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Equilibrium, Kinetic, Thermodynamic and Thermal Stability Studies on Sorption of Ni (II) ions from Aqueous Solution using Dead Biomass of Fresh Water Green Algae *Cosmarium panamense*

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ABSTRACT

This study investigated biosorption of Ni(II) ion by fresh water dead algal biomass Cosmarium panamense from aqueous solution. The data showed that the maximum pH (pHmax) for efficient sorption of Ni(II) was 6 at which evaluated biosorbent dosage, initial concentrations of Ni(II) and sorption time were 0.1 g/50mL, up to 20 mg/L and 720 min, respectively. The experimental results were analyzed in terms of Langmuir and Freundlich isotherms. The Langmuir isotherm model fitted well to data of Ni(II) biosorption by Cosmarium panamense biomass as compared to the model of Freundlich. The kinetic studies showed that the sorption rates could be described better by a second order expression than by a more commonly applied Lagergren equation. The magnitude of the Gibbs free energy values indicates spontaneous nature of the sorption process. Due to its outstanding Ni(II) uptake capacity, Cosmarium panamense biomass proved to be an excellent biomaterial for accumulating Ni(II) from aqueous solutions.

Keywords: Biosorption, Ni(II), Kinetics, Thermodynamic.

INTRODUCTION

Water pollution is mainly due to inorganics, organics, sediments, radioactive materials and heavy metals [1]. Toxic heavy metals are released into the environment from a number of industries such as mining, plating, dyeing, automobile manufacturing and metal processing. The presence of heavy metals in the environment has led to a number of environmental problems. Nickel is widely used in stainless steel, electroplating, the manufacturing of magnetic tape, jewelry and coinage, in welding rods, as a catalyst in oil hydrogenation and coal gasification, dental procedures, electric storage batteries and pigments. It enters the human body through inhalation and ingestion, causing coughing, dyspenea, tachycardia, pneumonia, cerebral hemorrhage, asthma, insomnia and carcinoma of the lungs, nasal cavities, kidneys, stomach and prostate [2]. The contactness of nickel with skin results painful disease, nickel itch, which is followed by sudden death. Acute poisoning of nickel causes chest pain, tightness of the chest, shortness of breath etc [1]. Ni(II) is frequently encountered together in industrial wastewaters, such as mine drainage, metal plating, paint and ink formulation and porcelain enameling. Ni(II) is known environmental pollutant so its removal is of major importance as compared to other heavy metals [3].

New technologies are necessary so that the concentration of heavy metals liberated to the environment is within the levels allowed by law, at as acceptable cost. The biosorption, a process by which solids of natural origin or their derivatives are used to retain heavy metals, has great potential to achieve this objective [4]. The sorption of heavy metals on to these biomaterials is attributed to their constituents which are mainly proteins, carbohydrates and phenolic compounds which contain functional groups such as carboxyl, hydroxyl and amine that are responsible for the binding of metal ions [5][6].

The work is aimed at characterization of the biosorbent using Neutron activation analysis (NAA), fourier transform infrared (FTIR), Simultaneous thermal analysis (STA), scanning electron microscope (SEM) and energy dispersive X – ray (EDX); and studying the biosorption of Ni (II) ions from aqueous solution using dead biomass of fresh water green algae *Cosmarium panamense.* The equilibrium, kinetics and influence of different experimental parameters such as pH, biosorbent dosage, initial concentrations of Ni(II), sorption time and temperature on Ni(II) uptake were evaluated.

MATERIALS AND METHODS

2.1 Chemicals

Analytical Reagent Grade Chemicals and Distilled De-ionized water were used. They are: Conc. $HNO_{3(aq)}$, $NaOH_{(s)}$, $NaNO_{3(s)}$, $Ni(NO_3).6H_2O_{(s)}$. Ni(II) solutions of different concentrations were obtained by diluting the stock solution (1000mg/l) which was prepared using 0.01M $NaN0_3$. Standard acids and base solutions (0.1M HCl and 0.1M NaOH) were used for pH adjustments.

2.2 Equipments

Carbolite Furnace Model (GLM-3), Continent Microwave Oven (MW800G), Analytical Digital Balance (GR-200-EC), Top Loading Balance – XP500, Endecotts Sieve with Mechanized Shaker, Thermostat Water Bath Shaker, pH Meter (CRISON MICRO pH 2000), Atomic Absorption Spectrophotmeter, Shimatzu Fourier Transform Infra-red, Hitachis – 540 with Oxford Instruments 7497 EDAX,Using link ISIS Computer Software, SDT Q600 V4.1 Build 59.

2.3 Biosorbent preparation

Fresh algal biomass was collected from swimming pool located at Ahmadu Bello University, Zaria, Nigeria. Before use, it was washed several times with tap water and then with de-ionized water to remove impurities and salts. The biomass was sun –dried and then dried in an oven at 60^oC for 48hours. The dried algae biomass was cut, grinded in a mortar and subsequently sieved and particles with an average size 0.5mm was used for biosorption experiments.

2.4 Batch adsorption studies

The experiment was carried out at ambient temperature (25^oC) in a shaker water bath using 100ml conical flask as the reactor.

All the solutions was prepared in 0.01M $NaNO_3$ solution using de-ionized water. The $NaNO_3$ serve as background inert electrolyte that provides stability in the ionic strength of the solution throughout the experiment. The pH of the solution was adjusted to the required value throughout the experiment with 0.1M NaOH and 0.1M HNO_3. This gave only nitrate ion and sodium ion which are already in the medium without altering the chemistry of the ion of interest. The experiment was carried out as follows:

50ml of each of the working solution was measured using standard flask into three 100ml conical flask. This makes a triplicate for a given concentration i.e a set. 0.1g of the adsorbent was transferred into each of these conical flasks; the pH of the mixture was measured and adjusted to the desired pH – 5.02. Each set was agitated in the shaker at the same time for 3hrs and the set was left undisturbed on the desk for 24hrs to allow the system to equilibrate. After 24hrs the mixture was filtered through a whatman filter paper into 120ml polyethylene bottle. The first 5mls of the filtrate was discarded. This allows the filter paper to saturate with the solution. The concentration of the residual metal ion remaining in the solution was determined using AAS.

