

Research Paper

BIOSORPTION OF NICKEL AND COPPER IN A BINARY SYSTEM USING CHITOSAN DERIVED FROM CRABS

ABSTRACT

Aims: To ascertain the adsorptive potentials of crab shell derived chitosan for the removal of copper and nickel from solutions in a binary system in order to evaluate the competition of different metallic ions for the chelation sites of chitosan.

Study Design: Multifactorial Design.

Place and Duration of Study: Chemistry Department, The Federal University of Technology, Akure, Ondo State, Nigeria between April 2011 and December 2013.

Methodology: Chitosan was derived from crab shells through deacetylation process using 50% NaOH. The obtained chitosan was characterized by FTIR and used for removal of nickel and copper from aqueous mixture. Adsorption parameters such as pH, contact time, metal concentration, adsorbent dosage, and temperature were investigated.

Results: It was observed that optimum pH for the adsorption of both nickel and copper was 5. Maximum adsorption for both metals was within 120 minutes. Evaluation of the effect of temperature on adsorption showed that metal removal decreased with increase in temperature. The adsorption process was exothermic and this was reflected in the –ve values of ΔH^0 obtained. Isotherm studies showed that the adsorption process obeyed Freundlich model with high R^2 values.

Conclusion: Crab shell derived chitosan effectively removed copper and nickel ions from a binary solution. The removal process followed second order kinetic model and the sorption capacity is high.

Key words: Biosorption; heavy metals; chitosan; kinetics; isotherms; thermodynamic

1.0 Introduction

The amount of heavy metal ions released to the environment has been increasing significantly resulting from industrial activities and technological development. Heavy metal ions present in wastewaters are often released by various industries such as mining, electroplating, electronic equipment, and battery manufacturing processes. The wastewater commonly contains Cu, Ni, Cd, Cr, and Pb which are not biodegradable and their accumulation in ecological system can cause harmful effects to human, animals and plants. The excessive exposure to nickel can lead to severe damage of lungs, kidneys, skin dermatitis, and cancer [1]. Copper consumption in high doses can cause serious toxicological concerns since it can be deposited in the brain, skin, liver and pancreas. As a result, various studies have been conducted on the removal of heavy metal ions in wastewaters which includes ion-exchange, reverse-osmosis, electro-coagulation, chemical precipitation, neutralization, and adsorption [2]. Recently, adsorption has attracted considerable interest especially from cheap and abundantly available agricultural waste material such as maize tassel, banana peel, sawdust, wheat straw, soybean straw, and *Pinus sylvestris* sawdust [3].

Biosorption is a proven technology for the removal of metal ions from synthetic and real industrial effluents. The high cost of activated carbon the major adsorbent widely used has motivated scientists into the search for new low cost materials. Chitosan a natural biopolymer

has been used for some decades in water purification processes. Most of the applications had been in the field of oil pollution control. Water purification plants throughout the world use chitosan to remove oil, grease, and fine particulate matters that cause turbidity in wastewater streams [4]. The biosorbents prepared from shrimp chitin and crab chitosan were tested for their removal and recovery efficiency for Cd(II), Cr(III) and Ni(II) ions [5, 6]. The removal of Cu (II) from aqueous solutions was studied using chitosan [7]. The aim of this work is to ascertain the adsorptive potentials of crab shell derived chitosan for the removal of copper and nickel from binary mixture. The basic objectives of the study include; (1) to study the adsorption characteristics of Cu(II) and Ni(II) on chitosan under equilibrium, (2) to understand the kinetics and (3) to model the adsorption process. For this purpose, the effect of various factors affecting the adsorption process, such as time of contact, initial pH of the solution, adsorbent dose and metal ion concentration were investigated.

2. Materials and methods

2.1 Materials

All reagents used in this study were of analytical grade. Experimental solutions were prepared by diluting the stock solution to the required concentration using de-ionized distilled water. The pH of each experimental solution was adjusted using HCl or NaOH. The concentration of residual metals was determined with atomic absorption spectrometer (Bulk 210VGP).

2.2 Preparation of chitosan

Crab shells used were obtained from seafood market in Lagos Nigeria, thoroughly washed and sun-dried for 3 days before taken to mill to reduce the particle size. Chitosan was extracted from the crab shell according to the procedure reported in [8]. The powdered crab shell samples were

first treated with 1.2N NaOH (1g per 10ml) and boiled at 60-65°C for 3h to deproteinize. The sample was washed with distilled water until it became neutral. Demineralization was accomplished by treating with 0.7N HCl (1g per 10ml) and boiling at 60-65°C for 15 minutes. The chitin obtained was converted to chitosan by deacetylation using 50% NaOH and boiled at 100°C for 3h. The sample was then thoroughly washed with distilled water and oven-dried. The obtained chitosan was further purified by dissolving in acetic acid, filtering and reprecipitating.

