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Screening of agricultural waste for Ni(II) adsorption: Kinetics, equilibrium and thermodynamic studies

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This study reports the adsorption of Ni(II) ions onto waste powders prepared from egg plant (EGP), sweet potato (SWP) and banana peels (BNP). The influence of adsorption parameters, such as pH, contact time, adsorbent weight, adsorbate concentration and temperature were investigated. Equilibrium was described by the Langmuir and Freundlich models. Ni(II) uptake was very fast reaching a maximum within 20 min of adsorbent contact with metal solution. Comparison of removal capacities for EGP, SWP and BNP indicated that EGP was more effective in removing Ni(II) from aqueous solution. The kinetic data fitted the pseudo second order model. Thermodynamic parameters ΔH and ΔS were negative which suggest that adsorption process was spontaneous. The results of Fourier transform infrared (FTIR) indicated several binding and chelating ions, such as carboxyl, carbonyl and hydroxyl groups on the biomaterials surfaces were responsible for Ni(II) adsorption.

Key words: Adsorption, nickel, biomaterials, kinetics, equilibrium, thermodynamics.

INTRODUCTION

Metals are used in a variety of applications and are thus present in municipal and industrial effluents and landfills. These metals commonly include calcium, sodium, magnesium, potassium, iron, manganese, arsenic, cadmium, nickel, lead, chromium, mercury, cobalt, copper and many others. Their pollution of the natural environment has become a serious problem (Riaz et al., 2009). They are present in virtually every area of modern consumer goods such as construction materials, cosmetics, medicines, processed foods and fuel sources. They have been reported to have toxic and/or carcinogenic effects on human health, and their removal is important for the sustenance of a healthy environment (Forster and Wase, 1997). Ni(II) ion is one of the heavy metals frequently encountered in raw wastewater streams from landfill leachate, mine drainage, metal finishing and forging. Concentrations up to 130 mg/l have been reported in these water stream (Patterson, 1985). It

is bio-accumulated by marine animals and may directly enter the human food chains, thus presenting a high health risk to consumers (Diniz and Volesky, 2005). Even at low concentration it can be toxic to organisms. Acute poisoning by Ni(II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, cyanosis and extreme weakness (Malkoc and Nuhoglu, 2005).

Many physicochemical treatment technologies, such as flotation, coagulation-flocculation, chemical oxidation, membrane processing, ion exchange and adsorption onto activated carbon have been used for the removal of heavy metals from municipal and aqueous wastewater streams (Dean et al., 1972; Sheng et al., 2004). These technologies suffer certain disadvantages which range from high running cost for chemical purchase and a consistent high sludge volume which is produced after concentration of the metal (Silva et al., 2004). Membranes applied for micro filtration are susceptible to fouling due to formation of biological slimes and this poses a significant problem to the continuous use of the technology.

Adsorption onto activated carbon is one of the most extensively applied physicochemical processes for the

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removal of pollutants from leachates and wastewaters (Enzminger et al., 1987). Although, activated carbon is widely applied for pollutant removal, natural low-cost materials (biomaterials) have also been successfully employed as adsorbents for heavy metal removal from aqueous solutions and wastewaters. The reduced running cost has been the focal point for such research (Juang and Shiau, 2000; Lacour et al., 2001; King et al., 2007). The recent attention in this field is evident in the number of articles currently being published on the use of low cost agricultural waste for metal removal from aqueous solution (Odoemelam et al., 2011; Gupta et al., 2009, 2003; Subbaiah et al., 2011; Opeolu et al., 2009).

Peelings, also known as skin, are the outer protective layers of a fruit or vegetable currently gaining wide attention as biosorbent in water treatment. Peelings of different fruits such as, orange, banana, water melon, cassava, mango, etc., have been used as adsorbents for the removal of different pollutants from wastewater (Bhatnagar and Sillanpää, 2010; Li et al., 2008). The use of mango peel waste for the adsorption of Cd(II) and Lead(II) has been reported (Iqbal et al., 2009a, b).

Volesky and Holan (1995) earlier noted that tedious experimental screening of readily available biomaterial types is the basis for discovering new biomaterials. To the best of our knowledge, heavy metal adsorption of these materials, egg plant (EGP) and sweet potato (SWP) has not been reported. Banana peels (BNP) has been reported as effective and inexpensive biomaterials for cadmium removal from waste water (Memon et al., 2008). In this study, we report the adsorption property of three readily available agriculture wastes (EGP, SWP and BNP) as possible adsorbents for heavy metal, namely nickel in aqueous solution. The kinetics, thermodynamic and other adsorption related parameters determined under optimized conditions were investigated.

MATERIALS AND METHODS

Preparation of biosorbents

Batch samples of banana, egg plant and sweet potato peels was collected from fruit and vegetable market in Cape Town and were washed copiously with tap, distilled and deionized water. Samples were dried to constant weight in convection oven at 50 to 60°C, communized, ground and screened to 75 μm. Samples were then stored in pre-labeled plastic bottles and preserved in desiccators until the time of use. Powder from egg plants peels, sweet potato peels and banana peels were labeled EGP, SWP and BNP, respectively.

Preparation of chemicals

All chemicals used were of analytical grade and were obtained from Sigma-Aldrich Company. 1000 mg/L stock solution of Ni(II) was prepared by dissolving 4.4786 g $NiSO_4.6H_2O$ in 1 L distilled-deionized water. The pH of the solution was adjusted using 0.1 M NaOH or HCl. Working solutions of Ni(II) in the range of 5 to 220 mg/L were then prepared from the stock solution by appropriate

dilution of the stock with distilled-deionized water.

Fourier transform infrared (FTIR) analysis of samples

FTIR absorption spectra of EGP, SWP and BNP were obtained using the potassium bromide (KBr) pellet method. Approximately, 1 mg of finely powdered dry sample was mixed with 250 mg of dry potassium bromide and ground to fine powder in an agate mortar. The mixture was transferred into a die and compressed to form a pellet (13 mm diameter) by the use of hydraulic press. The pellet was carefully removed from the die, placed in the holder and the spectra of the samples were recorded over the range 400 to 4000 cm^{-1} using FTIR (Perkin Elmer[TM] Spectrum 1000).

Effect of adsorbent dose

The effect of varying amounts of EGP, SWP and BNP on the adsorption of Ni(II) was studied by adding 0.025, 0.05, 0.1, 0.2, 0.4 and 0.6 g of the biosorbents corresponding to 1, 2, 4, 8, 16 and 24 g/L, respectively, in each of 50 ml conical flasks containing 25 ml of 100 mg/L Ni(II). Contact time and pH were kept constant at 120 min and pH 5, respectively. Residual Ni(II) in each filtrate solution was analyzed by atomic absorption spectrophotometer (AAS) (Model Perkin Elmer 3300).

Percentage Ni(II) removal was calculated according to Equation 1:

$$\text{Biosorption (\%)} = \frac{C_o - C_e}{C_o} \times 100$$

where C_o and C_e are initial and equilibrium metal concentrations, respectively.