The amount of the metal adsorbed was calculated using the equation below

- $q_e = \frac{V\,(C_o - C_e)}{M}$

Where q_e is the amount of adsorbate ion adsorbed in milligram per gram of the adsorbent, C_o is the initial concentration of the metal ion before adsorption process, C_e is the equilibrium concentration of the metal ion in the filtrate after adsorption process and M is the mass in gram of the adsorbent, V is the volume of the solution.

RESULTS AND DISCUSSION

3.1 Characterization of the Biosorbent

Table 1:Physicochemical parameters of the algal biomass *Cosmarium panamense*

Parameters	Native algal Biomass
pH of 1% Solution	6.73
Bulk Density (g/cm^3)	0.687
Moisture content (%)	7.53
Dry Matter (%)	92.6
Ash Content (%)	29.3

Table 2: Elemental analysis of the Native algal biomass *Cosmarium panamense* using Neutron Activation Analysis (NAA)

Elements	Native Algal Biomass	Elements	Native Algal Biomass
Mg (%)	0.70 ± 0.07	Sc (ppm)	3.34 ± 0.10
Al (%)	2.44 ± 0.07	Cr (ppm)	4.50 ± 0.70
Ca (%)	0.40 ± 0.04	Fe (%)	1.00 ± 0.03
Ti (ppm)	BDL	Co (ppm)	6.60 ± 0.4
V (ppm)	16.00 ± 2.00	Zn (ppm)	BDL
Mn (ppm)	70.00 ± 7.00	Rb (ppm)	8.50 ± 2.20
Dy (ppm)	BDL	Cs (ppm)	BDL
Na (%)	0.06 ± 0.001	Ba (ppm)	27.00 ± 4.00
K (%)	0.32 ± 0.03	Eu (ppm)	BDL
As (ppm)	BDL	Tb (ppm)	NA
Br (ppm)	20.00 ± 0.40	Lu (ppm)	0.03 ± 0.004
La (ppm)	13.4 ± 0.40	Hf (ppm)	BDL
Sm (ppm)	3.10 ± 0.20	Ta (ppm)	BDL
Yb (ppm)	0.26 ± 0.03	Sb (ppm)	0.15 ± 0.03
U (ppm)	BDL	Th (ppm)	BDL

Table 3.Summary of Elemental Analysis using EDAX

Native Biomass	Nickel Treated Biomass
Carbon	Carbon
Oxygen	Oxygen
Aluminium	Alumninum
Niobium	Niobium
Chlorine	Chlorine
Copper	Copper
----------	Silicon
----------	--------
	Nickel

Table 1 showed that all the phyiscochemical properties of the algal biomass *Cosmarium panamense* are within acceptable range required for a good biosorbent except for the ash content which is very high (29.3%). It has been reported that high ash content suggest good presence of inorganic constituents and hence, reduces the overall activity of activated carbon and also reduces the efficiency of reactivation [7]. This therefore suggest that there is

high presence of inorganic constituents in the algal biomass of *Cosmarium panamense*. Hence, the poor activity of its carbon predicted.

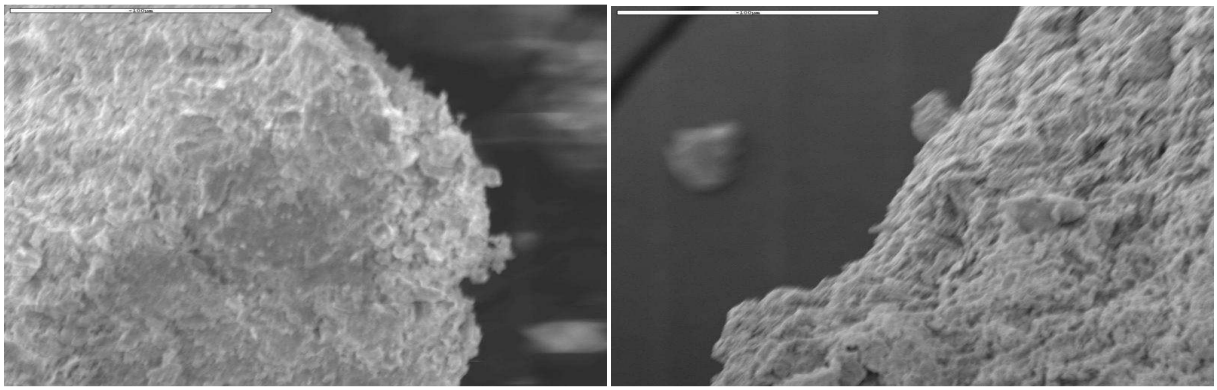
High elemental quantities of Aluminum(Al), Magnesium(Mg), Calcium(Ca), Sodium(Na), Iron(Fe), Potassium(K), and Manganese(Mn) was found in the native sample (Table 2). Hence, the sample showed high metal content. The metal content is usually the non-volatile inorganic constituents present in the carbons. This suggested the reason why the ash content was extremely high. It is important to state here that the chemical nature and concentration of these metals constituents may sometimes interfere with the carbonization and/or activation process either positively or negatively. Energy Dispersive X – ray detect only elemental quantities up to 0.1%. It was also observed that the number of elements detected by the energy dispersive x – ray on the biomass before and after biosorption varies (Table 3 and Fig.2). This is due to the surface interactions of each of this heavy metal (Ni^{2+}) ions on the surface binding sites of the algal biomass during biosorption resulting to complexation and ion – exchange which affects the availability of these elements for detection. This goes in line with the reports in literature by Ahalya *et al*.,[8] that Non – metabolism dependent biosorption mechanism is a rapid process that include precipitation, physical adsorption, ion – exchange, and complexation.