2.3 FTIR Spectral Analysis

FTIR spectral and surface area analysis Fourier transform Infrared spectra of biosorbent before and after adsorption of metal ions were recorded in the frequency range of 400–4000 cm^{-1} using FTIR spectrophotometer. The samples were formed into pellets with KBr.

2.3 Equilibrium Sorption Studies

The effect of pH on metal removal was studied using 50ppm Cu (II) and nickel (II) solutions prepared from the stock solutions. 0.5g of the chitosan was weighed into reaction vessels containing 25ml of each metal solution of a particular (1 – 8) pH mixed together and agitated for six hours. At the expiration of this period the solutions were filtered into clean sample bottles and taken for metal analysis. The effect of sorbent resident time was monitored by allowing 0.5g of chitosan to interact with 25ml each of 50ppm mixed metal solutions at designated pH and specific duration.

To establish the effect of metal concentration and temperature on the biosorption process and subsequent evaluation of sorption isotherm and thermodynamic parameters, six (6) different concentrations from 25 – 500ppm and five (5) temperature ranges (room temperature – 65°C)

were considered. Equilibration was done for 2h using 0.5g chitosan and pH5 metal solutions. The effect of competitive ions was also studied using, KCl and CaCl₂ salts at concentrations of 0.2, 0.4, 0.6, 0.8, 1.0M. Recovery of bound metals unto chitosan was actualized using 0.1, 0.2 and 0.3 M HCl solution

All experiments were done in triplicates and mean of all reported. After each experiment, the solutions were filtered using whatman filter paper and the filtrates were analyzed for respective Cu and Ni contents.

2.4 Metal Uptake

The metal uptake q_e was calculated according to the mass balance equation below:

$$q_e = \frac{(C_o - C_e) V}{W \cdot 1000} \quad (1)$$

where q_e is the amount adsorbed per unit mass of adsorbent (mg g⁻¹), C_o and C_e are the metal ion concentrations in mgL⁻¹ before and after adsorption for time t , V is the volume of adsorbate in ml, and W (g) is the weight of the adsorbent.

3. Results and Discussion

3.1 Characterization of the derived chitosan

The FTIR spectrum of chitosan before adsorption clearly showed a marked change from chitin spectrum as reported by Palpandi et al, (2009) due to the removal of acetyl groups from the amino nitrogen indicates the presence of predominant peaks at 3394.28 cm⁻¹ (–OH and –NH

stretching), 2987.2 and 2901.4 cm^{-1} ($-\text{CH}$ stretching), 1629.53 cm^{-1} ($-\text{NH}$ bending in $-\text{NH}_2$), 1393.3 cm^{-1} ($-\text{NH}$ deformation vibration in $-\text{NH}_2$), and 1065.5 cm^{-1} ($-\text{C}-\text{O}-\text{C}-$ stretching). The $\text{C}=\text{O}$ stretching frequency at 1640 cm^{-1} was missing in the spectrum of chitosan thus confirming a high degree of deacetylation of chitin to pure chitosan.

3.1 Effect of pH on the adsorption of nickel (II) and copper (II) ions

The pH study of the adsorption of metals is useful in determining the optimum sorption of metal ions. It is a well known fact that pH of the medium affects the solubility of the metal ions and the concentration of the counter ions on the functional group of the biomass [9]. The result of the pH study indicated that in the binary mixture, the optimum pH of copper (II) and nickel (II) ions were at 5.0. The quantity of the metal ions removed at this pH is only slightly higher than what was obtained at pH 4.0. In a work involving the adsorption of copper from a monolytic aqueous solution by chitosan in prawn shell, pH 4.0 was also recorded as optimum [10]. The percentage removal of Cu(II) and Ni(II) increased considerably from pH 1 to pH 5. The low level of metal ion uptake by the biosorbent at lower pH values could be attributed to the increased concentration of hydrogen (H^+) ions which compete along with Cu(II) and Ni(II) ions for binding sites on the biomass. As the pH is lowered, the overall surface charge on the beads become positive, which will inhibit the approach of positively charged metal cations. At pH values above the isoelectric point, there is a net negative charge on the surface and the ionic point of ligands such as carboxyl, hydroxyl and amino groups are free so as to promote interaction with the metal cations. This would lead to electrostatic attractions between positively charged cations such as Cu(II) and Ni(II) and negatively charged binding sites [11, 12].