Effect of pH

The effect of pH on the adsorption of Ni(II) by each biomaterial was studied by weighing 0.4, 0.4 and 0.05 g of SWP, EGP and BNP, respectively, into each of 50 ml conical flasks containing 25 ml of 100 mg/L Ni(II) solutions after appropriate pH adjustment. pH was studied in the range of 2 to 8 pH units. Residual Ni(II) was measured in filtered solutions and percentage removal was calculated according to Equation 1.

Effect of contact time

The effect of contact time on the adsorption process was studied in both batch and semi-batch mode. Batch experiments were conducted by varying contact time of optimized adsorbents masses with 50 ml of 100 mg/L Ni(II) ion solution at a pH 5 and 298K. Contact times were 1, 3, 5, 10, 15, 20, 25, 30, 60, 90 and 120 min. Semi-batch experiments were conducted by contacting 0.8, 0.8 and 0.1 g of EGP, SWP, BNP, respectively, with 50 ml of 100 mg/L Ni(II) in a conical flask. Samples were drawn from the flask at regular intervals, filtered and analyzed for residual Ni(II).

Effect of initial Ni(II) concentration

Ni (II) standard solutions ranging from 5 to 220 mg/L were prepared from the stock solution. Optimized biosorbent amount was weighed into 25 ml of metal solution for 2 h and residual metal was determined in filtered solutions. The data obtained were then used to test the fitness of the sorption process to Langmuir and Freundlich isotherms.

Effect of temperature

The effect of temperature on the adsorption was studied in the range of 295 to 333K at fixed initial ion concentration of 100 mg/L for 90 min and at pH 5.

RESULTS AND DISCUSSION

FTIR results

The comparative FTIR spectrum of EGP, SWP and BNP is as shown in Figure 1. The band at 3416 to 3447 cm^{-1} was assigned to OH in free alcohols. The band at 2921 to 2929 cm^{-1} was assigned to C-H stretching (Li et al., 2007). The band at 1617 to 1637 cm^{-1} was assigned to the asymmetric stretching of –COO- in ionic carboxylic group .The band at 1384 cm^{-1} was assigned to symmetric –COO- stretching in pectin (Farinella et al., 2008). The band at 1021 to 1054 cm^{-1} was assigned to C-OH stretching in alcohols. The deformation vibration of carbonyl stretching at 1245 cm^{-1} by Guilbaud et al. (2003) was observed in the FTIR spectrum of SWP. The FTIR spectra of the Ni(II) loaded adsorbents are as shown in Figure 2. After metal loading, the C=O deformation band (1384 cm^{-1}) in pectin remained constant while shifts occurred in the ionic carboxylic bands indicating an interaction of this functional groups with the adsorbed Ni(II). Significant shifts were also observed in the O-H stretching band at 3416 to 3447 cm^{-1}. For example, the 3447 cm^{-1} band in EGP shifted to 3421 cm^{-1}. After adsorption, the 1734 cm^{-1} band appeared in the spectra of all the adsorbents. This band has been attributed to the stretching vibration of C=O band due to non-ionic carboxylic groups, as in carboxylic acid or their esters (Iqbal et al., 2009a, b; Li et al., 2007). The spectrum on Figure 1 shows that all the biomaterials possess ionic carboxylic functional groups. The appearance of the non-ionic C=O band in the metal loaded spectra may indicate the interaction of the ionic carboxylic acid with Ni(II) ion, leading to a non-ionic C=O after metal loading. The functional groups in BNP were verified from earlier reports (Memon et al., 2008). Those for EGP and SWP were unavailable in the literature. Table 1 represents the FT-IR adsorption bands (wave numbers cm^{-1}) of biomaterials and Ni(II) loaded biomaterials.

Effect of adsorbent dose

The effect of adsorbent dose on the adsorption of Ni(II) by EGP, SWP and BPN is as shown in Figure 3. Adsorbent dose varied from 0.025 to 0.6 g for the three biomaterials. It was observed that the percentage adsorption increased with increasing adsorbent dose, reaching an optimal at 0.4 g for EGP and SWP, corresponding to 62 and 41% removal, respectively. The percentage removal for BNP reached a maximum at 0.05

g corresponding to 29% Ni(II) ion removal. At adsorbent doses higher than 0.4 g for EGP and SWP, and 0.05 for BNP, there was no significant increase in the percentage Ni(II) removed by the biomaterials. These respective values for EGP, SWP and BNP were therefore selected as optimum biomaterial utilized in other aspects of this study.

Effect of pH

To examine the effect of pH on the biosorption efficiency, several experiments were performed at different pH ranges from 2 to 8 as shown in Figure 4. Biosorption of Ni(II) was very low at pH 2. At this acidic pH, the proton concentration in solution is high and they compete with free metal cations for adsorption sites on the surface of the biomaterial (Zafar et al., 2007). The results indicate that relatively little biosorption took place at pH 2 and only 32.7, 10.7 and 1.9% of Ni(II) ions were adsorbed on EGP, SWP and BNP, respectively. Increasing pH from 2 up to the range 3 to 6 brought about a rapid increase in the removal efficiency. Adsorption of Ni(II) on the biomaterials reached its maximum at the following pH values: pH 5 for EGP (61% removal), pH 4 to 5 for SWP (40% removal) and pH 5 for BNP (31% removal). pH 5 was therefore selected for further studies. After pH 6, cloudy precipitates of Ni(II) were visible in solution and thus were inaccessible for Ni(II) adsorption by the biomaterials.

Effect of initial ion concentration

The effect of varying initial concentration (5 to 220 mg/L) of Ni(II) on the adsorption onto EGP, SWP and BNP is as shown in Figure 5. The apparent capacity of the adsorbents increased with increasing concentration of Ni(II) ions reaching a maximum removal at 100 mg/L. Percentage removal was 62.5, 40.2 and 26.1% for EGP, SWP and BNP, respectively at 100 mg/L. In all experiments conducted at varying concentration of Ni(II) ions, the percentage removal followed the trend EGP> SWP > BNP. The adsorption behavior exhibited by the biomaterials indicates that surface saturation was dependent on initial metal ion concentration and reached a maximum at 100 mg/L. In an earlier study, Zafar et al. (2007) showed that Ni(II) adsorption by protonated rice barn at varying concentration of Ni(II) ions reached a maximum percentage removal at 100 mg/L of Ni(II) ions. Metal diffusion through biomaterial surface by intraparticle diffusion was identified as the controlling factor for this observed trend (Zafar et al., 2007).

