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Equilibrium, Kinetic and Thermodynamic Parameters of the Biosorption of Ni^{2+} from Aqueous Solution by *Streblus asper*

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Abstract: The biosorption of Ni^{2+} by *Streblus asper*, biomass was investigated in single metal solution. Batch kinetic studies were carried out in order to determine effect of adsorbent and adsorbate dose, pH of solution, agitation time and temperature on biosorption of *Streblus asper*. The maximum Ni^{2+} biosorption was obtained at pH 6.0. The equilibrium nature of Ni^{2+} biosorption was described by the Freundlich and Dubinin-Radushkevich isotherms. The value of n, the intensity of adsorption, is ≈2 indicating that Ni^{2+} is favourably biosorbed by *Streblus asper*. The saturation capacity, q_m, of Ni^{2+} by *Streblus asper* was calculated to be 40.48 mg g^{-1}. The value of the mean free energy of biosorption was calculated to be 4082.48 kJ mol^{-1} which indicates that the biosorption may occur via a chemical ion-exchange mechanism. The results of the thermodynamic investigations indicated that the adsorption reactions were spontaneous ($\Delta G<0$), endothermic ($\Delta H>0$) and irreversible ($\Delta S>0$). The pseudo second-order kinetic model was used to analyse the kinetic data. The second order rate constants for the biosorption of Ni^{2+} from solutions by *Streblus asper* was evaluated to be 1.35 g mg^{-1} min^{-1}.

Key words: *Streblus asper*, heavy metals, Ni (II) biosorption, adsorption isotherms, parameters

INTRODUCTION

Human activities such as industrial and domestic activities have led to an increase in the amount of metals discharged into the environment. Nickel, zinc, copper, lead and cadmium, mercury are the most common inorganic pollutants found in industrial effluents. These metals are widely distributed in the air, water and soil and their concentrations have been found to be above the normal permissible limits. The high concentrations of these concerned heavy metals pose worrisome health risks to life because of their hazardous nature. Ni^{2+} is contained in stainless steel, nickel electroplating, battery and manufacturing of accumulator, pigments and wastewaters from ceramic industries (Aksu, 2002).

Small amounts of nickel are needed by the human body to produce red blood cells, however, can become mildly toxic in excessive amounts. Short-term over-exposure to nickel is not known to cause any health problems but long-term exposure can cause a decrease in body weight, heart and liver damage and skin irritation. The Environmental Protection Agency (EPA) does not currently regulate nickel levels in drinking water. Nickel can accumulate in aquatic life.

A myriad of techniques such as precipitation, evaporation, adsorption, ion exchange, membrane processing, solvent extraction are employed for treatment of heavy metals. These methods require high capital and operational costs and may also be associated with the generation of secondary wastes, which pose treatment problems (Bodek *et al*., 1998; Ajmal *et al*., 2000; Wong *et al*., 2000). Biosorption is a type of sorption that is based on the use of sorbent obtained various types of biomaterials or biomass. Biosorption has been found economical for removal of heavy metals from waste-waters. Biosorption of heavy metal on biosorbents is based on the various mechanisms which include physical adsorption, ion exchange, complexation and precipitation (Schiewer and Volesky, 1999; Volesky *et al*., 2003; Beolchini *et al*., 2006). Biosorption may not necessarily consist of a single mechanism. Biosorption utilises the ability of biological materials to accumulate heavy metals from waste streams by either metabolically mediated or purely physico-chemical pathways of uptake (Fourest and Roux, 1992).

The purpose of this research was to investigate the biosorption capacity of *Streblus asper* (sand paper leaves) as efficient biosorbent for removal of heavy metal from aqueous solution by batch process. *Streblus asper* used for this study is inexpensive, widely grown and available in large quantity (abundant) in most of the West African countries.

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MATERIALS AND METHODS

Preparation of biosorbent and nickel solution: The leaves of a sand paper plant, *Streblus asper*, were used for the purpose of the research work. The leaves were collected from botanical garden located within the University of Ibadan, Ibadan, Nigeria. These leaves were washed with ordinary water to remove dirt and then with de-ionized water. These were subsequently oven-dried at 80°C for 24 h. The dried samples were pulverised using an electric blender and sieved using a 400-mesh copper sieve. This formed biosorbent used for the experiment. The prepared biosorbent was then stored in a clean air-tight glass bottle prior usage.