3.2 Effect of contact time

The relationship between concentration adsorbed at any time per unit mass (Q_t) and adsorbent resident time (T) for both metal ions is presented in Fig. 1. The amount of the adsorbed metal ions increased as the time elapsed. Similar finding was recorded in a study on Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads [13]. Cu(II) removal was rapid with over 95% adsorbed in the first 10min of interaction. The optimum contact time was achieved at 90min for Cu(II). Ni(II) ion removal was a lot more gradual than Cu(II) with only about 83% of nickel removed in the first 10min of interaction. Optimum time for Ni(II) was 150min. apparently in a mixed metal solution, the adsorbent chitosan from crab has preference to copper than to nickel. Cumulatively more Ni(II) than Cu(II) were removed. After this equilibrium period, the amount of metal adsorbed did not change significantly with time. The fast adsorption at the initial stage was probably due to availability of sufficient number of vacant sites on the surface of the adsorbent.

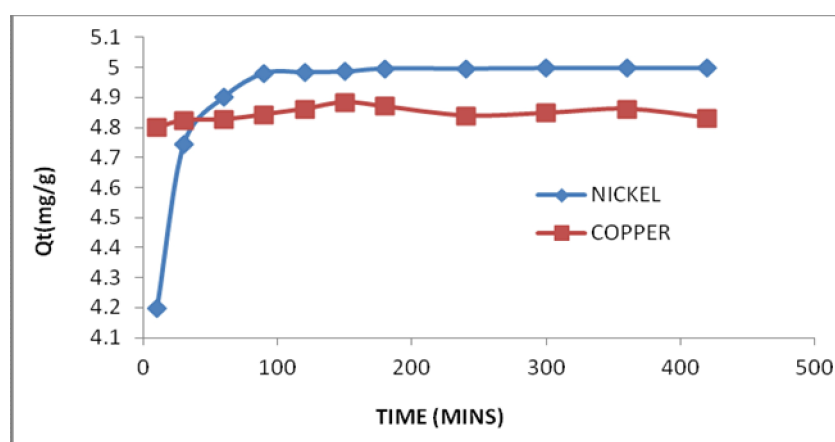


Figure 1: Effect of contact time on biosorption of Cu (II) and Ni(II)

3.3 Kinetics of copper and nickel adsorption

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the Lagergren pseudo-first order and pseudo second order equations are applied to model the kinetics of nickel and copper adsorption onto Chitosan in a binary system.

3.3.1 Pseudo-first-order kinetic model

The pseudo-first-order rate expression based on solid capacity is generally expressed as follows [14]

$$\frac{dq}{dt} = k_{ad}(q_e - q_t) \quad (2)$$

Where, q_e is the amount of copper metal adsorbed at equilibrium (mg/g), q_t is the amount adsorbed (mg/g) at time t , k_{ad} is the rate constant (L/min). After integration and applying boundary conditions, $t = 0$ to t and $q = 0$ to q_e ; equation (2) becomes:

$$\text{Log } (q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \quad (3)$$

The plot of $\log (q_e - q_t)$ against Time should give a straight line graph where the following parameters, k_{ad} and q_e can be deduced from the slope and the intercept respectively. From the data presented in table 1, its obvious that the sorption process failed to comply with Lagergren's pseudo-first- order kinetic model. It has been observed that in most cases, the first order equation of Lagergren does not fit well for the whole range of contact time [15].

3.3.2 Pseudo-second-order model

The pseudo-second-order equation is also based on the sorption capacity of the solid phase [16]. It predicts the behaviour over the whole range of data and is in agreement with chemisorption being the rate controlling step. pseudo-second-order equation is expressed as

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \quad (4)$$

Where k_2 is the rate constant of second order adsorption (g/mg.min). For the same boundary conditions the integrated form of equation (4) becomes:

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

The initial sorption rate, h (mg/ g. min), at $t = 0$ is defined as

$$h = k_2 q_e^2 \quad (6)$$

Where q_e and h values were derived from the slope and intercept of plot t/q against t . Fig. 2 shows that the model can be applied for the entire adsorption process and confirms that the sorption of copper and Nickel follows the pseudo-second-order kinetic model with high R^2 values for the adsorption process.

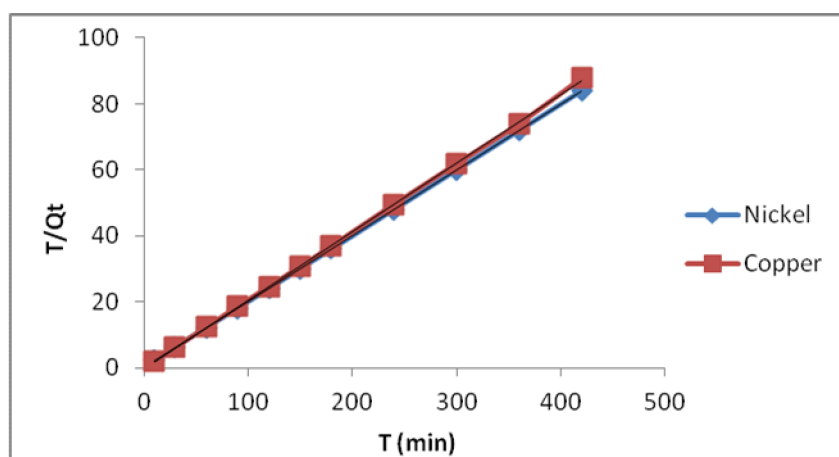


Fig. 2: Pseudo-second-order kinetic plots for adsorption of Cu(II) and Ni(II) in a binary solution

