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Batch equilibrium biosorption of Ni(II), Cr(III) and Co(II) from solution using Bitter leaf (*Vernonia amygdalina*): kinetics, isotherm, and thermodynamics

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Abstract

The removal of Ni(II), Cr(III), and Co(II) from aqueous solution using *Vernonia amygdalina* (Bitter leaf) as biosorbent was studied. The FTIR characterization showed the presence of ionizable groups and lone pairs that could participate in the binding of metal ions in solution. Among the four kinetic studies tested, the adsorption process was best represented by pseudo-second order kinetics. Equilibrium data were better represented by Freundlich isotherm than Langmuir isotherm. The biomass dosage based on this study showed that the dosage of the biomass significantly affected the uptake of the metal ions from solution. Thermodynamic parameters such as standard Gibbs-free energy (ΔG), standard enthalpy (ΔH), standard entropy (ΔS), and the activated energy (A) were calculated. The order of spontaneity of the biosorption process was found to be Ni(II) > Cr(III) > Co(II). The activation energy for the biosorption of each of the metal ions was less than 42kJ/mol at 318K which indicated that each was a diffusion controlled process. The calculated entropy shows that the order of disorder is Ni(II)>Co(II).

Key words: Bitter leaf, Vernonia amygdalina, Ni(II), Cr(III), Co(II), isotherm

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1. Introduction

Heavy metal pollution is a major environmental problem today because they cause pollution that threatens human health and the ecosystem. They are not biodegradable and tend to accumulate in living organisms [1]. Water pollution due to heavy metals present is an issue of great environmental concern [2]. The conventional methods used for the removal of these metal ions are known to have demerits. Biosorption has the merits of low cost and environmental friendliness over the conventional methods of removing metal ions from solution [3]. Bitter leaf (Vernonia amygdalina) was named after the botanist, William Vernon. Its botanical name is Vernonia and it belongs to the family of Asteraceae. It is a small shrub that grows in the tropical Africa. It is called bitter leaf because of its bitter taste. The Bitter leaf plant's uses range from antimicrobial to decorative. These chemical substances possess the ability of detoxification and recovery of toxic or valuable metals from industrial discharges. Some of the principal chemical Barbarinde et al., 2013

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constituents found in Bitter leaf herb are a class of compounds called steroid glucosides – type vernonioside B1, anthelminthic anti-parasitic properties [4]. These components contain functional groups that could remove metal ions from solution. This forms the basis for utilizing the bitter leaf for its potential in the uptake of nickel, chromium and cobalt ions from solution.

2. Materials and methods

2.1. Biomass Preparation

Vernonia amygdalina was harvested from Ago-Iwoye, Ogun State, Nigeria. The leaves were carefully collected inside a sac rinsed with distilled water, air dried immediately and kept dry till time of usage.

2.2. Preparation of solution

All chemicals used in this study were of analytical reagent grade and were used without further purification. Standard solutions of Ni(II), Cr(III) and Co(II) used for this study were prepared from NiCl₂.6H₂O, Cr(NO₃)₃.9H₂O and CoSO₄.7H₂O, respectively. The working solutions with different concentrations of the metal ions were prepared by appropriate dilutions of the stock solution immediately prior to their use with distilled water. The initial pH of the solution was adjusted accordingly with a pH meter. Thermostated water bath (Haake Wia Model) was used as the medium for the process. The concentration before and after biosorption before and after biosorption of each metal ion was determined using a Perkin-Elmer analyst 700 flame Atomic Absorption Spectrophotometer (AAS) with deuterium background corrector. Fourier Transform Infrared (FTIR) spectra of dried unloaded biomass and metal loaded biomass are recorded at 400-4000cm⁻¹, using a Shimadzu FTIR model 8400 S spectrophotometer.

2.3. Batch biosorption study

The biosorption study was determined by batch experiments by contacting 0.5g of the *Vernonia amygdalina* (Bitter leaf) with 25ml of each metal ion solutions under different conditions for a period of time in a glass tube. The biosorption studies were conducted at 25°C using thermostated water bath to determine the effect of pH, contact time, and initial metal ion concentration on the biosorption. The residual metal ions were analyzed using AAS. The amount of metal ion biosorbed from solution was determined by difference and the mean value calculated.