Effect of temperature
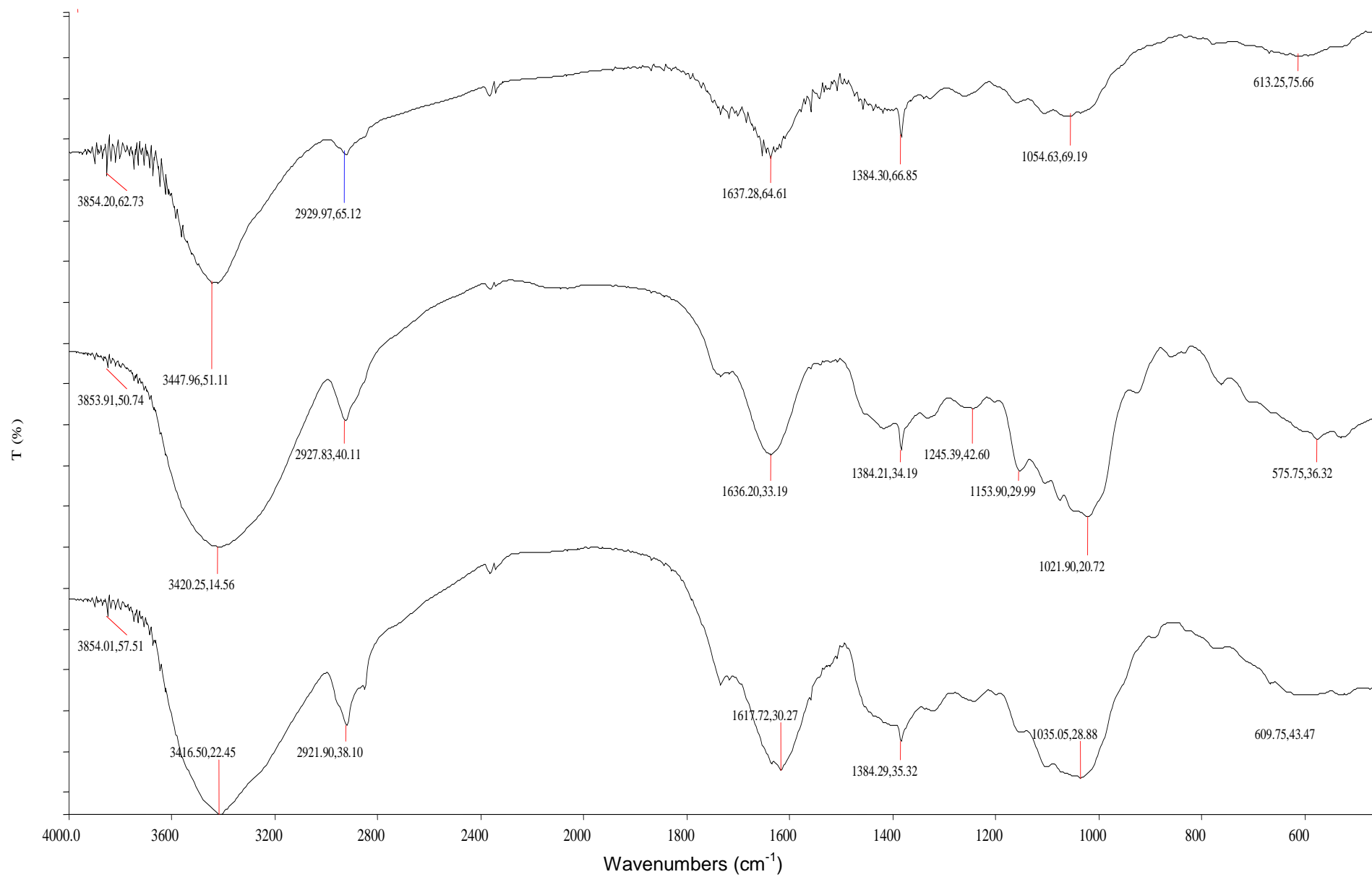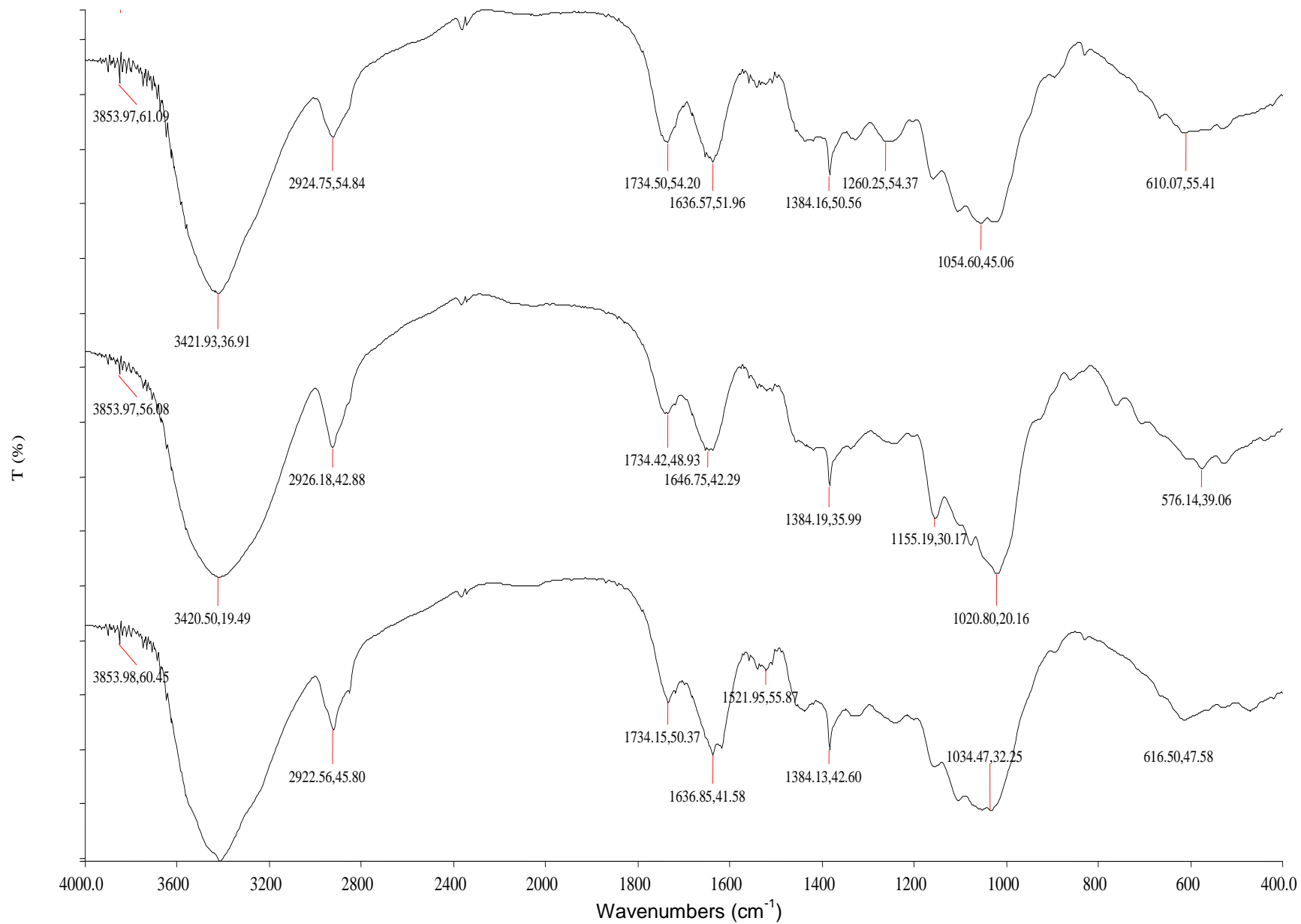