Presented in table 1 are the parameters of 1st and 2nd order kinetic models. Q_e estimated tallied with the experimental values for both Copper and Nickel indicating that Second order kinetics best explained the sorption kinetics.

Table 1: pseudo first order and pseudo second order kinetic model parameters

Metal ion	Pseudo first order				Pseudo second order		
	K (dm ³ /g)	R ²	Q _e (mg/g) estimated	Q _e (mg/g) experimental	K (dm ³ /g)	R ²	Q _e (mg/g) estimated
Cu (II)	0.001	0.020	0.071	4.88	-0.014	0.999	4.83
Ni (II)	0.009	0.255	0.109	5.00	0.016	1.00	5.03

3.3.3 Elovich model of adsorption

Elovich model for adsorption is based on the kinetics of gas chemisorptions on heterogeneous solid surfaces [17]. The Elovich equation is given as;

$$dq/dt = \alpha \exp(-\beta qt) \quad (7)$$

Where α is the initial sorption rate (mol/g min) and β is the desorption constant (g/mol). Assuming $\alpha\beta t \ll 1$, applying the boundary conditions $Q_t = 0$ at $t = 0$, eq. (6) becomes

$$qt = \beta \ln(\alpha\beta) + \beta \ln t \quad (8)$$

Thus, the constants can be obtained from the slope and the intercept of a straight line plot of qt against $\ln(t)$. Low values of R^2 for nickel (0.746) and copper (0.414) obtained (fig. not included) showed that the sorption process did not strongly fit into Elovich model.

3.3.4 Intra-particle diffusion

The most commonly used technique for identifying the mechanism involved in the adsorption process is the intra-particle diffusion model given as equation 9:

$$q = k_d t^{1/2} + 1 \quad (9)$$

Where K_d is the intra-particle diffusion rate constant. If intra-particle diffusion occurs, then plot of q_t against $t^{1/2}$ in fig. 3 should be linear and the line should pass through the origin if the intra-

particle diffusion was the only rate limiting parameter controlling the process. The plots in the figure are multi linear with two distinct regions indicating two different kinetic mechanisms. The initial curved region corresponds to the external surface uptake and the second stage relates the gradual uptake reflecting intraparticle diffusion as the rate limiting step. Based on the results it may be concluded that intra particle diffusion is not only the rate determining factor.

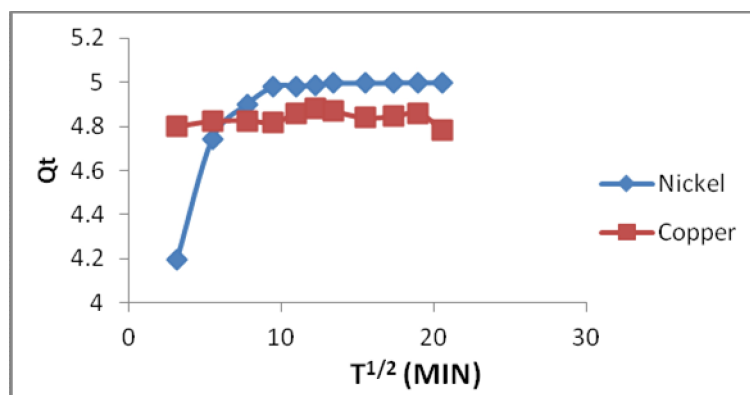


Fig. 3: Intra- Particle Diffusion Plot for adsorption of Cu(II) and Ni(II)

3.4 Effect of initial concentration

It has been suggested that the removal of nickel from solutions depends on the initial concentration of nickel ion. The decrease in initial concentration increased the amount of nickel removed [18]. In this study, for an initial concentration of 25ppm, the percentage nickel removal decreased with increase in temperature. Similar trends were observed for the other metal ion concentrations as shown in fig. 4. For copper, in fig. 5, under the same experimental conditions, increase in the initial concentration resulted in decrease in copper removal even at 298, 308, 318, 328 and 338K. The decrease in adsorption as concentration increases may be due to the reduction in the number of available functional groups and active sites on the adsorbents [19]. Notwithstanding the decrease observed as concentration increased, the removal rate of 94% of nickel was observed at 338K as against 99% at 298K for an initial concentration of 25ppm. Even

at 500ppm, the adsorbent had the capacity of removing 88% and 83.67% at 298 and 338K respectively.