2.4. Effect of pH on biosorption

The effect of pH on the biosorption of the metal ion was carried out within pH 1-7 for Ni(II) and pH 1-6 for Cr(III) and Co(II) to prevent the precipitation of metal ions. This was done by contacting 0.5g of Bitter leaf with 25ml of 100mg/L metal ion solution in glass tubes. The pH of each solution was adjusted to the desired value by drop wise addition of 0.1M HNO₃ and/or 0.1M NaOH. The glass tubes containing the mixture were left in a water bath for three hours. The biomass was removed from the solution by decantation. The residual metal ion concentration in the solution was analyzed. The optimum pH was determined as the pH with the highest biosorption of each metal ion.

2.5. Effect of contact time on biosorption

The biosorption of the metal ions by Bitter leaf was studied at various time intervals (0-300min) and at the concentration of 100mg/L. This was done by contacting 0.5g of *Vernonia amygdalina* with 25ml of 100mg/L of metal ion solution at optimal pH. The Bitter leaf was left in solution for different periods of time. At predetermined time, the glass tubes were withdrawn from the bath, and the residual metal ion concentration in solution was determined using AAS. The amount of metal ions biosorbed was calculated for each sample.

2.6. Effect of initial concentration on biosorption

Batch biosorption study of metal ion was carried out using a concentration range of 10-100mg/L. This was done by contacting 0.5g of *Vernonia amygdalina* (Bitter leaf) with 25ml of 100mg/L of metal ion solution at optimal pH. Two glass tubes were used for each concentration. The tubes were left in a thermostated water bath maintained at 25°C for the predetermined optimum time. The leaves were removed from the solution, and the concentration of residual metal ion in each solution was determined.

2.7. Effect of Temperature on Biosorption

The batch biosorption process was studied at different temperatures within the range 20°C-50°C in order to investigate the effect of temperature on the biosorption process. This was done by contacting 0.5g of *Vernonia amygdalina* with 25ml of 100mg/L of metal ion solution at optimal pH and time.

2.8. Statistical Analyses

The curve fittings of the data obtained were performed using Microcal Origin 6.0 software.

3. Results and Discussion

3.1. Physical Characterization of Vernonia amygdalina

Phytochemical screenings of the leaf extracts revealed the presence of alkaloids, saponins, tannins and glycosides. These components account for its bitter taste [5]. Therefore, the functional groups present on the bitter leaf would form active sites for sorption on the material surface. The FT-IR spectra of dried unloaded, Ni-loaded, Cr-loaded and Co-loaded Vernonia amygdalina were taken to obtain information on the nature of possible interactions between the functional groups of Vernonia amygdalina biomass and the metal ions as presented in Figure 1. Analysis of the FT-IR spectra showed the presence of ionizable functional groups which are able to interact with cations [3, 6-9]. This implies that these functional groups would serve in the removal of positively charged ions from solution. The IR spectra pattern of the biomass showed distinct and sharp absorptions indicative of the existence of the functional groups such as -NH, -OH, C-O, CO and C-O groups as shown in Figure 1. These bands are due to the functional groups of Vernonia amygdalina (Bitter leaf) that participate in the biosorption of Ni(II), Cr(III) and Co(II). On comparison, there are clear band shifts and decrease in intensity of bands as reported in Table1. The FT-IR spectra of the Vernonia amygdalina (Bitter leaf) biomass indicated slight changes in the absorption peak frequencies due to the fact that the binding of the metal ions causes reduction in absorption frequencies. These shifts in absorbance observed implies that there were metal binding processes taking place on the active sites of the biomass.