Scanning electron microscope clearly revealed the surface texture and morphology of the algal biomass before and after biosorption at 500x magnification (Fig.1). Uneven surface texture along with a lot irregular surface format was observed. SEM photos displayed evidently that over the biosorption period, the surface morphology of the native algal biomass had undergone remarkable physical disintegration resulting to emergence of protrusions and rough surface area. Similar SEM observations were reported by Gupta and Rastogi [9], Shakirullah *et al*., [2], Sethuraman and Balasubramanian[10] and Wilke *et al.*, [11].

Thermal stability of the algal biomass *Cosmarium panamense* before and after biosorption was evaluated by simultaneous thermal analysis. This was performed by TGA – DSC curves with a heating rate of 50^{o}C/min under nitrogen atmosphere within the temperature range of 50 – 600^{o}C and DSC scanning range of 0 – 120mcal/sec (Fig.3). The biomass samples showed two step decomposition process but the heat required for thermal degradation was higher after biosorption, which is as a result of the ionic bond formed after biosorption. Also the percentage weight residue after was lower after biosorption, which suggests that biosorption affects the inorganic content of the biomass. The stability showed by the biomass suggests that the biomass is responsible for the biosorption of these metal ions. This was similarly reported by researchers [12][9].

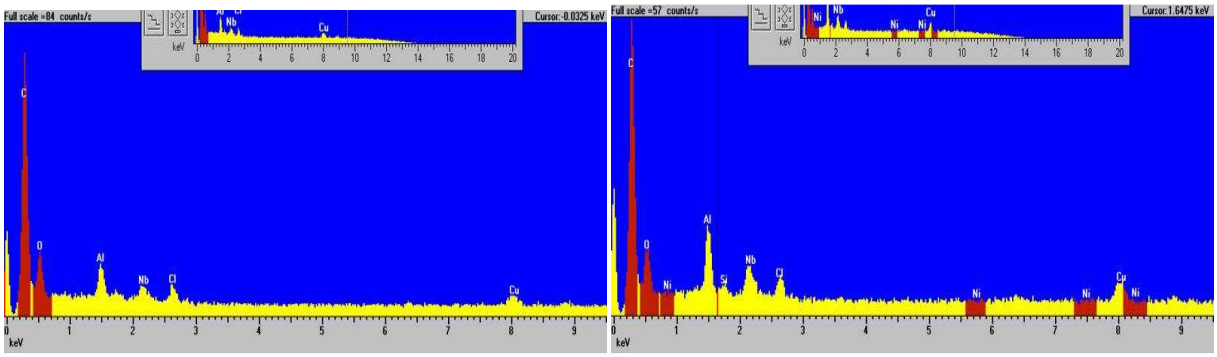
The FTIR spectra of native and Ni^{2+} treated algal biomass in the range of 500 – 5000cm^{-1} were performed to have an idea of which functional groups were responsible for the biosorption process (Fig.4). It was observed from that the absorbance peaks of the different heavy metal ions treated algal biomass were slightly lower than the absorbance peaks of native algal biomass. Band shift that appeared at 534.3cm^{-1} represents the C – N – S scissoring which are found in polypeptide structure [9] and Si – O – Si bend of the silica group [13]. This further supports the earlier detection of silicon by EDAX in the algal biomass sample. The absorption band observed at 1030.99cm^{-1} could be assigned to C – N, C – OH and P – O – C stretching vibrations of amines and Proteins fractions [14][15][16]; polysaccharides [17] and phosphonate groups respectively [18][19]. The peak appearing at 1435.09cm^{-1} could be attributed to C – H bending of methyl and methylene functional group [20][21][17]. The absorption band at 1654.01cm^{-1} may be as a result of –C = C (characteristics of alkene), - C = N, - C = O stretching and N – H bending of amines or amide I and amide II band of amide bond of protein peptide bonds [9][15][21][16][20]. The peak observed at 2927.08cm^{-1} could be assigned C – H stretching of methyl and methylene group in cell wall structure [14][15][10] and asymmetric stretching of carboxylate anion (- COO^{-}) [18][9]. The display of strong broad – OH (H bonded) and – NH stretch of carboxylic and amine band respectively were also observed in the region of 3453.66cm^{-1} [15]. The spectra analysis indicate the presence of ionizable functional groups namely amino, amide, carboxyl, phosphonate, hydroxyl, silica, methyl and methylene group which are able to interact with proton or metal ions. The peaks appearing at 621.1 and 3335.03cm^{-1} could be attributed to – NH bending of amines and – NH and – C – H stretching of proteins and alkynes respectively [16][20].

The FTIR spectra result obtained is consistent with published FTIR spectra reports by other researchers [21][18][19][17][20][14][16][15][9].



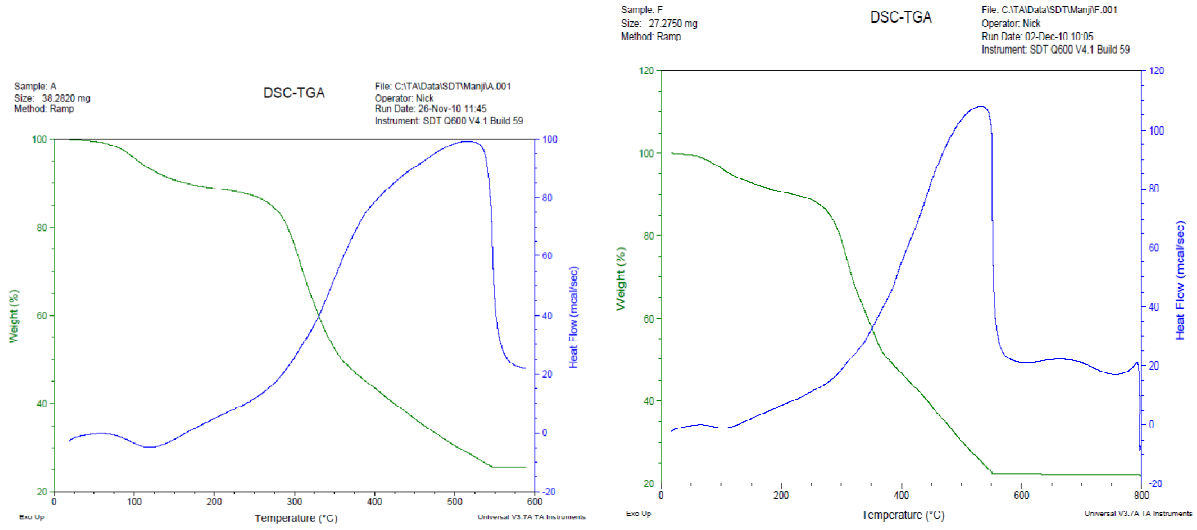
(a) **(b)**

Fig.1 SEM micrograph at 500x magnification of the different algal biomass (a) Native (b) Ni^{2+} treated algal biomass