All the reagents used in this study were of analytical grade. A stock solution of Ni^{2+} was obtained by dissolving Ni $(NO_3)_2$. $6H_2O$ salt in deionised water and the accurate concentration of Ni^{2+} in the stock solution was measured using Atomic Absorption Spectroscopy (AAS) and the solution was used for further experimental solution preparation.

Batch biosorption experiments

Influence of initial metal concentration on biosorption: The solutions of Ni^{2+} was prepared by diluting 5.0 mmol dm^{-3} stock solution of nickel. The range of concentrations of prepared Ni^{2+} solutions varied from 0.15 to 5 mmol dm^{-3}. Biosorption experiments were carried out in 100 mL centrifuge bottles using 20 mL of Ni^{2+} solution with 0.4 g of the dried biosorbent, *Streblus asper*. The pH of each solution was measured adjusted to 6.0 on pH meter. The biosorption medium was placed in a thermostated water bath shaker and agitated at 200 rpm for 10 min at 25°C. For all the experiments carried out, the agitated solution mixtures were filtered using Whatmann No. 1 filter paper and 10 mL of each supernatant (Ni^{2+}) was then taken and analysed for the residual metal content by AAS. Each experiment was carried out in duplicate under identical conditions for all the experiments.

Effect of contact time on biosorption: The 0.4 g of *Streblus asper* was treated with 20 mL of 0.3 mmol dm^{-3} solution of Ni^{2+} at pH 6.0. Agitation time intervals chosen for the analysis varied from 5 to 180 min.

Effect of biosorbent dose: Between 0.20 and 2.0 g of biosorbent were added to 20 mL of 0.3 mmol dm^{-3} solutions of Ni^{2+} at pH 6.0. The solutions of the mixtures were agitated for 10 min on a thermostated water bath shaker at 200 rpm.

Influence of pH on biosorption: The 0.4 g of a sample of *Streblus asper* were added to 20 mL of 0.3 mmol dm^{-3} solutions of each of Ni^{2+} solution at 25°C in 100 mL centrifuge bottles. The experiments were carried out at pH 3, 4, 5, 6, 7, 8 and 9. The accuracy of pH measurements was±0.1. The reaction mixtures were then agitated for 10 min on a thermostated water bath shaker at 200 rpm.

Effect of temperature on biosorption: Twenty milliliter of 0.3 mmol dm^{-3} solution of each metal at the optimum pH 6.0 was contacted with 0.4 g of *Streblus asper* at a constant temperature in a thermostated water bath shaker for 10 min. The agitated solution mixtures were then filtered using Whatmann No. 1 filter paper. The experiments were performed at different temperatures between 20 and 50°C. The accuracy of temperature measurements was ±1°C.

Treatment of experimental data: Biosorption equilibrium data were modelled using the Freundlich and Dubinin and Radushkevich (1947) (D-R) models. Kinetic and thermodynamic parameters for the biosorption process were evaluated.

Calculation of metal uptake: Metal uptake by *Streblus asper* was calculated using the mass balance equation, which is shown in Eq. 1:

$$q=\frac{(C_o - C_e)V}{S} \quad (1)$$

where, q is the metal uptake (mg metal g^{-1} dry weight); V (L) is the volume of metal-bearing solution contacted with the biosorbent; C_o is the initial concentration of metal in solution (mg L^{-1}); C_e is the final concentration of metal in solution (mg L^{-1}); S is the dry weight (g) of biosorbent used.

RESULTS AND DISCUSSION

Effect of pH on biosorption: Investigation of biosorption capability of *Streblus asper* for Ni^{2+} at different pH values (3-9) is illustrated in Fig. 1. The percentage of biosorption of Pb^{2+} metal uptake increased from 15 to 58% between pH 3.0 and 8.0 (Fig. 1). The highest% biosorption was observed at pH 6. Effect of pH became apparent from pH 4 to 8 and an increase in metal uptake was observed for Ni^{2+} uptake. Therefore, biosorption of Ni^{2+} is pH dependence.