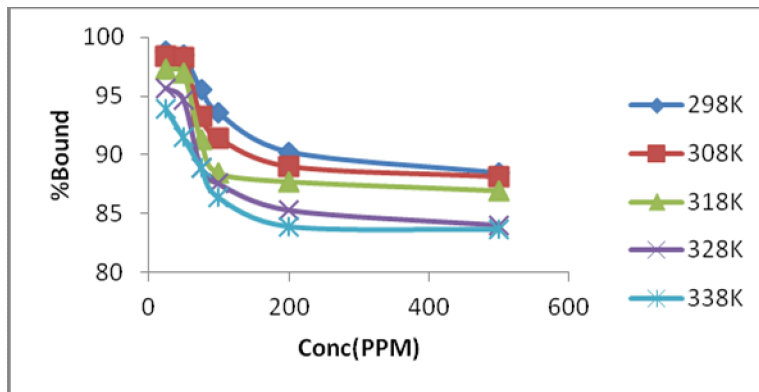


Fig. 4: Plot of effects of initial concentration for Ni(II)sorption

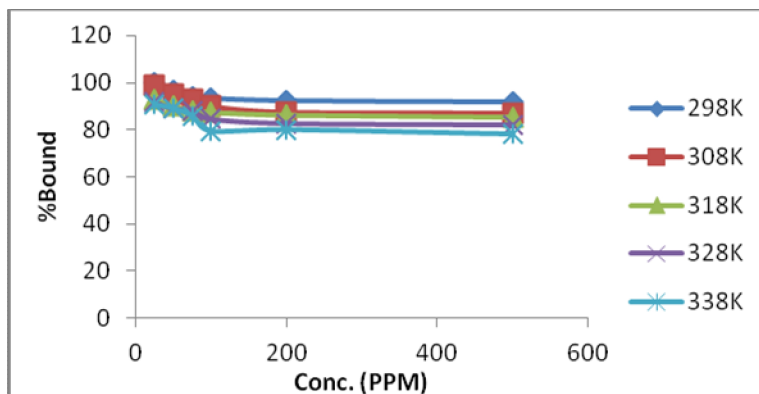


Fig. 5: Plot of effects of initial concentration for Cu(II) sorption

3.5 Equilibrium isotherm models

Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich and Temkin isotherms. Analysis of these models is important in developing equations that best represent the sorption processes

3.5.1 The Langmuir Isotherm

The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface. The Langmuir isotherm is given as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (10)$$

Where q_m and K_L are the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively [18]. The low R^2 values for both nickel and copper adsorption at 298K, 308K, 318K, 328K and 338K in Figs. 6 and 7 and table 2 showed that the isotherm data fairly fit into the Langmuir model.

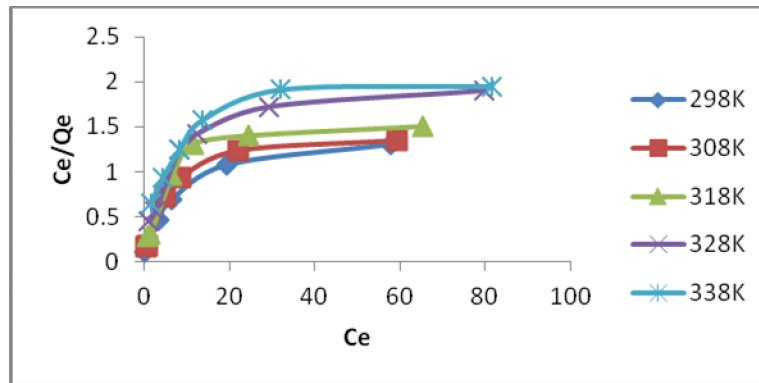


Fig. 6: Plot of Langmuir isotherm for Ni(II) sorption

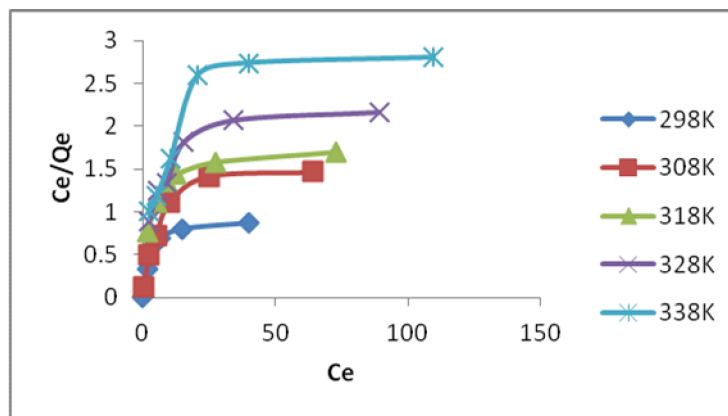


Fig. 7: Plot of Langmuir isotherm for Cu(II) sorption

3.5 The Freundlich Isotherm

The Freundlich isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption [20]. The logarithmic linear form of Freundlich isotherm may be represented as;