3.2. Effect of Solution pH on Metal Ion Biosorption

The pH of the solution usually plays an important role in the biosorption of the metal ions [10]. It is an important parameter governing the uptake of heavy metals by biosorption process as it not only affects metal species in solution, but also influences the surface properties of biosorbents in terms of dissociation of binding sites and surface charge [11]. The net charge of the sorbate and that of the sorbent are dependent on the pH of the solution. At low pH, the metal ion uptake is inhibited by net positive charge on the sorbent and the competition between the metal ions and the hydrogen ions in solution. As the pH increases, the negative charge density on biomass increases as a result of deprotonation of the metal binding sites on the biomass, consequently, the biosorption of the metal ions increases. Figure 2 shows the variation of the metal ions biosorbed on *Vernonia amygdalina* at various solution pH values. For the three metal ions, the biosorption increased as the pH increased from pH 1 to 7 for Ni(II) and pH 1-6 for Cr(III) and Co(II). The increase observed in the biosorption with increase in pH implies that ion exchange process was involved.

The reaction involved the biosorption of metal ion (represented as M^{x+}) from the liquid phase to the solid phase, the biosorbent with lone pair of electron (represented as \ddot{A}) and can be considered as a reversible reaction with an equilibrium being made between the two phases as schematically shown below for a divalent metal ion in solution:

 $\ddot{A} + M^{2+} \rightleftharpoons A - M \tag{1}$

3.3. Biosorption Kinetics

Figure 3 illustrates the dynamic biosorption process of the three metal ions on Vernonia amygdalina. It was observed that the biosorptive quantities of the three metal ions on the Bitter leaf increase with increasing contact time. In each case, biphasic kinetics are observed: an initial rapid stage (fast phase) where biosorption is fast and contributes to equilibrium uptake and a second stage (slow phase) whose contribution to the metal ion biosorbed is relatively smaller. The fast phase is the instantaneous biosorption stage, it is assumed to be caused by external biosorption of metal ion to the biomass surface. The second phase is a gradual biosorption stage, whose diffusion rate is controlled. Finally, the biosorption sites are used up, the uptake of the metal ion reached equilibrium. This phase mechanism has been suggested to involve two diffusion processes, external and internal, respectively [12]. The biosorption of each of the metal ions eventually achieves equilibrium, although their rates of uptake and times of reaching equilibrium are different. This might be due to the differences in hydrated ionic sizes of the metal ions [13].

In order to establish the mechanism of the biosorption of Ni(II), Cr(III), and Co(II) on *Vernonia amygdalina*, four kinetic models were obtained. These are the pseudo-first-order, pseudo-second-order, the elovich kinetic model and the intraparticle diffusion model equations. One of such models is the Lagergren pseudo-first-order model which considers that the rate of occupation of the biosorption site is proportional to the number of the unoccupied sites [9].

$$rate = -\frac{d[A]}{dt} = k [A]^{n}$$
⁽²⁾

Which can also be written as

$$\frac{d}{dt}q_t = k_1(q_e - q_t) \tag{3}$$

Integrating between the limits $q_t = 0$ at t = 0 and $q_t = q_t$ at t = t, we obtain

$$\log \left[\frac{q_e}{(q_e - q_t)} \right] = \frac{k_1}{2.303} t \tag{4}$$

This can be rearranged to obtain a linear form

$$\log(q_{e} - q_{t}) = \log q_{e} - \frac{k_{1}}{2.303}t$$
⁽⁵⁾

where k_1 is the Lagergren rate constant of the biosorption (\min^{-1}) ; q_e and q_t are the amounts of metal ions sorbed $(\operatorname{mg/g})$ at equilibrium and at time t, respectively. The plot of $\log(q_e - q_t)$ versus t for the biosorption of metal ions on Bitter leaf at initial concentration of 100 mg L⁻¹ should give a straight line for a process that follows first-order kinetic model. The data was equally subjected to the pseudo-second-order kinetic model. The pseudo-second-order kinetic model as

$$\frac{d}{d_t}q_t = k_2(q_e - q_t)^2 \tag{6}$$

On integrating between boundary conditions, we have

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{7}$$

On rearrangement, we have

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(8)

Where k_2 is the equilibrium rate constant of pseudo-secondorder biosorption process (g mg⁻¹ min⁻¹). However, plots t versus t/q_t showed good fitness of experimental data with the pseudo-second-order kinetic model for different initial concentration of the metal ions as represented in Figure 4.