Sorption of heavy metals from aqueous solutions depends on properties of adsorbent and molecules of adsorbate transfer from the solution to the solid phase. It has been also reported that biosorption capacities for heavy metals are strongly pH sensitive and that adsorption increases as pH of solution increases (Yin *et al*., 1999). For example, Ni^{2+} exists in different forms in aqueous solution and the stability of these forms is

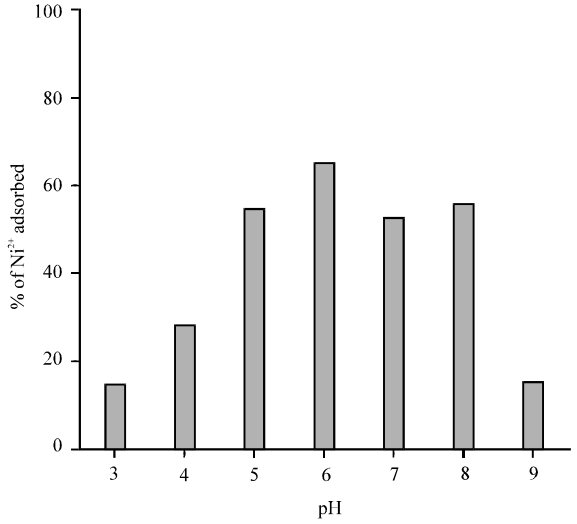

Fig. 1: Effect of pH on biosorption of Ni^{2+} by *Streblus asper* (C_o = 100 mg L^{-1}; biosorbent dosage, 0.4 g; agitation time = 10 min; T = 25°C)

dependent on the pH of system (Kandah and Meunier, 2007). This result, therefore, shows that high pH favours Ni^{2+} biosorption by *Streblus asper*. At a very low pH, concentration of H^+ ions exceeds that of the Ni^{2+}. H^+ ions compete with Ni (II) ions for the surface of the adsorbent which would prevent the Ni^{2+} ions from reaching the binding sites of the biosorbent. The metal removal is hinder at pH<4 because of competition between proton ions and nickel ions for the binding sites and complex formation.

At a very high pH, the Ni^{2+} get precipitated due to hydroxide anion forming a nickel hydroxide precipitates (Malkoc and Nuhoglu, 2005). For this reason, the optimum pH value was selected to be 6.0 for other subsequent experiments carried out. Above pH 8, Ni^{2+} tends to form nickel hydroxide precipitates.

Effect of biosorbent dose: Biosorbent dose has a great influence in biosorption process. The number of binding sites available for adsorption is a function of biomass dose added into the solution (Zafar *et al*., 2007). Effect of biosorbent dose on biosorption capacity of Ni^{2+} on *Streblus asper* is shown in Fig. 2. The result showed that metal uptake values decreased with an increase in biomass quantity. An increase in biomass quantities strongly affects the amount of metal removed from aqueous solutions. This could be attributed to interference between binding sites at higher concentrations (Sampedro *et al*., 1995). Reduction in metal uptake with increasing biomass concentration was attributed to an insufficiency of metalions in solution

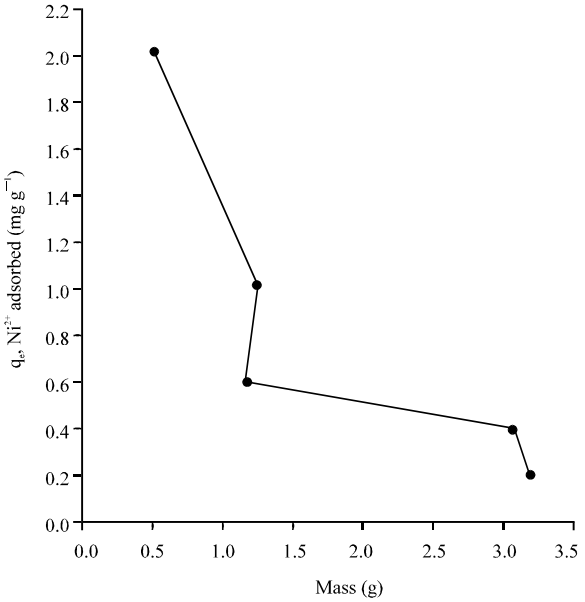

Fig. 2: Effect of biosorbent dose on biosorption of Ni^{2+} by *Streblus asper* (initial metalion conc. = 100 mg L^{-1}; agitation time = 10 min; pH = 6.0; temperature = 25°C)