$$\log q_e = \log K_F + 1/n_F (\log C_e) \quad (11)$$

Where K_f (L/g) and $1/n_f$ are the sorption capacity and sorption intensity respectively. Q_e is the amount of metal adsorbed per unit mass of sorbent (mg/g) at equilibrium; C_e is the equilibrium concentration of heavy metal ion (mg/g).

A plot of $\log q_e$ versus C_e in fig. 8 at different temperatures indicates conformity with Freundlich Isotherm with high R^2 values for nickel metal ion. Similar result was displayed by the adsorption of copper metal ion in figure 9 with high R^2 values.

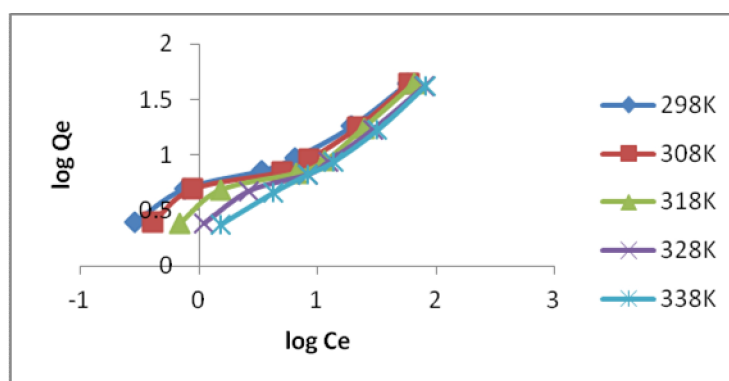


Figure 8: Plot of Freundlich isotherm for Ni(II) sorption

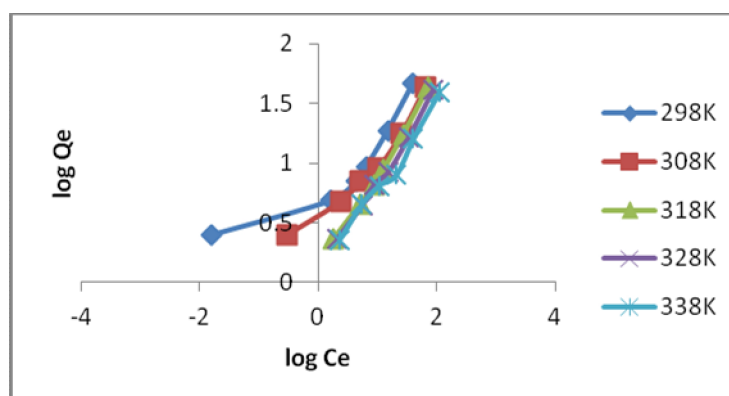


Figure 9: Plot of Freundlich isotherm for Cu(II) sorption

Table 2: Langmuir and Freundlich isotherm parameters for Ni (II) and Cu (II) Adsorption

Metal ions	Temp. (K)	Langmuir parameters			Freundlich parameters		
		q_m (mg/g)	K_l	R^2	K_F (dm ³ /g)	n_F	R^2
Ni (II)	298	0.025	84.11	0.60	0.006	0.52	0.96
	308	0.029	71.34	0.61	0.093	0.49	0.94
	318	0.031	61.35	0.62	0.191	0.61	0.94
	328	0.026	53.15	0.60	0.331	0.65	0.97
	338	0.022	46.61	0.75	0.537	0.71	0.99
Cu (II)	298	0.031	81.33	0.53	0.013	0.42	0.98
	308	0.029	61.82	0.62	0.112	0.42	0.94
	318	0.017	48.63	0.56	0.741	0.79	1.00
	328	0.020	37.85	0.60	0.759	0.76	0.99
	338	0.028	29.26	0.50	0.794	0.72	0.98

The Temkin Isotherm

The Temkin isotherm has generally been applied in the following linear form [21]