The data were equally subjected to the Elovich kinetic model given by

$$q_t = A + B \ln t \tag{9}$$

and the intraparticle diffusion equation given as

$$R = K_s t^{\nu} \tag{10}$$

The intraparticle diffusion equation has been used to indicate the behaviour of intraparticule diffusion as the rate limiting step in the biosorption process. R is the percent metal ions biosorbed, K_s is the intraparticle diffusion constant, t is the contact time, while b is the gradient of the linear plot. In the linear form, equation (10) turns to

$$\log R = b \log t + \log K_s \tag{11}$$

The correlation coefficients obtained were found to be highest for the pseudo-second-order kinetics as it was found to be in excess of 0.9 as presented in table 5. On comparison of the values of \mathbb{R}^2 for the experimental points, the pseudosecond-order kinetic model is the best kinetic model to predict the dynamic biosorption of Ni(II), Cr(III) and Co(II) on Bitter leaf similar to what was reported for Banana leaf [13]. The result shows that the rate of biosorption of the metal ions is of the order Co(II) > Ni(II) > Cr(III). The biosorption capacity is in the order Co(II) > Ni(II) > Cr(III). The differences observed in the rate of biosorption as well as in the biosorption capacity may be accounted for in terms of the differences in ionic charges and hydrated ionic sizes of the ions in solution [13].

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Fig. 1. FTIR spectra of the free and metal bound Vernonia amygdalina (Bitter leaf)

Absorption band (cm ⁻¹)					
Metal ion				Functional groups	
	Before	After	Difference		
Ni(II)		3383.26	36.65	N-H Stretch (Amine)	
Cr(III)	3346.61	3373.61	27	N-H Stretch (Amine)	
Co(II)		3383.26	96.44	N-H Stretch (Amine)	
Ni(II)		1726.35	3.86	C=O, Stretch (Aldehyde)	
Cr(III)	1722.49	1734.06	11.57	C=O, Stretch (Aldehyde)	
Co(II)		1734.06	11.57	C=O, Stretch (Aldehyde)	
Ni(II)		1643.41	-15.43	C=O Bend (Amide)	
Cr(III)	1658.84	1653.05	-5.79	C=O Stretch (Amide)	
Co(II)		1653.06	-5.78	C=O Stretch (Amide)	
Ni(II)		1442.8	0	N=O Stretch (Nitro)	
Cr(III)	1422.80	1458.30	35.5	N=O Stretch (Nitro)	
Co(II)		1456.30	35.5	N=O Stretch (Nitro)	
Ni(II)		699.32	30	C-O-C Stretch (Dialkyl, Ester)	
Cr(III)	669.32	719.47	50	C-O-C Stretch (Dialkyl, Ester)	
Co(II)		669.32	0	C-O-C Stretch (Dialkyl, Ester)	

 Table 1: FT-IR Spectra Characteristics of Vernonia amygdalina (Bitter leaf) before and after biosorption of Ni(II), Cr(III) and Co(II) for 3 hours.



Fig. 2. pH dependence profile for the biosorption of Ni(II), Cr(III), and Co(II) using Bitter leaf (Vernonia amygdalina).



Fig. 3. Contact time dependent profile for the biosorption of Ni(II), Cr(III), and Co(II) using Bitter leaf (Vernonia amygdalina).



Fig. 4. Pseudo-second-order for the biosorption of Ni(II), Cr(III), and Co(II) using Bitter leaf (Vernonia amygdalina).



Fig. 5. Freundlich Isotherm for biosorption of Ni(II), Cr(III) and Co(II) by Bitter leaf (Vernonia amygdalina).



Fig. 6. Percentage Efficiency for the biosorption of Ni(II), Cr(III) and Co(II) by Bitter leaf.



Fig. 7. Effect of biosorbent dose on the biosorption of Ni(II), Cr(III) and Co(II) by Bitter leaf (*Vernonia amygdalina*) at 100mg/L initial metal ion concentration.



Fig. 8. Thermodynamic plots for the biosorption of Ni(II), Cr(III) and Co(II) by Bitter leaf (*Vernonia amygdalina*) at 100mg/L initial metal ion concentration.

Table 2: Pseudo-second-order parameters for the biosorption of Ni(II), Cr(III) and Co(II) by Bitter leaf (Vernonia amygdalina).