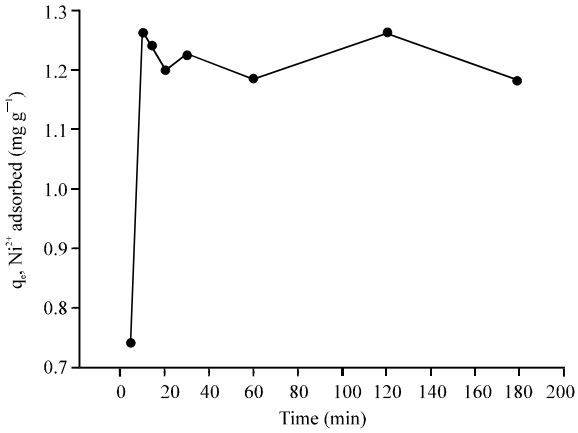

Fig. 3: Effect of agitation time on the biosorption of Ni^{2+} by *Streblus asper* (initial metalion conc. = 100 mg L^{-1}; biosorbent dosage, 0.4 g; pH = 6.0; temperature = 25°C)

with respect to available binding sites (Fourest and Roux, 1992). For the purpose of this present study, biomass dose of 0.4 g was chosen for all the experiments. This biomass dose was found to be an optimum value.

Effect of contact time on biosorption capacity: Effect of agitation time for Ni^{2+} biosorption in aqueous solution by *Streblus asper* is presented in Fig. 3. Maximum biosorption was observed for Ni^{2+} at 10 min of agitation.

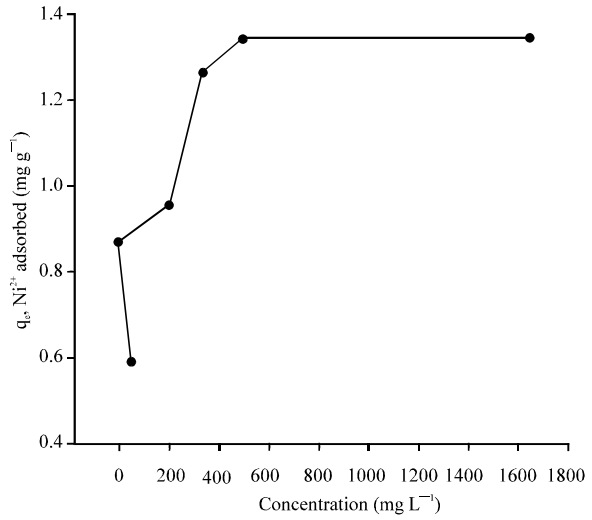

Fig. 4: Effect of Ni^{2+} concentration on biosorption by *Streblus asper* (biosorbent dosage, 0.4 g; agitation time = 10 min; pH = 6.0; temperature = 25°C)

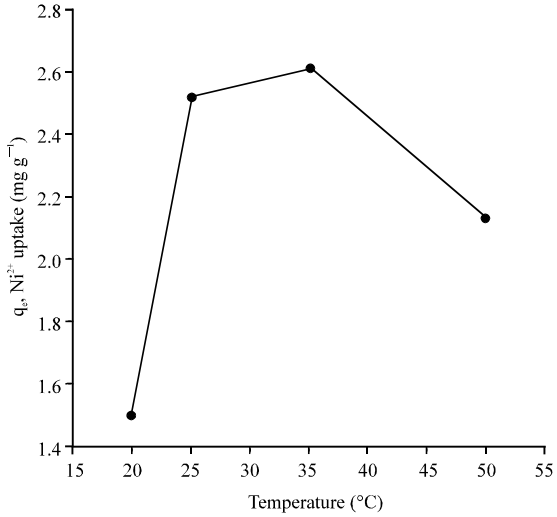

Fig. 5: Effect of temperature on the biosorption of Pb^{2+} by *Streblus asper* (initial metalion conc. = 100 mg L^{-1}; biosorbent dosage, 0.4 g; agitation time = 10 min; pH = 6.0)

The biosorption process was rapid and reached equilibrium within 10 min.