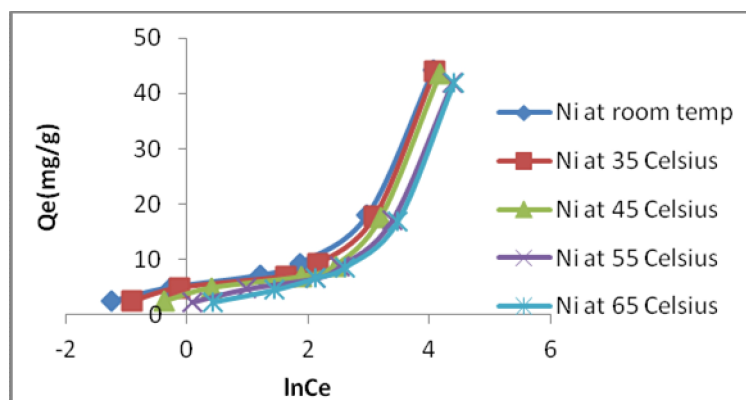
$$q_e = B \ln A + B \ln C_e \quad (12)$$

$$B = RT/b \quad (13)$$

Where A (L/g) is Temkin isotherm constant, b (J/mol) is a constant related to heat of sorption, R is the gas constant and T is the absolute temperature in Kelvin.

In figure 10, the values of R^2 for Nickel were deduced. At 298K, R^2 was found to be 0.73 at 298K; 0.69 at 308K; 0.69 at 318K; 0.74 at 328K and 0.77 at 338K respectively. Similar results were observed in the adsorption of Copper in figure 11. The values of R^2 in the adsorption of copper did not show strong conformity with Temkin isotherm due to low R^2 values.

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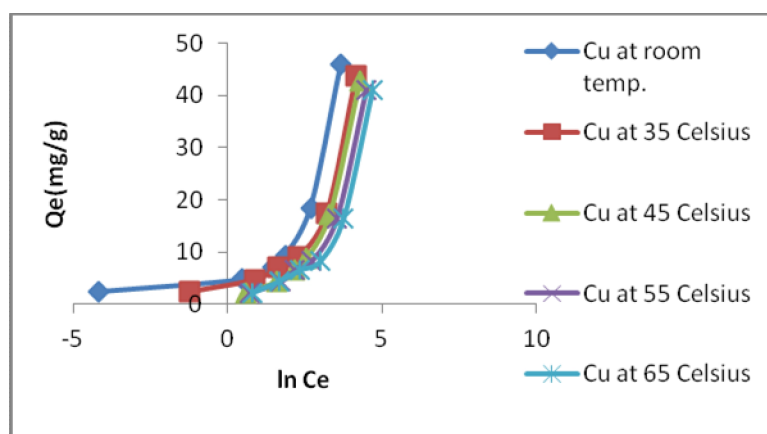


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Figure 10: Plot of Temkin for Nickel at different temperatures

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Figure 11: Plot of Temkin for Copper at different temperatures

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297 Temperature studies

298 Effect of temperature on adsorption of Ni (II) and Cu (II) ions was studied by conducting
 299 different sets of experiments at different concentrations of 25, 50, 75, 100, 200 and 500 ppm at
 300 25, 35, 45, 55 and 65°C. Fig. 12 and 13 showed that adsorption of nickel and copper ions
 301 decreased respectively with increase in temperature. A similar submission that adsorption
 302 capacities increased with decreasing temperature and indicating that the adsorption process was
 303 exothermic was reported in the study adsorption of phenol onto activated phosphate rock [22].

Increase in temperature apparently implies increase in kinetic energy such that the metal ions could be so mobile and the entropy very positive. This certainly will not support physical adherence onto the surface of the adsorbent.