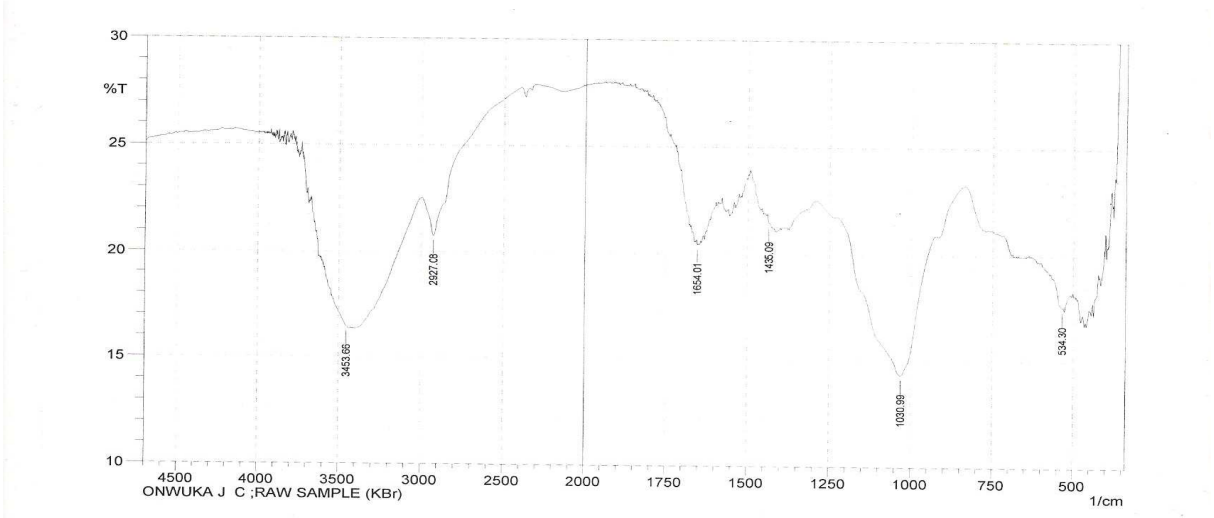
(a) **(b)**

Fig.2 EDAX Profile of the different algal biomass (a) Native (b) Ni^{2+} treated algal biomass.

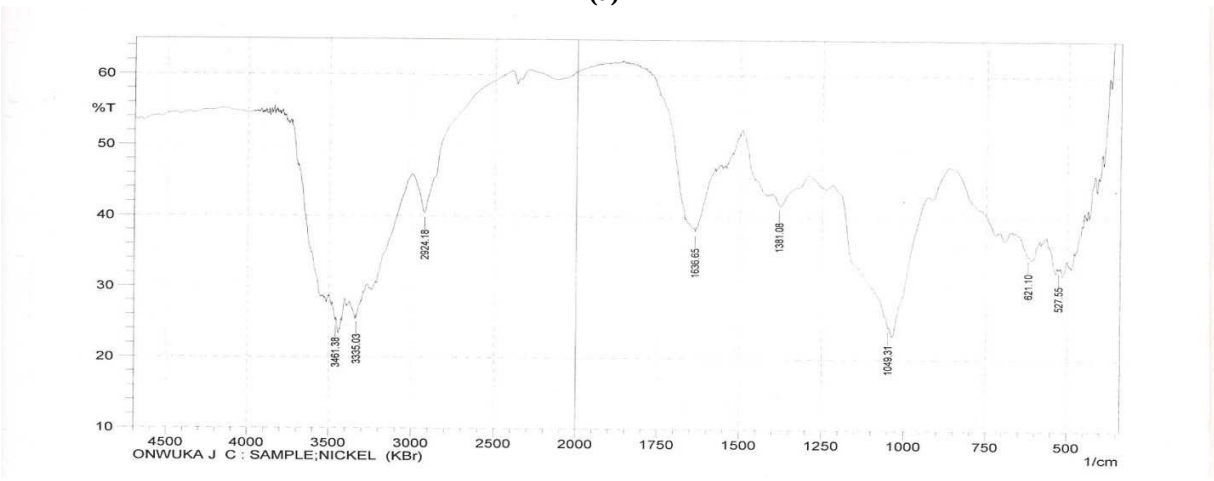


(a) **(b)**

Fig.3 Thermogram of the algal biomass (a) Native (b) Ni^{2+} treated algal biomass degradation.



(a)



(b)

Fig.4. FTIR Spectra of algal biomass (a) Native (b) Ni^{2+} treated algal biomass

3.2 Biosorption of heavy metal ions

3.2.1 Effect of initial metal ion concentration

This was carried out at constant biomass concentration, pH, and temperature by varying the initial metal ion concentration (5, 10, 15, 20, and 25ppm) of Ni^{2+}. It was observed that as the initial metal ion concentration of the metal was increased, the metal uptake also increased (Fig.5). It has been reported that with increasing metal ion concentration, the specific sites are saturated and vacant sites are filled and at low concentrations adsorption sites took up the available metal more rapidly or quickly while at higher concentrations metal ions need to diffuse to the biomass surface by intra particle diffusion and greatly hydrolyzed ions will diffuse at a slower rate [22][23][24].