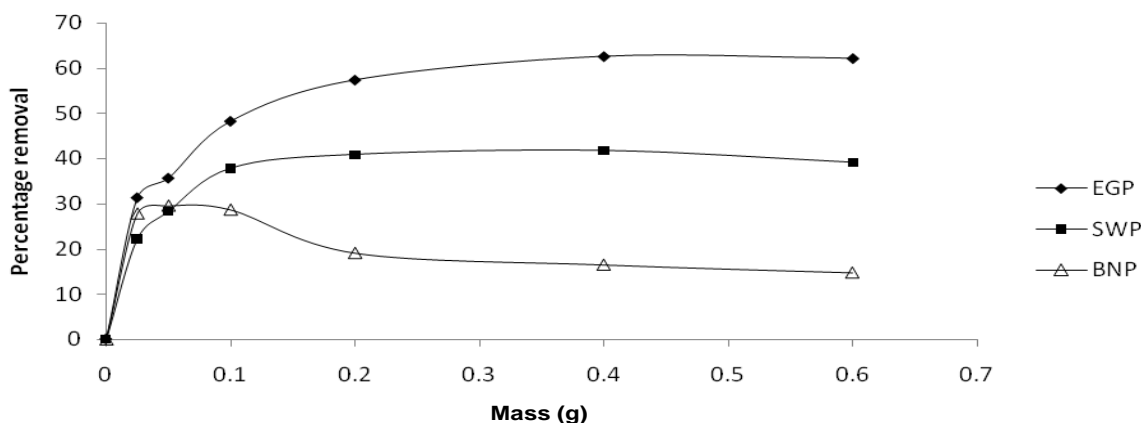
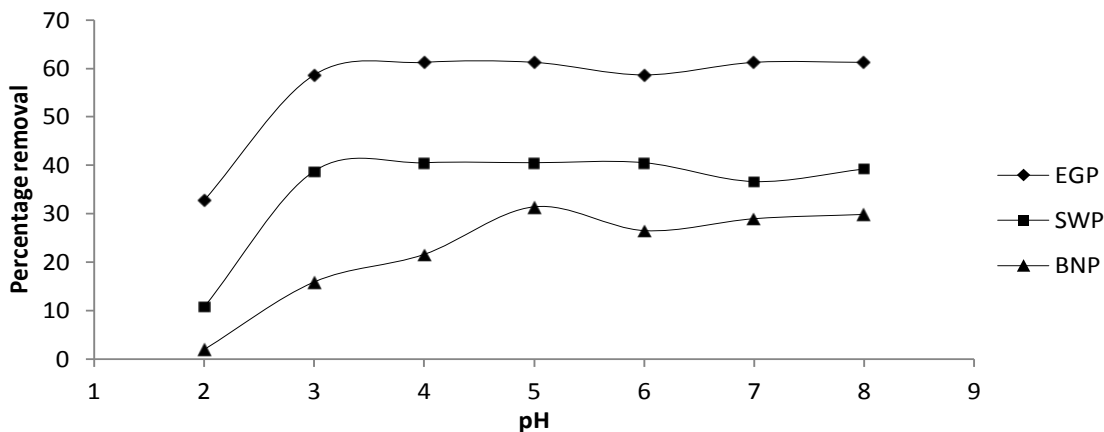The effect of temperature on adsorption of Ni(II) onto