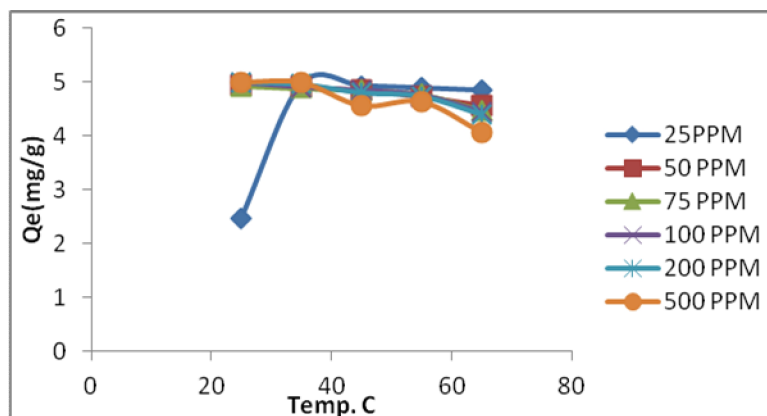


Fig.12. Effect of temperature on adsorption of nickel

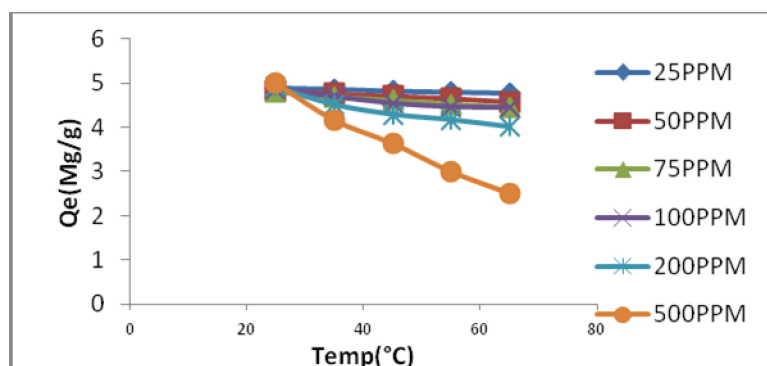


Fig. 13: Effect of temperature on adsorption of copper

Sorption Thermodynamics

Thermodynamic parameters such as change in Gibb's free energy ΔG° , enthalpy change, ΔH° and entropy change, ΔS° were determined using Van't Hoff equation.

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (14)$$

317 $\Delta G^{\circ} = -RT \ln K_d$ (15)

318 Where K_d is the equilibrium constant obtained from Langmuir's plot; T is temperature. (K), and
 319 R is gas constant ($\text{Jmol}^{-1}\text{K}^{-1}$). The values of ΔH° and ΔS° for nickel and copper respectively and
 320 the parameters are presented in table 3. The values of ΔG° were -ve showing that the sorption
 321 reaction is feasible, and the values of ΔH° were also -ve, suggesting exothermic process.

322 **Table 3: Thermodynamic parameters of Ni (II) and Cu (II) ions**

METAL	- ΔG° (KJ/mol)					- ΔH° (KJ/mol)	- ΔS° (J/mol)
	25°C	35°C	45°C	55°C	65°C		
Nickel	10.975	10.930	10.885	10.839	10.794	12.327	4.5349
Copper	10.913	10.569	10.225	9.881	9.537	21.161	34.3889

323

324 Effect of adsorbent dose

325 The effect of adsorbent load on the removal of the metals was studied at various dosages of 0.25,
 326 0.50, 0.75, 1.00, 1.50 and 2.00g. For the two metals (Cu (II) and Ni (II)), there was increase in
 327 adsorption with increase in dosage. This was expected, since as number of adsorbent particles
 328 increases, more surface areas are available for metal uptake. Same trend was reported by [23].
 329 The increment observed from 4.79mg/g to 4.99mg/g for nickel however is about 4% showing
 330 that the crab shell derived chitosan was really effective even at reduced dosage.

331

332 Adsorption capacity

333 The potency of the adsorbent and its re-usability can be measured from its sorption capacity.
 334 After 10 cycle of using the same dose of adsorbent, it was observed that removal efficiency was

reduced from 4.95mg/g to 2.47mg/g for Nickel and 4.85mg/g to 3.07mg/g for copper. These results show that the same sorbent could still be viable beyond 10 cycles.

Ionic strength

The effect of metal interference on adsorption capacity investigated showed a gradual drop in percentage nickel and copper bound as 0.2, 0.4, 0.6, 0.8 and 1.0M KCl or CaCl₂ were added. Adsorption of nickel and copper was higher with K⁺ interference than Ca²⁺. Reduction in metal adsorption in the presence of interfering cation can be related to the nature of ion pairs involved. Similar report was submitted in [24] using Ca and Na ions in the adsorption of nickel on kaolinite.

Recovery of Bound metals

Recovery of bound nickel and copper from the sorbent was effected using different concentrations of HCl. Desorption of Ni (II) and Cu (II) ions are most pronounced using 0.3M HCl. Up to 57% of bound nickel and only about 33% of bound copper were recovered from the adsorbent. It had also been reported that greater percentage metal recovery was actualized using 0.3M HCl [25]. Lower percentage of copper recovered from this adsorbent further supports the earlier suggestion that in this binary mixture of copper and nickel, intraparticle diffusion had taken place and indeed more pronounced in copper uptake by the crab shell derived chitosan.

Conclusion

Biosorption has been demonstrated as a useful alternative to conventional systems for the removal of toxic metals. The adsorption data of Cu²⁺ and Ni²⁺ ions showed that pseudo-second

order model was more suitable than pseudo first order model. Temkin model and Langmuir model did not strongly correlate with the adsorption data due to low R^2 values while Freundlich isotherm model described the adsorption data adequately going by the high values of R^2 for both nickel and copper metals. Thermodynamic parameters of the adsorption process showed that the Gibbs's free energy, ΔG° values were negative, indicating feasible adsorption process; the enthalpy change, ΔH° values were also negative which showed that the adsorption process was exothermic. Maximum adsorption capacity for the copper and nickel in this study was found to be 4.88 mg g^{-1} and 5.0 mg g^{-1} respectively.

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