3.2.1.1 Biosorption modeling

To estimate the sorption capacity of the algal biomass, the isotherm data were analyzed using adsorption type isotherm models. The Langmuir and Freundlich isotherms are the most commonly used for solid – liquid phase isotherms. These isotherms relate the amount of metal ion sorbed at equilibrium per unit weight of the sorbent, q_e(mg/g) to the sorbate concentration at equilibrium, C_e(mg/l). The linearized form of Langmuir isotherm can be expressed as:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{bq_{max}C_e} \quad \text{.....(1)}$$

Where; q_e is the amount of adsorbate adsorbed per gram of dried adsorbent at equilibrium (mg adsorbate/g of dried adsorbent), q_{max} is the constant relating to the maximum amount of adsorbate ion bound per g of adsorbent for a monolayer (mg/g), b is Langmuir constant or adsorption coefficient or the adsorption affinity (l/mg) for binding of adsorbate on the adsorbent sites and C_e is equilibrium (residual) adsorbate concentration in solution after sorption (mg/l).

The values of q_{max} and b can be calculated from the intercept $\left(\frac{1}{q_{max}}\right)$ and slope $\left(\frac{1}{q_{max}b}\right)$ of the plot $\frac{1}{q_e}$ against $\frac{1}{C_e}$ as illustrated in Figures 6(a).

The Freundlich isotherm model describe non – ideal sorption onto heterogeneous surfaces involving multilayer sorption. The isotherm model linearized form is given as

$$lnq_e = lnK_F + \frac{1}{n} ln\, C_e \quad \text{..... (2)}$$

Where, q_e is the amount of adsorbate adsorbed per unit weight of biosorbent, K_F is Freundlich Constant measuring adsorption capacity(L/mg), C_e is equilibrium concentration of the adsorbent in solution(mg/l), n is constant related to adsorption efficiency and energy of adsorption or adsorption intensity of the adsorbent.

Figures 6(b) shows Freundlich isotherm model the different heavy metal ions biosorption and the isotherm constants and correlation coefficients, R^2, are also listed in Table 4. A plot of lnq_e against lnC_e gives a straight line with a slope, 1/n and an intercept of lnK_F. The K_F value increases with the total adsorption capacity of the adsorbent to bind the adsorbate. The numerical value of n is a useful index to determine favorability of the adsorption.

Table 4: Langmuir and Freundlich isotherm constants for the biosorption of the Selected Metal ions on algal biomass (*Cosmarium panamense*).

Metals	Langmuir Constant				Freundlich Constant		
	q_{max}(mg/g)	b(Lmg^{-1})	b(Lmol^{-1})	R^2	$1/n$	K_f(mg/g)	R^2
Nickel	10.73	0.10	5900	0.9778	0.73	1.06	0.9667

It was observed from the correlation coefficients(Table 4), that Ni^{2+} sorption data are well fitted in Langmuir model of sorption. In other words, the equilibrium data were well represented by Langmuir isotherm equation when compared to Freundlich isotherm because Langmuir isotherm possess higher correlation coefficient than Freundlich isotherm. The high degree of correlation for the linearized Langmuir relationship suggest monolayer sorption on specific sites or single surface reaction [9].

The value of $1/n$ in Table 4 falls within 0 – 1 range which strongly suggest favorable adsorption. The n values for the biosorbent used, was found to be greater than one, indicating that adsorption of Ni(II) is favorable [25].

3.2.2 Effect of biosorbent dose

Figure 7 showed that as the biosorbent dose increases, the removal efficiency increases while the metal uptake decreases. Therefore, 0.05g of the adsorbent comparatively showed the lowest removal efficiency and highest adsorption capacity while 0.25g of the adsorbent gave the highest removal efficiency and lowest adsorption capacity. It has been reported by Pattabhi *et al.*, [1] that increase in biomass concentration increases the level of biosorption due to the overall increase in surface area of the biomass which in turn increases the number of binding sites. Saradhi *et al.*,[24] explained that the metal uptake (mg/g) decreases with increase in biosorbent dose due to the interference of inter – particle cohesive forces, interference of binding sites, desorption due to abrasion, turbulence and reduce mixing due to large mass of the biosorbent while Rastogi and Gupta [9], attributed this to the fact that at higher adsorbent dose, the availability of higher energy sites decreases with a larger fraction of lower energy sites occupied. High biomass concentration can exert a shell effect protecting the active sites from being occupied by metal and this results to lower specific metal uptake [26].

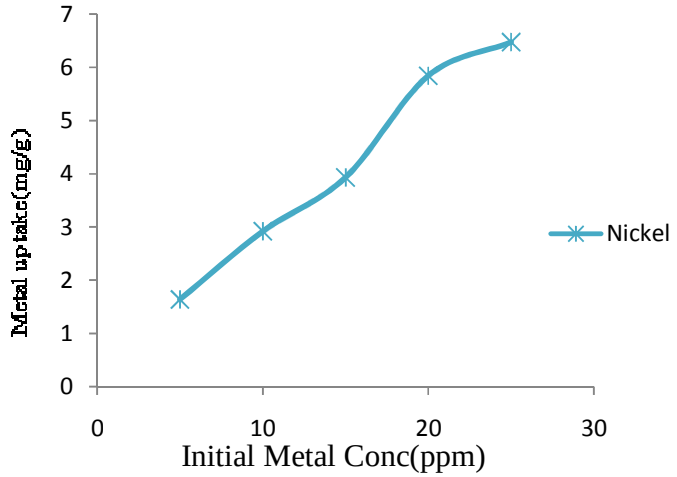
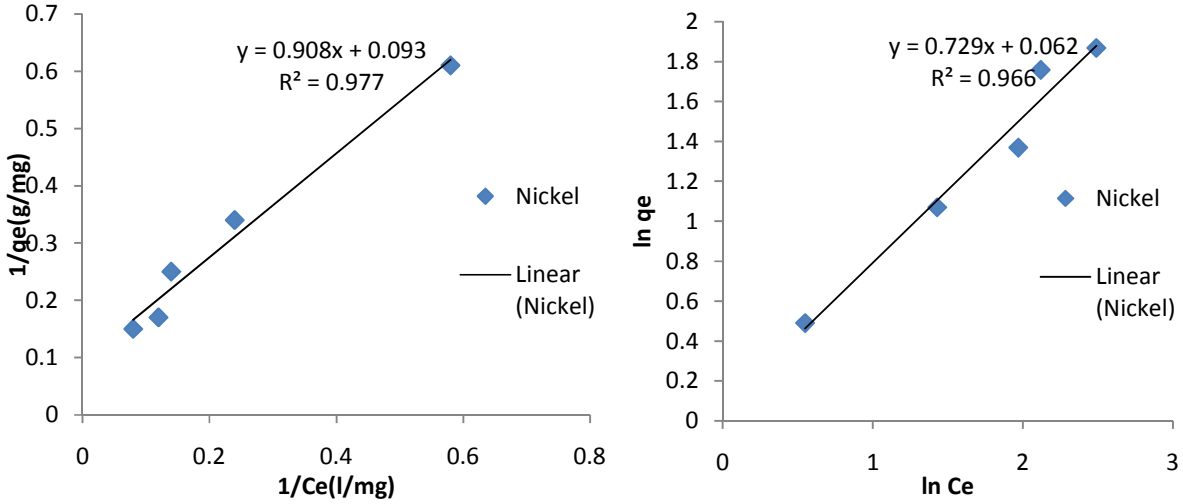