Figure 1. FTIR spectrum of biomaterials; from above EGP, SWP and BNP.

Figure 2. FTIR spectra of Ni (II) loaded biomaterials; from above EGP-Ni, SWP-Ni and BNP-Ni.

Table 1. FT-IR adsorption bands (wavenumbers cm^{-1}) of biomaterial and Ni(II) loaded biomaterial.

| Functional groups	EGP	EGP-Ni(II)	SWP	SWP-Ni(II)	BNP	BNP-Ni(II)
OH free alcohols	3447	3421	3420	3420	3416	3417
C-H stretching	2929	2924	2927	2926	2921	2922
C=O stretching vibration (non ionic)	-	1734	-	1734	-	1734
COO- asymmetric stretching (ionic)	1637	1636	1636	1646	1617	1636
COO- symmetric stretching	1384	1384	1384	1384	1384	1384
C=O deformation stretching	-	-	1245	-	-	-
C-OH stretching in alcohols	1054	1054	1021	1020	1035	1034

Figure 3. Effect of adsorbent dose on adsorption of Ni (II) ions from aqueous solution at pH 5.

Figure 4. Effect of pH on adsorption of Ni (II) ions from solution.

EGP, SWP and BNP was investigated at five different temperatures between 295 and 333K. The results are as shown in Figure 6. For EGP and SWP, the percentage removal decreased sharply as the temperature increased from 295 to 303K, remaining fairly constant from 303 to 323K before reducing sharply again at 333K. BNP on the other hand, presented a different behavior as the percentage removal increased slightly with increase in temperature. The BNP plot reaches a maximum at 313K before reducing sharply as temperature was increased from 323 to 333K. A similar result was presented for the adsorption of Cd(II) using *Moringa oleifera* and *Moringa stenopetala* biomaterial (Mataka et al., 2010). The observed decrease in Ni(II) percentage removal with increasing temperature is suggestive of weak binding interaction between the active sites and the Ni(II) ion
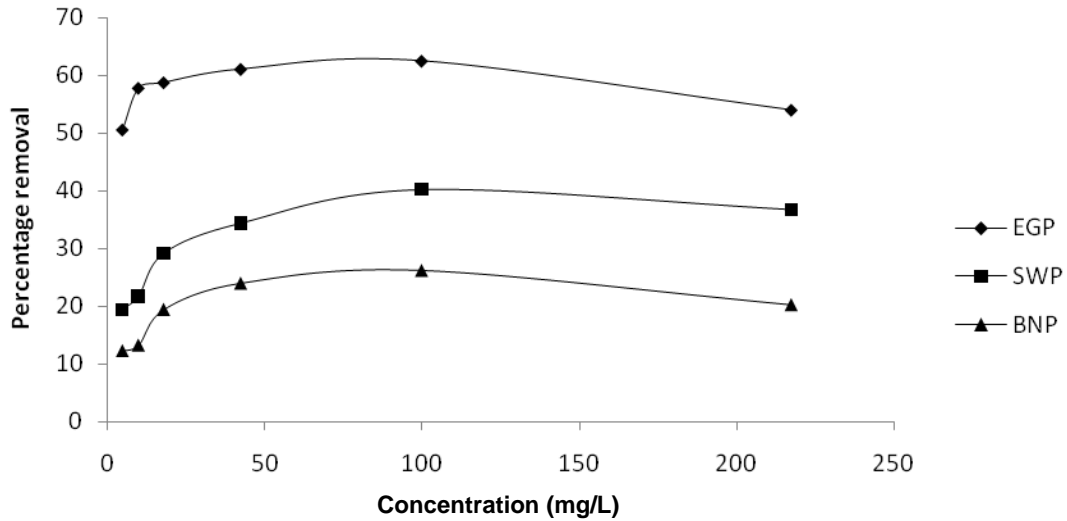
Figure 5. Effect of initial metal concentration on adsorption of Ni (II) from solution at pH = 5 and 298K.
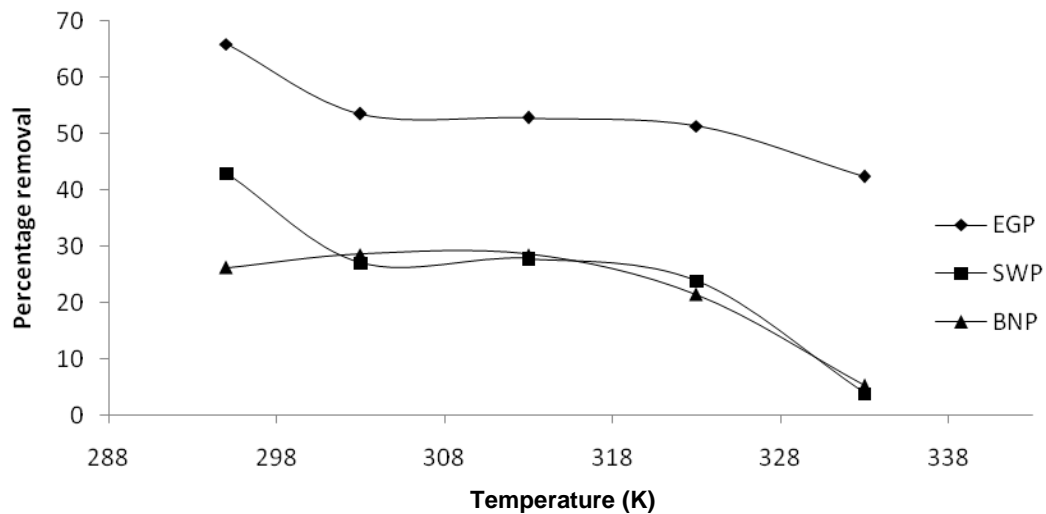
Figure 6. Effect of temperature (K) on the adsorption of Ni (II) ions by EGP, SWP and BNP. (time = 60 min ; pH = 5).

which support physisorption (Panday et al., 1986). Furthermore, physical adsorption reactions are exothermic; hence, the extent of adsorption generally increases with a decrease in temperature (Salinas et al., 2000).
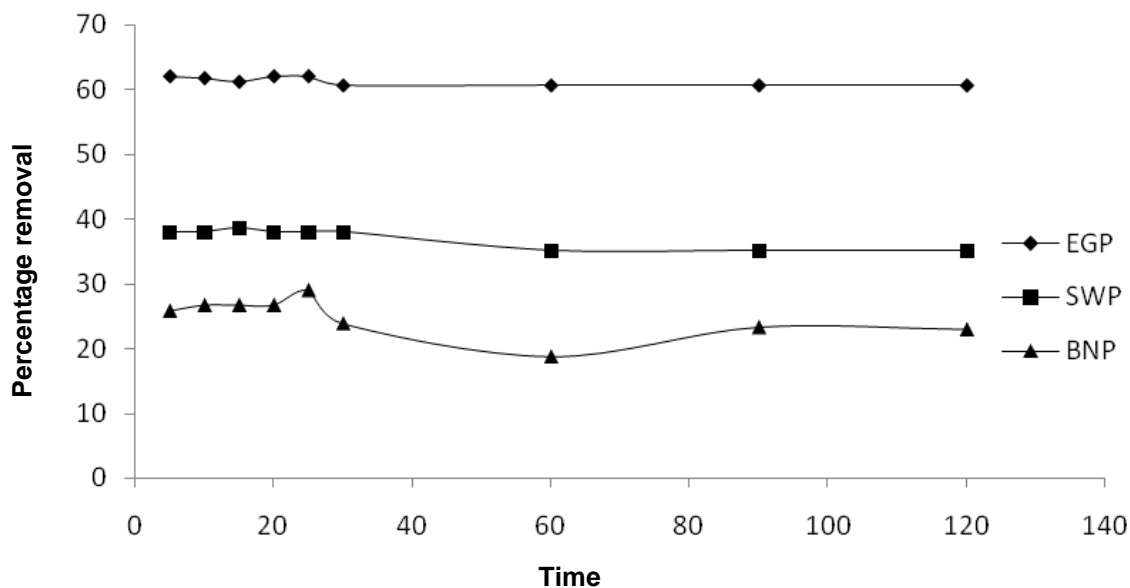
Effect of time

Batch experiments

Equilibrium time is an important parameter for an economical wastewater treatment system. It helps to study the biosorption mechanism and is required to obtain an insight of the rate of the biosorption. With the help of kinetics data, the rate determining step of the transport mechanism and thus the modelling and the design of the process can be described (Farooq et al., 2011). The effect of contact time on the adsorption of Ni(II) on EGP, SWP and BNP in batch mode is as shown in Figure 7. Maximum percentage removal for SWP (39%) and BNP (28%) occurred within 5 min of contact, while maximum percentage removal for EGP (65%) occurred after 20 min. A dynamic system existed between the Ni(II) ions and the biomaterials; the concentration of Ni(II) ions adsorbed by each biomaterial
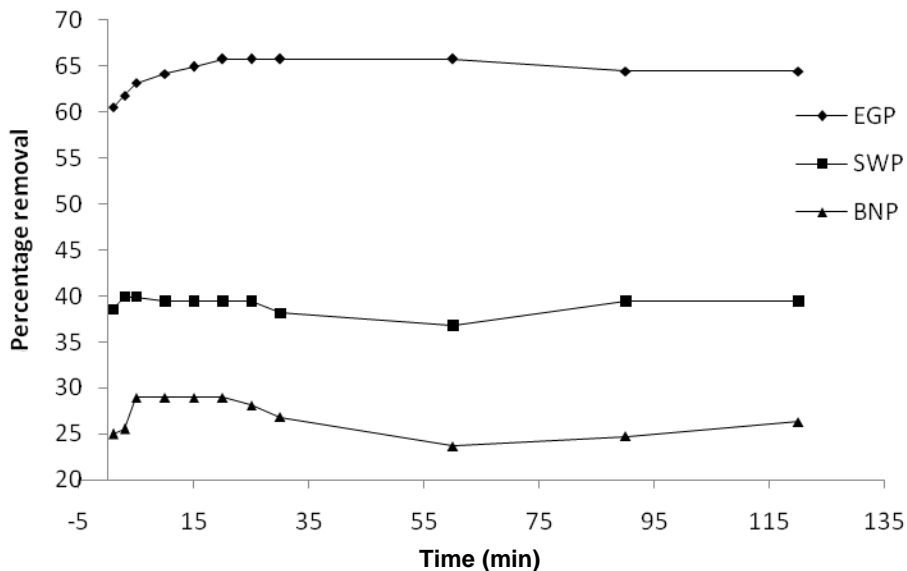
Figure 7. Effect of contact time (batch mode) on adsorption of Ni (II) ions by EGP, SWP and BNP.