Metal ion	$q_e(mg/L)$	k ₂ (gmg ⁻¹ min ⁻¹)	\mathbf{R}^2	SD	
Ni(II)	61.728	5.206 x 10 ⁻⁴	0.993	0.097	_
Cr(III)	53.248	7.108 x 10 ⁻⁴	0.992	0.996	
Co(II)	108.225	2.080 x 10 ⁻⁴	0.997	0.049	

Table 3: Freundlich Isotherm parameters for the biosorption of Ni(II), Cr(III) and Co(II) by Bitter leaf (Vernonia amygdalina)

Metal ion	1/n	$\mathbf{K_{f}}$	R	SD	
Ni(II)	1.176	0.300	0.998	0.0279	
Cr(III)	0.635	1.083	0.995	0.0174	
Co(II)	0.212	2.706	0.999	0.0006	

Table 4: Thermodynamics parameters for the biosorption of Ni(II) and Co(II) by Vernonia amygdalina (Bitter leaf).

Metal ion	ΔH^{\prime} (kJmol ⁻¹)	$\Delta S^{\circ}(JK^{-1}mol^{-1})$	\mathbf{R}^2	A (kJmol ⁻¹) (303K)	A (kJmol ⁻¹) (318K)
Ni(II)	17.846	+73.58	0.985	2.537	2.661
Cr(III)	3.120	+24.23	0.959	2.5223	2.647
Co(II)	3.796	+20.13	0.848	2.5229	2.648

3.4. Biosorption Isotherm

Fig.5 illustrates the biosorption isotherm of Ni(II), Cr(III) and Co(II) on Bitter leaf (*Vernonia amygdalina*). The equilibrium biosorption q_e increases with increase in metal ion concentration. The Freundlich and Langmuir isotherms were employed to calculate the biosorption capacity. The Freundlich isotherm is an empirical equation describing adsorption onto a heterogenous surface. The Freundlich isotherm is expressed as

$$\log \Gamma = \frac{1}{n} \log C_e + \log K_f \tag{12}$$

Where K and $\frac{1}{n}$ are the Freundlich constants related to the

biosorption capacity and biosorption intensity of the biosorbent, respectively.

The linear form of the Langmuir equation is expressed as

$$\frac{1}{\Gamma} = \frac{1}{b_m} \frac{1}{C_e} + \frac{1}{\Gamma_m}$$
(13)

Where Γ , Γ_m and b_m are the Langmuir parameters. The results showed that the regression coefficient obtained for Freundlich isotherms are higher than for Langmuir isotherm. The parameters of the Freundlich isotherms show that the Freundlich isotherm is a better isotherm than the Langmuir isotherm and are presented in Table 3.

3.5. Biosorption Efficiency

The result of the study on the effect of initial metal ion concentration on biosorption efficiency is shown in Figure 6. The plots show that the biosorption efficiency of the biomass reduces with increase in the initial metal ion concentration for Cr(III) and Co(II) which might be due to increase in effective collision between the metal ions and the active sites in the biosorbent having more ions than at lower concentration. On the other hand, the biosorption efficiency increased with the increase in initial metal ion concentration for Ni(II). The biosorption efficiency (E) for each metal ion was calculated as

$$E = 100 \left(\frac{C_i - C_e}{C_i} \right) \tag{14}$$

Where C_i and C_e are the initial and the equilibrium metal ion concentrations (mgL⁻¹), respectively.

3.6. Effect of Biomass Dosage on Biosorption

The effect of biomass dosage on biosorption efficiency is reported in Figure 7. The general trend of increase in the three metal ions biosorbed with increase in biomass dosage indicates an increase in uptake due to more binding sites on the biomass available for biosorption. This is due to the fact that increase in biomass dosage leads to increase in the number of active sites available for biosorption. Hence, amount of metal ions available for biosorption per gram of biosorbent will be less when the amount of biosorbent is increased. The difference in biosorption capacity q (mg/g) at the same initial metal ion concentration and contact time may also be attributed to the difference in their chemical affinities and ion exchange capacity, with respect to the chemical functional group on the surface of the biosorbent. This trend has been reported for other biosorbents [14].

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