Fig.5: Effect of initial metal ion concentration



(a) **(b)**

Fig.6: Isotherm modeling for Ni^{2+} biosorption (a) Langmuir (b) Freundlich biosorption isotherm for Ni^{2+} biosorption

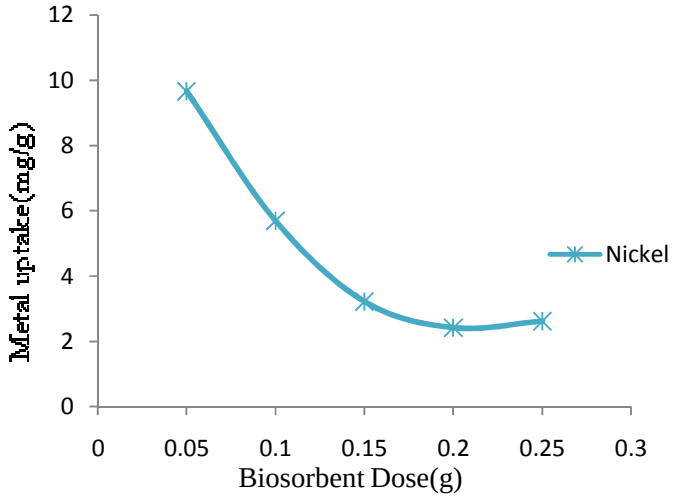


Fig.7: Effect of biosorbent dose

3.2.3 Effect of contact time

The contact time was evaluated as one of the important parameters affecting the biosorption efficiency [27]. Fig.8 showed that the maximum adsorption for Ni^{2+} (5.69mg/g) occurred at 90min. It was also observed that process of adsorption was high at the initial stage and became slower while approaching the equilibrium stage. This is obvious due to the fact that more number of vacant negatively charged sites are available initially on the surface of the adsorbent and the sites are gradually filled up while approaching equilibrium and completely filled at equilibrium [24]. Contact time were further used to generate the rate of the reaction.

3.2.3.1 Biosorption kinetics

In order to investigate the mechanism of biosorption and potential rate controlling step, pseudo first order and pseudo second order kinetic models were used to test the equilibrium data

The pseudo first-order equation [28] is generally expressed as [29]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{.....(3)}$$

Where q_e and q_t are the amount of sorbate adsorbed on adsorbent at equilibrium and time *t*, respectively (mg/g), and k_1 is the rate constant of first order adsorption (min^{-1}).

The plot of $\log(q_e - q_t)$ versus t will give a straight line and the value of k_1 can be evaluated from the slope of the graph, $-\frac{k_1}{2.303}$, while $q_{e\,(\text{calculated})}$ is obtained from the intercept, log q_e, of the graph as illustrated in Fig.9(a).

The linearized second-order kinetic model is expressed as [30]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{.....(4)}$$

Where, k_2 is the pseudo-second-order rate constant of adsorption (g $mg^{-1}min^{-1}$). The plot of $\frac{t}{q_t}$ versus t will give a linear relationship with $\frac{1}{q_e}$ and $\frac{1}{k_2 q_e^2}$ as a slope and intercept, respectively. The values of q_e and k_2 can be determined from the slope and intercept as illustrated in Fig.9(b).

Table 5: Comparison between adsorption rate constants, q_e estimated and correlation coefficient associated to the Lagergren pseudo first – and second – order adsorption.

	Pseudo First – Order Model			$q_{e\,\text{exp.}}$ (mg/g)	Pseudo Second – Order Model		
	$q_{e\,(\text{cal})}$	$K_1(min^{-1})$	R^2		$q_{e\,(\text{cal})}$	$K_2(gmg^{-1}min^{-1})$	R^2
Nickel	1.440	0.003	0.3066	5.69	6.49	0.009	0.9948

It was observed that the correlation coefficient for pseudo second order model is higher than that of pseudo first order (Table 5). Hence, the correlation coefficient and calculated adsorption capacity of the Ni^{2+} sorption by pseudo first order model are not satisfactory, which suggest that it is dependent on initial concentration. However, Pseudo second order adsorption model is more suitable to describe the adsorption kinetics of Ni^{2+} on algal biomass and this relies on the assumption that biosorption may be the rate-limiting step [9]. The obtained kinetic information has a significant practical value for technological applications, since kinetic modeling successfully replaces time and material consuming experiments, necessary for process equipment design [23]. This is supported by reports by Gupta and Rastogi [9], Mahamadi and Torto [31], Krishnaiah *et al.*, [17], Anasri *et al.*, [15].