Figure 8. Effect of time on Ni (II) adsorption (Semi-batch mode) using EGP, SWP and BNP.

reduced after reaching the maxima and equilibrium was only established after 60 min of contact. Similar results have been reported using other biosorbents for the uptake of different heavy metals (Prasanna et al., 2006; Bueno et al., 2008; Lawal et al., 2010). Metal uptake by biomaterial has been regarded to occur in phases, usually beginning with an initially fast adsorption phase where the adsorbate reaches a maximum within 5 to 15 min after solid liquid contact (Volesky and Holan, 1995).
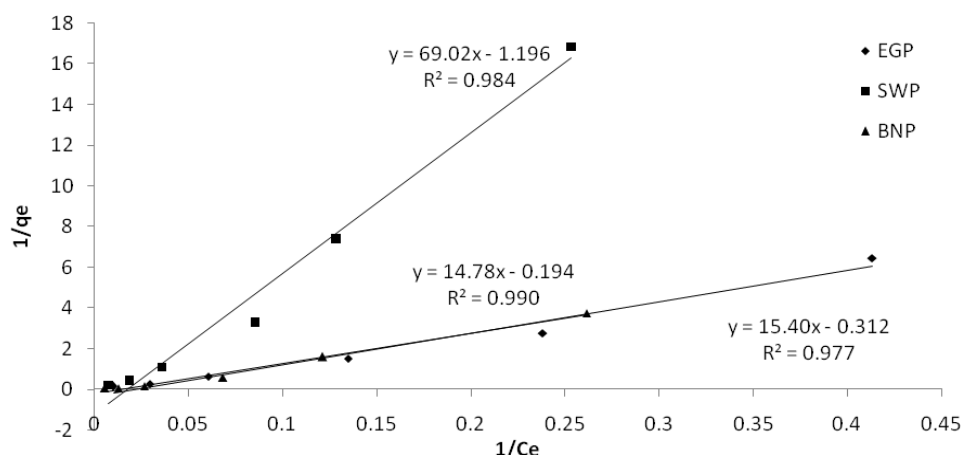
Semi-batch experiments

Figure 8 showed that the results of semi-batch adsorption experiments for Ni(II) on EGP, SWP and BNP varied as a function of time. The weighed masses correspond to the optimal masses obtained from previous experiments. The results showed that the biomaterials reached their maximum percentage removals very quickly, (< 25 min). Reduction in percentage removal was observed after

Table 2. Percentage removal and q_e obtain in batch and semi-batch experiments.

	Batch		Semi-batch	
	Removal (%)	q_e (mg/g)	Removal (%)	q_e (mg/g)
EGP	65	3.9	61	3.4
SWP	39	2.3	38	2.1
BNP	28	13.7	28	12.8

Figure 9. Langmuir isotherm for adsorption of Ni (II) ion onto EGP, SWP and BNP.

reaching the maxima and equilibrium was achieved after 60 min of contact. Similar observation was noticed in the batch experiments. This may be as a result of desorption of the metal from the surface of the biomaterial before attaining equilibrium with the Ni(II) solution. The maximum quantity adsorbed (q_e) for the biomaterials at optimum time were 3.43 mg/g (20 min), 2.13 mg/g (25 min) and 12.85 mg/g (25 min) for EGP, SWP and BNP, respectively. The higher q_e for BNP obtained in our calculations is due to the small mass of the material optimized for the study. Higher masses of BNP as shown in Figure 3 did not bring about appreciable removal of Ni(II) ions. Recommended usage for BNP would be to apply it in small doses in repeated experiments. Comparative results from the batch and semi batch process are as shown in Table 2. There was no significant difference from results obtained using both methods.

Adsorption isotherms

Adsorption isotherms are used to describe equilibrium data and are important for developing equations that can be used to compare different biosorbents under different operational condition. Equilibrium data obtained in this study was fitted to the widely applied Langmuir and Freundlich models.

Langmuir (1918) isotherm is the most commonly used

adsorption isotherm and is linearized by Equation 2:

$$\frac{1}{q_e} = \frac{1}{q_m K_L}\left[\frac{1}{C_e}\right] + \frac{1}{q_m} \tag{2}$$

where C_e is the concentration of the adsorbate solution (mg/L) at equilibrium, q is the adsorption capacity (mg/g) and b is related to the energy of adsorption (L/mg). Values of q_m were calculated from the linear plot of $1/q_e$ against $1/C_e$ (Lawal et al., 2010).

The Freundlich (1907) isotherm is the most frequently used to describe the adsorption of inorganic and organic compounds in solution. The logarithmic form of the model is presented in Equation 3:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{3}$$

where K_f and n are constants incorporating all factors affecting the adsorption process (adsorption capacity and adsorption intensity). Values of K_f and n were calculated from the slope and intercept of the plot of log q_e against log C_e.

Figures 9 and 10 show the Langmuir and Freundlich plots for the biomaterials, respectively. A summary of the
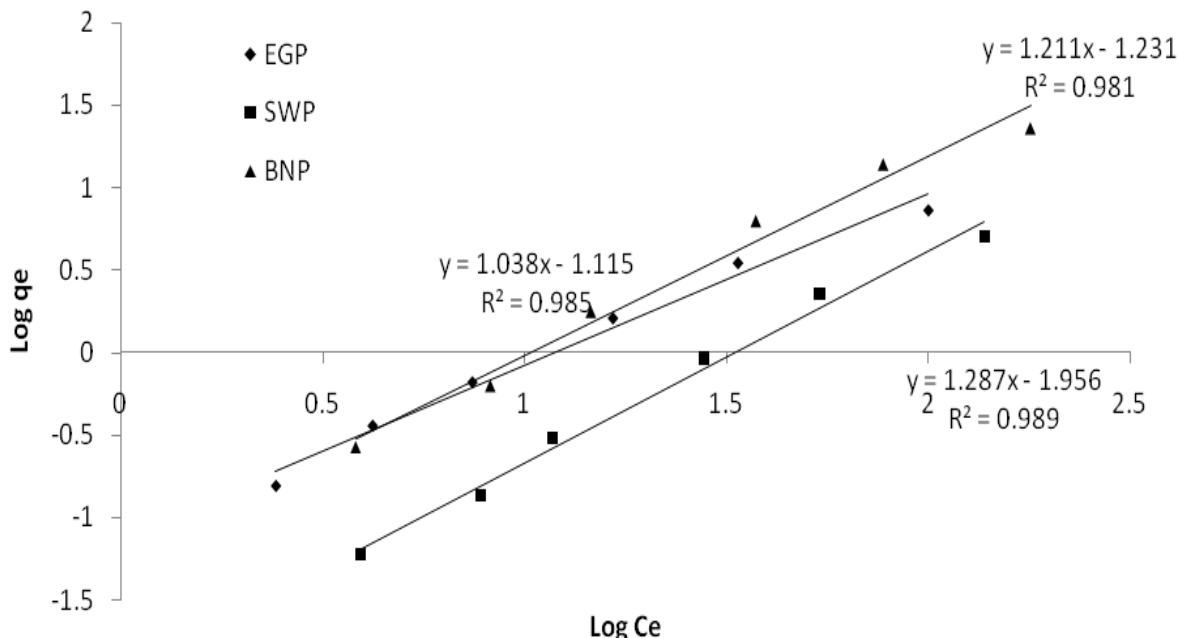
Figure 10. Freundlich isotherm for adsorption of Ni (II) ion onto EGP, SWP and BNP.