Effect of initial Ni^{2+} concentration: The apparent capacity of *Streblus asper* was determined for Ni^{2+} at varying Ni^{2+} concentrations but fixed biosorbent dose. Figure 4 shows the relation between biosorption capacities and the metal ion concentrations which shows that the metal uptake is directly proportional to metal ion concentration in solution. In general, the data indicated that sorption capacity increased with increase in initial metal ion concentration of Ni^{2+}. The initial metal concentration is an important factor that provides an important driving force to overcome all mass transfer resistance of Ni^{2+} between the aqueous and solid phases (Nuhoglu and Malkoc, 2009). At moderate concentrations of Ni^{2+}, biosorption sites took up the available Ni^{2+} rapidly. At higher concentrations, on the other hand, Ni^{2+} needs to diffuse to the biomass surface by intraparticle diffusion.

Effect of temperature on biosorption of Ni^{2+}: The equilibrium uptake of Ni^{2+} by *Streblus asper* was affected by temperature and increased with increasing temperature up to 35°C which is an optimum temperature in relation to this work (Fig. 5). Biosorption of Ni^{2+} was endothermic up to this optimum temperature because the extent of biosorption increased with increasing temperature. Above the optimum temperature, the biosorption decreased with increasing temperature. The adsorption mechanism, chemical or physical is an important indicator to describe the type of level of interaction between the adsorbate and adsorbent. Decreasing in adsorption with increasing temperature indicates physical adsorption while increasing in adsorption with increasing in temperature signifies chemisorption. However, there are a number of contradictory cases in the literature (Kara *et al*., 2003). The biosorption of Ni^{2+} by *Streblus asper* may involve both physical and chemical adsorption. This effect may be due to the fact that at higher temperatures, an increase in active sites occurs due to bond rupture.

Adsorption isotherms: Biosorption isotherms are important for understanding the mechanisms of the biosorption process. Present data fitted well into the Freundlich and Dubinin and Radushkevich (1947) isotherm. To examine the relationship between metal uptake (q_e) and aqueous concentrations $(C)_e$ at equilibrium, biosorption isotherm models were used for fitting the data of which the Dubinin and Radushkevich (1947) equations are the widely used. The linearized Freundlich isotherm is given in Eq. 2. This isotherm assumes that the biosorption process takes place on heterogeneous surfaces, and that the biosorption capacity is related to the concentration of biosorbent at equilibrium:

$$\text{Log}\, q_e = \log K_f + \frac{1}{n}\log C_e \quad (2)$$

where, K_f (L g-1) and n (dimensionless) are Freundlich biosorption isotherm constants that reveal the extent of

Table 1: Freundlich and Dubinin–Radushkevich isotherm parameters for the biosorption of Ni^{2+} by *Streblus asper*

Freundlich Isotherm			Dubinin–Radushkevich			
R^2	K_f (L g^{-1})	n	R^2	q_m (mg g^{-1})	β (mol^2 kJ^{-2})	E(kJmol^{-1})
0.827	0.10	1.58	0.937	40.48	3×10^{8}	4082.48

the biosorption and the degree of nonlinearity between solution concentration and biosorption, respectively. q_e is the Ni^{2+} biosorbed on the biosorbent (mg/g dry weight) while C_e is the final concentration of Ni^{2+} (mg L^{-1}) in the solution. A plot of log q_e against log C_e, for the biosorption of Ni^{2+} by *Streblus asper* was made to determine the value of K_f and n from the intercept and the slope, respectively.

Dubinin and Radushkevich (1947) does not assume a homogeneous surface or a constant biosorption potential. The D-R isotherm model distinguishes between the physical and chemical biosorption. Eq. 3 shows the linear form of the D-R isotherm (Dubinin and Radushkevich, 1947).

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (3)$$

where, β is a constant that is related to the mean free energy of biosorption per mole of the biosorbate (mol^2 kJ^{-2}); q_m is the theoretical saturation capacity mol g^{-1} and ε is the Polanyi potential.