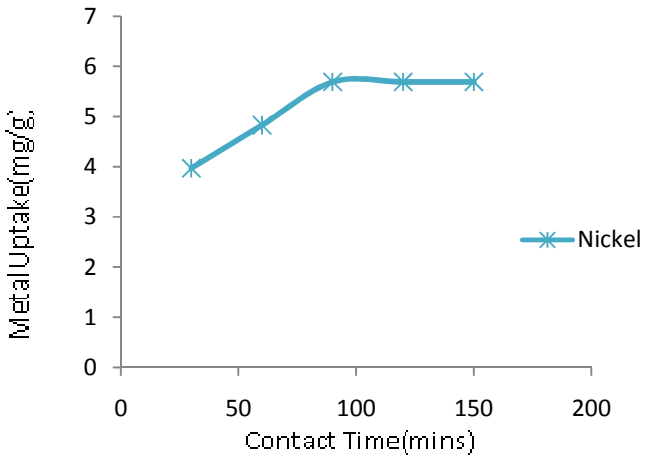
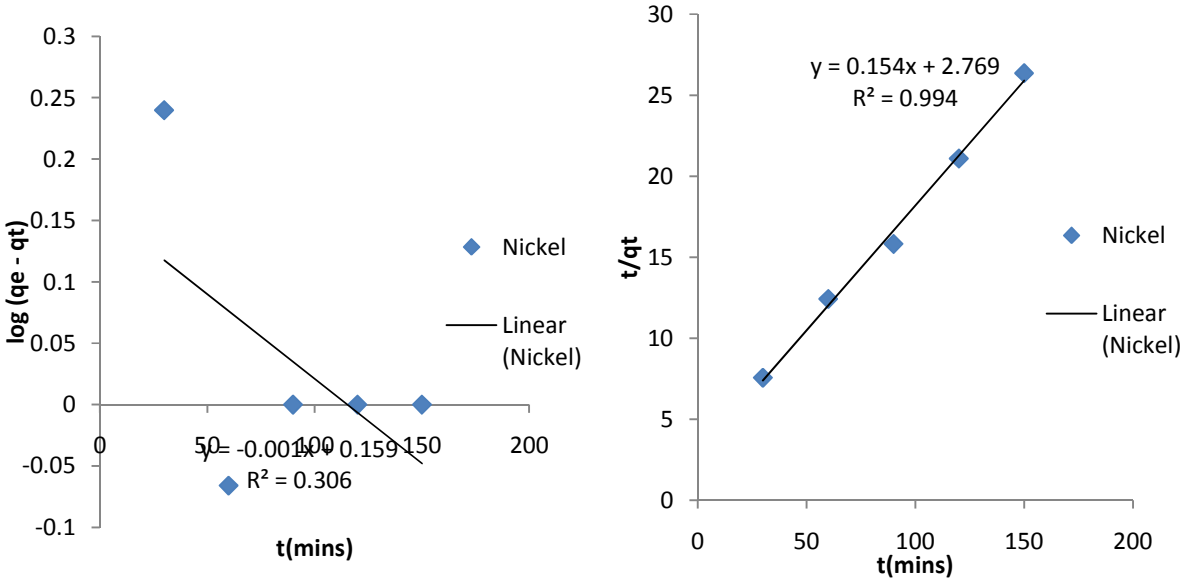


Fig.8: Effect of contact time



(a) **(b)**

Fig.9: Kinetic modeling for Ni^{2+} biosorption (a) pseudo first order (b) pseudo second order kinetic modeling

3.3.3 Effect of initial solution pH

It was observed from Fig.10 that as the solution pH of Ni^{2+} solution was increased, the adsorption capacity first increased from 2 pH to pH 6 and then decreased at pH 8. This may be attributed to the negative charge of the overall surface charge on the cells as the pH is increased. Hence, the positively charged nickel species (Ni^{2+}) bind through electrostatic attraction to negatively charged functional groups on the surface of biosorbents and biosorption increased [14][10][32]. Also at pH higher than 6, formation of insoluble metal hydroxides or anionic hydroxide complexes of metal ions takes place restricting the true biosorption studies. This is consistent with the results obtained for the other adsorbent systems [33][31][26][15][1].

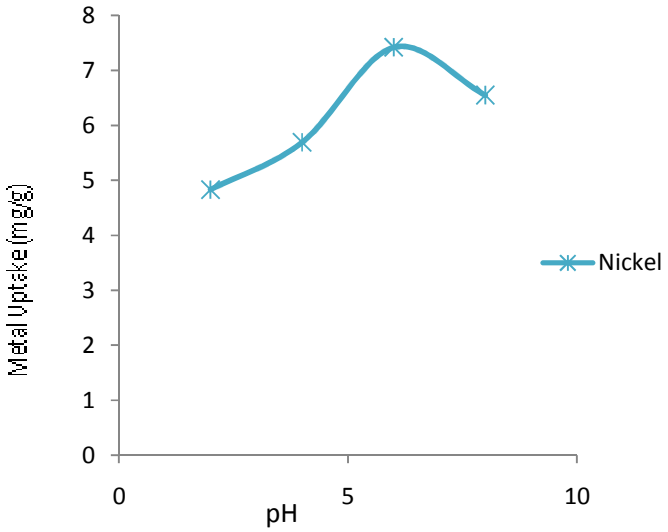


Fig.10: Effect of initial solution pH

3.3.4 Effect of Temperature

It was observed that the metals showed increase in adsorption capacity with increase in temperature (Fig.11). This could be due to increase in average kinetic energy of the metal ions in solutions containing the adsorbent which increases the number of metal ions interacting with the adsorbent surface by increasing the rate at which the metal ions hit the binding sites at the surface of the adsorbent thus increasing the adsorption capacities. The equilibrium data obtained was further used for thermodynamic modeling to determine the enthalpy, entropy and free energy of the adsorption reaction at different temperatures.