Table 3. Adsorption isotherm parameters for Ni (II) removal by EGP, SWP and BNP.

		Langmuir			Freundlich	
	$q_{exp\ 100\ (mg/L)}$	q_m	K_L	R^2	n	R^2
EGP	3.5156	3.205	0.128	0.9772	0.962	0.9855
SWP	2.2656	0.509	0.005	0.9844	0.776	0.9895
BNP	13.75	5.133	0.013	0.9906	0.825	0.9816

calculated parameters for each model is presented in Table 3. Based on the regression values, the Freundlich isotherm better describes the nature of the adsorption process between Ni(II) and EGP or SWP ($R^2 > 0.98$). The Freundlich model assumes a multi-layer coverage of the biosorbent surface by Ni(II) ions by interactions which are exclusively physical in nature (Araújo et al., 2007). The adsorption of Ni(II) by EGP and SWP may therefore be physical in nature. However, since the Langmuir model also gave a high regression (> 0.97) for the adsorption of Ni(II) by EGP and SWP, then both models may be applied to describe the nature of the adsorption process.

Kinetics of adsorption process

In order to investigate the mechanism of the adsorption of Ni(II) ions by EGP, SWP and BNP, the pseudo first and pseudo second order kinetic models were used to evaluate the experimental adsorption data. These empirical mathematical models which describe adsorption data have been proven as useful tools for

scale up process optimization (Senthilkumaar et al., 2006; Sciban and Klasnja, 2003).

1. The pseudo first order kinetic model (Lagergren, 1898).

$$log(q_e - q_t) = log\,q_e - \frac{K_1 t}{2.303} \qquad (4)$$

where qe and qt are the amount of the adsorbate adsorbed at equilibrium and at time t, respectively, in mg/g, k_1 is the first order rate constant (min^{-1}) and t is time (min).

2. The pseudo second order kinetic model as proposed by Ho and McKay (1999).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

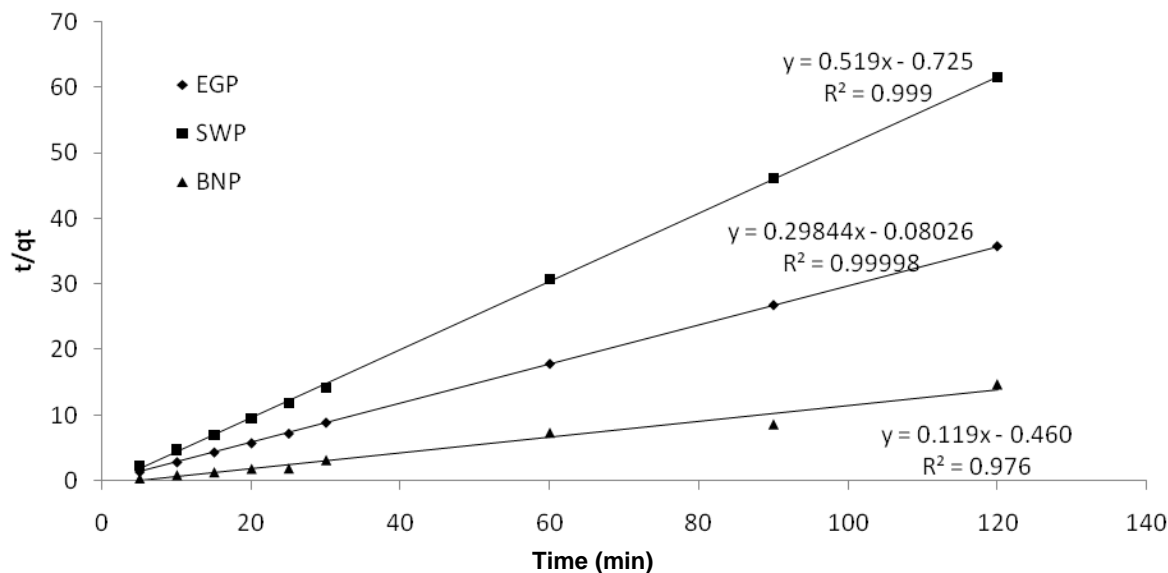where k_2 is the pseudo second order rate constant. The

Figure 11. Pseudo-second order plot for semi-batch experiments using EGP, SWP and BNP.

product of the pseudo second order rate constant k_2 and the square of the equilibrium quantity qe is defined as h_o, the initial adsorption rate (mg/g/min). Equation 5 then becomes:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$
(6)

Figures 11 and 12 show the pseudo-second plot for semi-batch and batch experiments, respectively. The kinetic plots for the pseudo second order equations presented higher regression value ($R^2 > 0.995$) when compared with the pseudo first order plots ($R^2 < 0.95$). The values of the pseudo second order parameters for the two semi-batch experiments and the batch experiment are presented in Table 4. While identical R^2 values were obtained in all experiments, the values of K_2, q_e and h_o varied with mass of the adsorbent applied and also with the mode in which the experiment was conducted. For example, the values of q_e and h_o for EGP and SWP increased when a lower mass of the adsorbent was applied in the semi-batch experiments, while the rate constant K_2 decreased. The second order kinetic parameters were also dependent on the experimental method adopted as the batch and semi-batch experiments did not produce identical results. There was no published data available for comparison of the results.

Thermodynamic studies

The results for Ni(II) ion adsorption as a function of temperature were modeled according to Equations 7 and 8 to obtain the thermodynamic parameters, free energy

change ΔG, enthalpy change ΔH and entropy change ΔS of the adsorption process.

$$\Delta G = -RTLn\,K$$
(7)

$$Ln\,K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$
(8)

where R is the universal gas constant (8.314 J/mol/K), T is the temperature (K) and K is the distribution coefficient (Lawal et al., 2010). The plot of Ln K versus 1/T for EGP is as shown in Figure 13. The thermodynamic parameter obtained from similar plots for SWP and BNP are presented in Table 5. The ΔG for Ni(II) adsorption by the three biomaterials was temperature dependent. The change in enthalpy (ΔH) and entropy (ΔS) were negative. This implies that the reaction was exothermic, being unfavorable at higher temperatures (Jiang et al., 2009). This is clear from effect of temperature results as shown in Figure 6. Decrease in adsorption with increase in temperature has been attributed to a weakening of adsorptive forces between the active sites of the adsorbents and adsorbate species and also between adjacent molecules on the adsorbed phase (Jiang et al., 2009).

