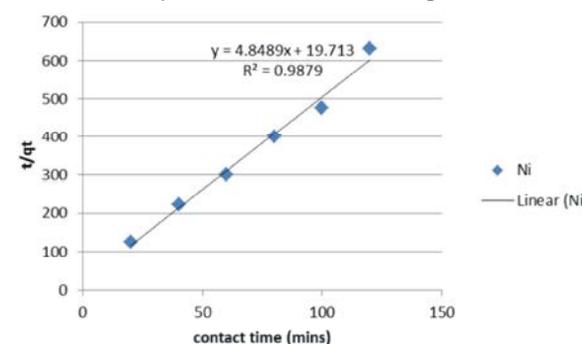


Fig. 15: Pseudo-Second order for biosorption of Ni(II) ions by *Citrus sinensis* mesocarp.

an energy barrier in the biosorption process. The negative value of ΔS° revealed that there was a decrease in the degree of disorderliness or randomness at the adsorbent-adsorbate interface during the biosorption of Pb(II), Cd(II) and Ni(II) ions on *Citrus sinensis* mesocarp. This is in line with what was reported by Babarinde *et al.* [10] and Babarinde *et al.* [16].

Adsorption Kinetics: The mechanism of the biosorption of Pb(II), Cd(II) and Ni(II) ions was tested using pseudo-first order [27] and pseudo-second order [28] kinetic models. The plot of pseudo-first order and pseudo-second order models shown in Figure 10-15 for the biosorption process by *Citrus sinensis* mesocarp.

Table 5: Pseudo-first order constants for the biosorption of Pb(II), Cd(II) and Ni(II) ions by *Citrus sinensis* mesocarp.

Metal ion	K_1 (g/mg/min)	q_e (mg/g)	R^2
Pb(II)	2.9×10^{-3}	0.083	0.0092
Cd(II)	14.7×10^{-3}	0.205	0.5344
Ni(II)	26.4×10^{-3}	0.048	0.082

Table 6: Pseudo-second order constants for the biosorption of Pb(II), Cd(II) and Ni(II) ions by *Citrus sinensis* mesocarp.

Metal ion	K_2 (g/mg/min)	q_e (mg/g)	R^2
Pb(II)	0.228	0.29	0.9523
Cd(II)	0.134	0.31	0.9179
Ni(II)	1.268	0.20	0.9879

The correlation coefficients (R^2) values were found to be highest for the pseudo-second order kinetic equation than for the pseudo-first order as shown in Table 5 and 6. The plot for the pseudo-second order model was linear as the R^2 value was approximately equal to 1 for all three metal ions. So the sorption of Pb(II), Cd(II) and Ni(II) ions could be best explained using the pseudo-second order kinetic model. The rate of sorption of the metal ions was in the order Ni(II)>Pb(II)>Cd(II) which may be due to differences in hydrated ionic sizes of the ions in solution. This is line with what was reported by Babarinde *et al.* [16].

CONCLUSION

The following conclusions can be made from this study,

- Contact time of adsorption was found to occur at 100 minutes for all three metal ions.
- Pseudo-second order kinetics model can be used to describe the binding of Pb(II), Cd(II) and Ni(II) ions on *Citrus sinensis* mesocarp.
- The biosorption data fitted the Langmuir isotherm model.
- The biosorption process was feasible and endothermic in nature but not spontaneous.

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