$\varepsilon = RT \ln (1+(1/Ce)$, where R (J mol^{-1} K^{-1}) is the gas constant and T (K) is the absolute temperature. A plot of ln q_e against ε^2, enabled the determination of the value of q_m (mol g^{-1}) from the intercept and the value of β from the slope. The constant β gives is related to the mean free energy, E (kJ mol^{-1}), of biosorption per mole of the biosorbate. The value of *E* can be evaluated using the relationship in Eq. 4 (Hasany and Chaudhary, 1996; Dubey and Gupta, 2005).

$$E = \frac{1}{(2\beta)^{\frac{1}{2}}} \quad (4)$$

The value of E gives information about the type of biosorption mechanism: either chemical ion-exchange or physical biosorption.

Table 1 reports the different parameters (R^2, K_f, n, q_m, β, E) obtained from Freundlich and Dubinin and Radushkevich (1947) isotherm models. The value of n is greater than unity which means that Ni^{2+} is favourably biosorbed by *Streblus asper*. The saturation capacity, q_m, of Ni^{2+} by *Streblus asper* was found to be 40.48 mg g^{-1}. The numerical value of the mean free energy of biosorption was calculated to be 4082.48 kJ mol^{-1}, indicating that the biosorption may occur via a chemical ion-exchange mechanism. Our data did not fit well into Langmuir isotherm.

Table 2: Thermodynamic parameters for the biosorption of Ni^{2+} on *Streblus asper*

			ΔG° (kJ mol^{-1})		
R^2	ΔH° (kJ mol^{-1})	ΔS° (kJ K^{-1} mol^{-1})	T_1=298 K	T_2=308 K	T_3=323 K
0.932	52222.73	176.53	-1509.95	-1824.48	-512.40

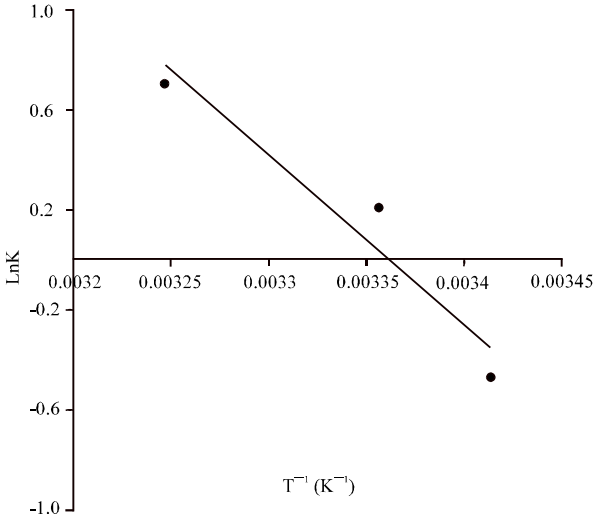

Fig. 6: Thermodynamic plot of the biosorption of Ni^{2+} by *Streblus asper*

Thermodynamic parameters: The standard Gibb's free energies of the biosorption of Ni^{2+} at different temperature are presented in Table 2. The negative values of Δ*G*° show that the biosorption process is feasible and spontaneous in nature. The values of enthalpy change (ΔH°) and entropy change (ΔS°) for the biosorption of each of the Ni^{2+} by *Streblus asper* were calculated from the slope of the plot of ln K versus T^{-1} as shown in Fig. 6. The values of the thermodynamic parameters are also presented in Table 2. The positive values of ΔH° for Ni^{2+} ions biosorption suggest the endothermic nature of biosorption and possible strong bonding between the metal ion and *Streblus asper* (Donmez and Aksu, 2002). The positive values of ΔS° for Ni^{2+} biosorption showed increased randomness at solid solution interface during the biosorption of the metalions on *Streblus asper* (Sarin *et al*., 2006).

Adsorption kinetic: Kinetic models were applied in this research work to test experimental data in order to determine the mechanism of biosorption of Ni^{2+} by *Streblus asper* and the potential rate-controlling steps, mass transport and chemical reactions. Pseudo first-order and pseudo second order kinetic models were tested. Figure 7 shows the pseudo second order kinetics for Ni^{2+}. Pseudo first-order model could not fit the experimental