3.3.4.1 Thermodynamic modeling

Thermodynamic parameters were obtained by varying the temperature conditions while other variables constant were kept constant [25]. The thermodynamic parameters such as change in standard free change energy (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) for adsorption process are calculated from binding energy constant, *b*, obtained from Langmuir equation using the following thermodynamic equations:

…….(5)

= - ……..…(6)

Where: R (8.314 J/mol K) is the gas constant, T (K) the absolute temperature and *b* (L/mol) is the Langmuir constant related to free energy or net enthalpy of adsorption. By plotting a graph of versus *T*, the values ΔH^o and ΔS^o can be estimated from the intercept and slope as illustrated in Fig.12

Table 6: Calculated values of Gibbs Free Energy in $Jmol^{-1}$ of themetals sorption process over the temperature range studied.

Temp.(K)	Nickel
300	-21656.4
313	-22594.8
323	-23316.7
333	-24038.6

Table 7:Thermodynamic parameters for the biosorption of the Metals on the algal biomass

	Nickel
	0.0106
($Jmol^{-1}$)	
	72.188
($Jmol^{-1}$ K^{-1})	

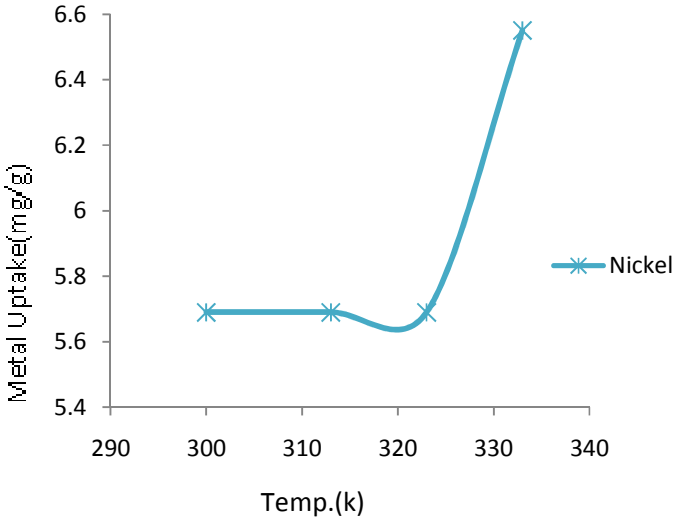


Fig.11: Effect of temperature

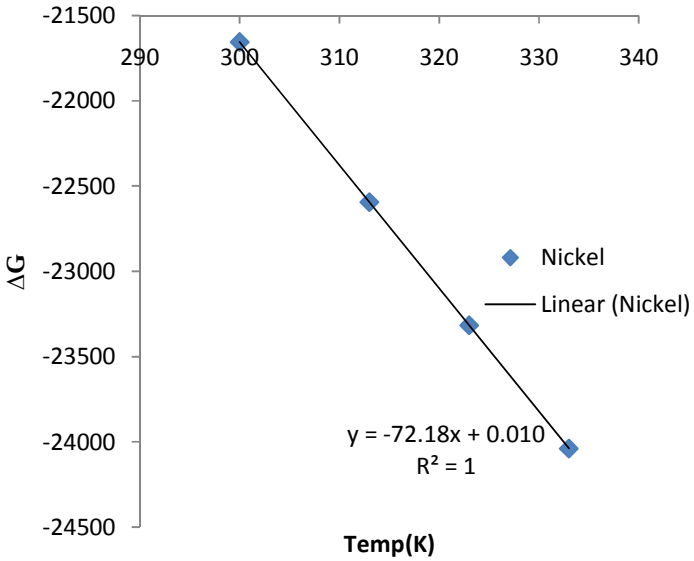


Fig.12: Thermodynamic modeling for Ni^{2+} biosorption.

Free energy change of the metal ions adsorption process was found to be negative (Table 6), suggesting spontaneous process. In general, it is of note that free energy up to −20 kJ/mol are consistent with electrostatic interaction between charged molecules and surface indicative of physiosorption while more negative than −40 kJ/mol involve chemisorption, free energy change values between −20 to −40 kJ/mol indicate that both physisorption and chemisorption were responsible for adsorption [23]. Thus, the magnitude of the free energy change values obtained

in this study indicates both physical and chemical mechanism for the adsorption of Ni(II) ions on to the *Cosmarium panamense* algal biomass, hence physiosorption and chemisorption were responsible for Ni(II) adsorption.

The values of enthalpy change for the sorption of the metal ions were positive(Table 7), which suggest endothermic reaction and could be attributed to increase in adsorption on successive increase in temperature while the positive values of entropy reveals increase in randomness at the solid – solution interface during the fixation of the different metal ions on the active sites of the biosorbent [9]. This could be as a result of high affinity for these metal ions by the binding sites on the surface of the algal biomass. Gupta and Rastogi, [9] reported that if adsorption process is endothermic, it means under the conditions the process becomes spontaneous because of the large positive entropy change.

CONCLUSION

- The batch studies conducted proves that biosorption of Ni(II) ions on dead biomass of green algae *Cosmarium panamense* species are dependent of initial solution pH, initial metal ion Concentration, biosorbent dosage, contact time, and temperature.
- It was found that the adsorption data for Ni(II) ion sorption was better fitted to Langmuir adsorption model. Hence, biosorption of Ni(II) ion on the algae biomass is a monolayer sorption process.
- Thermodynamic modeling showed that physiosorption and chemisorption process were involved in the biosorption of Ni(II) ions and these processes are spontaneous and endothermic .
- The availability of elements in the algal biomass, for detection are affected by biosorption of the metal ion on algal biomass. Hence, the inorganic status of the algal biomass are influenced by biosorption.
- Simultaneous thermal analysis reveals that both the native and Ni^{2+} treated algal biomass are thermally stable but with different energy and inorganic composition status.
- FTIR showed that carboxyl, hydroxyl, amines, amides, alkenes, alkynes, phosphonate and silica functional groups functional groups are responsible for the adsorption of Ni(II) ions.

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