Conclusion

In this study, the adsorption of Ni(II) from waste using EGP, BNP and SWP was investigated. The adsorption characteristics of these biosorbents were dependent on adsorbent dose, solution pH, initial Ni(II) ion concentration, contact time and temperature. Maximum adsorption
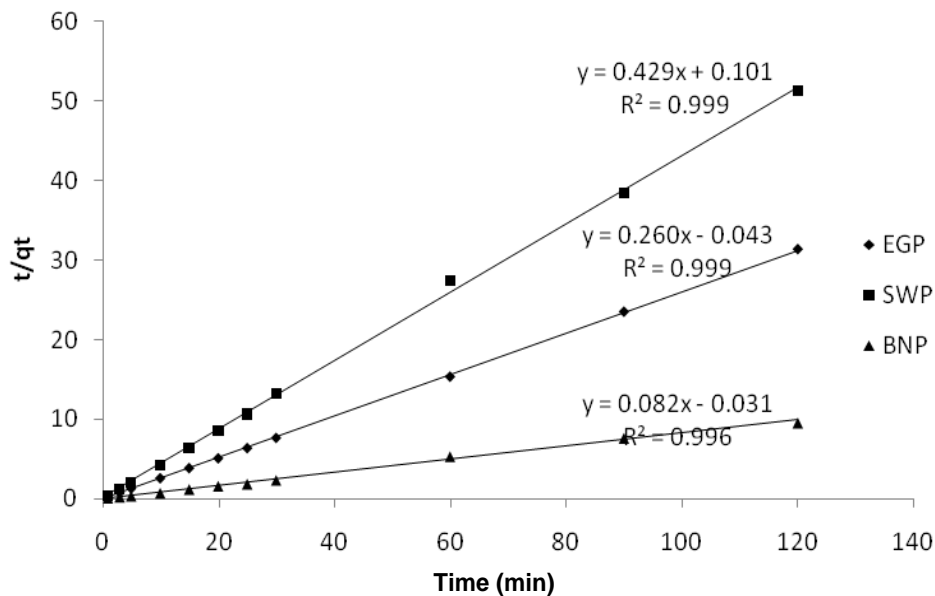
Figure 12. Pseudo-second order plot for batch experiments using EGP, SWP and BNP.

Table 4. Pseudo-second order parameters for semi-batch and batch sorption of Ni (II) using EGP, SWP and BNP in 50 ml solution.

	Semi-batch experiments (g)			Batch experiments (g)		
	0.8	0.8	0.1	0.8	0.8	0.1
	EGP	SWP	BNP	EGP	SWP	BNP
K_2 (g mg^{-1} min^{-1})	1.11	0.37	0.03	1.57	1.83	0.22
q_e (mg g^{-1})	3.35	1.93	8.36	3.83	2.32	12.07
h_o (mg g^{-1} min^{-1})	12.46	1.38	2.16	23.04	9.86	32.05
R^2	0.999	0.999	0.977	0.999	0.999	0.997
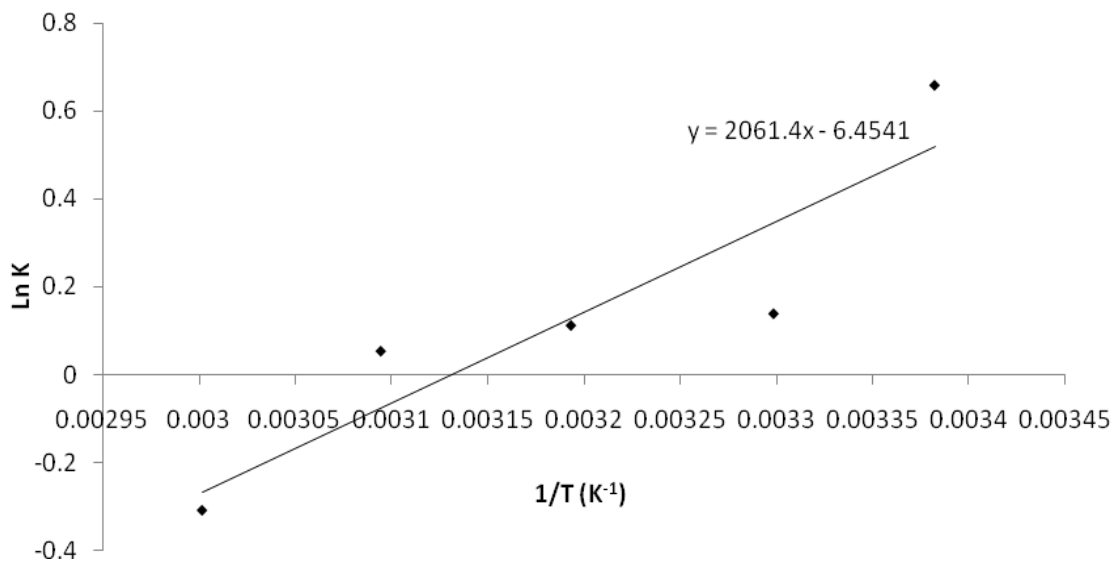
Figure 13. Thermodynamic profile of Ni (II) ion onto EGP.

Table 5. Thermodynamic parameters (ΔH and ΔS) for the adsorption of Ni (II) ion on EGP, SWP and BNP.

	ΔH (kJmol^{-1})	ΔS (JK^{-1} mol^{-1})	ΔG (kJ/mol) at various Temperatures (K)				
			295.65	303	313	323	333
EGP	-17.16	-53.66	-1.30	-0.893	-0.356	0.180	0.716
SWP	-50.98	-173.93	0.355	0.175	3.486	5.225	6.965
BNP	-32.2	-114.89	-0.982	-97.37	-96.22	-95.07	-93.92

occurred at pH 5 and 100 mg/L Ni(II) ion. Ni(II) removal was very fast, usually between 5 and 25 min. Percentage removal and q_e adsorbed for batch and semi batch experiment were identical irrespective of the mode in which the experiment was conducted. Selecting a method over the other would be based on convenience. Adsorption reactions were exothermic and spontaneous at low temperatures where exothermicity was important. All kinetic data fitted the pseudo second order kinetic equation (R^2 > 0.97). The FTIR indentified ionic carboxylic carbonyl carbon which showed shifts after metal loading indicating a possible interaction with Ni(II) ions. The hydroxyl functional group was also identified by FTIR. Also noticeable in the metal loaded spectra is the 1734 cm^{-1} corresponding to a non-ionic carbonyl carbon in carboxylic acids.

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