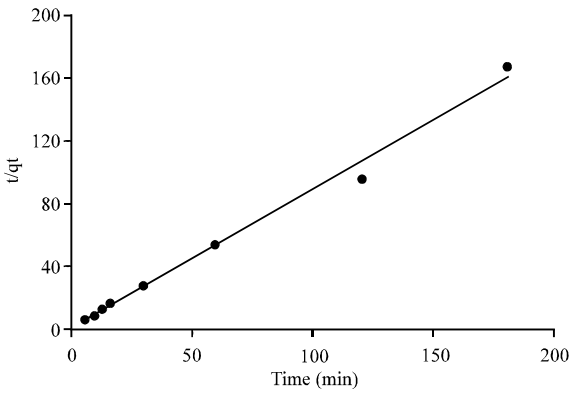

Fig. 7: The pseudo second-order plot for the biosorption kinetic study of Ni^{2+} by *Streblus asper*

Table 3: The pseudo second-order parameters for the kinetic study of Ni^{2+} biosorption by *Streblus asper*

Metal	R^2	k_2 (g $mg^{-1}min^{-1}$)	q_e (calc.) (mg g^{-1})	q_e (expt.) (mg g^{-1})
Ni^{2+}	0.992	1.350	1.125	1.260

data. This is because the coefficient of correlation for first-order kinetic model was <<1. The best fits, in the data range, were found to be the pseudo second order model, indicating that the rate-limiting step is a chemical biosorption process between Ni^{2+} and the *Streblus asper*. The pseudo second-order model is based on the assumption that biosorption follows a second-order mechanism. So, the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites (Zafar *et al*., 2007).

The values of the parameters; k_2 and q_{eq} and correlation coefficients, R^2, are shown in Table 3 for Ni^{2+}. The correlation coefficients obtained are approximately one ($R \approx 1$) and the adequate fitting of theoretical and experimental q_{eq} values for all the two metals suggest the applicability of second-order kinetic model based on the assumption that the rate limiting step may be the biosorption of Ni^{2+} and *Streblus asper* in explaining the kinetics of biosorption (Donmez and Aksu, 2002). The calculated value of q_{eq} (1.125 mg g^{-1}) closely agreed with experimental value (1.260 mg g^{-1}). The second order rate constants for the biosorption of Ni^{2+} from solutions by *Streblus asper*is 1.35.

CONCLUSION

The use of *Streblus asper* as biosorbent for removal of Ni^{2+} from aqueous solution was found to be a function of the initial solution pH, biosorbent dose, agitation time, temperature and the initial metal concentration of the solution. All these parameters highly affected the overall metal uptake capacity of the *Streblus asper*. Solution pH is an important parameter that affected the biosorption of Ni^{2+} by *Streblus asper*. Biosorption capacity was observed to increase from pH 2 to pH 8 for Ni^{2+}. A high metal uptake was observed between pH 5 and 8.

At the experimental pH and agitation time, equilibrium sorption capacity increased with increasing initial concentration of the metal ions in solution up to the highest concentration investigated (400 mg L^{-1}) for nickel (equilibrium concentration). The sorption capacity for nickel reached the maximum concentration of 400 mg L^{-1}. Sorption capacity was observed to decrease as the biosorbent dose increases from 0.4 to 3 g of Ni^{2+}. Increase in metal uptake was observed to be a function of temperature for nickel uptake, except that nickel uptake by *Streblus asper* reaches a maximum at 35°C.

The kinetics of nickel biosorption by *Streblus asper* shows that equilibrium sorption capacity occurs in 10 min. This process can be described by a pseudo second order model based on the assumption that the rate-limiting step may be chemical sorption or chemisorption. Freundlich and Dubinin and Radushkevich (1947) isotherm models were used to estimate the maximum nickel uptake and the affinity parameter that reflects the affinity of the material for the solute.

Perusing at the thermodynamic parameters, the negative values of the Gibb's free energy, $\Delta G°$, shows that the biosorption process is feasible and spontaneous. The positive values of the enthalpy, $\Delta H°$, show that the biosorption process is endothermic.

Hence, the values of the parameters obtained show that *Streblus asper* is a good biosorbent for the removal of heavy metals from wastewater. Overall, *Streblus asper* is a good biosorbent for removal of nickel from solution and most likely waste waters which implies that the biomass can be used in water treatment (purification). The leaves of *Streblus asper* are rough on surfaces. This characteristic might increase its biosorbent capacity.

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