Application of Citric Acid Modified *Annona squamosa* (Custard Apple) Bark Powder as Biosorbent to Remove Ni (II) From Waste Water

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ABSTRACT

Removal of the Ni (II) metal ions from aqueous solution was carried out using citric acid modified Annona squamosa bark powder. The modified biosorbent was characterized by Fourier transmission infrared, scanning electron microscope and X-ray difractometer techniques. The effect of solution pH, adsorbent dose, initial concentration of metal solution, contact time was investigated in a systematic manner. Experimental data were analyzed by kinetic parameters such as lagergrens pseudo-first order and pseudo-second order models and found that the biosorption of Ni (II) followed pseudo-second order model by its good correlation coefficient values which are very close to the unity. The equilibrium data were analyzed by using Langmuir, Freundlich, Dubnin–Radushkevich isotherm models. Among these isotherm models Langmuir model was fitted well with its good correlation coefficient and low Chi (χ) values. Desorption and recovery of the adsorbent were carried out using HCl solution by changing its concentration from 0.001 N to 0.25 N. The results concluded that the modified A. squamosa bark powder was an efficient, eco-friendly, and economically cheap adsorbent in the removal of Ni (II) ions from the aqueous medium.

1. INTRODUCTION

Industrial activity is being growing in recent years and releases incomparable volume of waste in the environment and causing the major effect to the environment. Among these pollutants, heavy metals are considered as the major pollutants that can cause the dangerous effects to the environment and mankind. Nickel is one of such heavy metals that observed in raw water bodies from industries of paint formulation, electro plating, non-ferrous metal and mineral processing, steam-electric power plants, porcelain enameling and copper sulfate manufacture [1]. Ni (II) belongs to the essential elements category and present as a component in a lot of enzymes. It involves in many biochemical, metabolic reactions such as ureolysis, hydrogen metabolism, methane biogenesis, and acidogenesis [2]. The redox biochemistry of nickel can cause serious health problems because this metal has several oxidative states that can interfere and damage the normal function of the organisms and cellular adsorption and results in the carcinogenic responses [3]. The poisoning of Ni (II) causes nausea, vomiting, chest pain, rapid respiration, dermatitis or nickel itch in men who worked in the nickel containing

industries [4]. Due to the increase in the number of health problems, the removal of these pollutants from the wastewater has received great attention. In order to remove heavy metals from industrial waste and detoxify these components micro-organisms such as algae, fungi, bacteria and other biomaterials used as adsorbents [5-8]. The biomaterials have distinct surface properties, and they can accumulate different types of pollutants. This accumulation process has distinct advantageous than the conventional removal of heavy metals from the wastewater bodies. This process is more efficient, highly selective, cost effective, easy to operate, and does not produce any chemical sludges in the treatment of large volumes of waste water containing low concentrations of heavy metals [9].

In this endeavor, biosorption as an alternative method to clean up the wastewater that has been contaminated with heavy metals by anthropogenic activities or by natural processes [10]. In the biosorption process the removal of heavy metals from waste water is mainly attributed by different mechanisms like ion exchange, chelation, complexation, physical adsorption, and

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surface micro precipitation and the biomaterials that has been used in this process are called as biosorbents [11]. The agro-wastes have attracted significant attention in choosing biosorbents for the removal of heavy metals from aqueous solutions, because of their abundance and low cost [12] (Figure 1).

The overall objective of this work was to determine the capability of citric acid (CA) modified *Annona squamosa* bark powder in the adsorption of Ni (II) from wastewater under equilibrium conditions. The effect of pH, adsorbent dose, initial metal ion concentration, contact time of adsorbent with metal solution was investigated. Kinetic parameters were determined by using pseudo-first order and pseudo-second order models. Equilibrium data were determined by different isotherm models.

2. EXPERIMENTAL

2.1. Chemicals and Equipment

All chemicals used in this study were analytical grade. Stock solution of the test reagent was made by dissolving the appropriate amount of $NiCl_2.6H_2O$ in double distilled water from a Merck Millipore-Q water system. Working standards were prepared by progressive dilution of stock nickel solution using double distilled water. Fresh dilutions were used in each experiment. The pH measurements were made using an Elico LI120 pH meter. Test solutions pHs were adjusted using dil. HCl and dil. NaOH. The metal concentrations in the samples were determined using an atomic adsorption spectrophotometer (Shimadzu Model AA-6300). It can detect a wide range of elements with a great sensitivity. The exact sensitivity depends on the specific element. Bruker alpha Fourier transmission infrared (FT-IR) spectrometer was used to know the functional groups present in the sample. The morphology of the adsorbent was determined by using scanning electron microscope (Model: EVO ma 15 manufactured by Carl Zeiss). Wide angle X-ray diffractometer (XRD) of CA modified custard apple bark (CAMAB) was taken from (XRD 6000, Shimadzu) by using Cu Kα radiation.

2.2. Biosorbent and Chemical Modification

The bark of *A. squamosa* tree was collected from S.V. University premises, Tirupati, Andhra Pradesh. The collected bark was washed several times to remove dirt from it and made into small pieces.
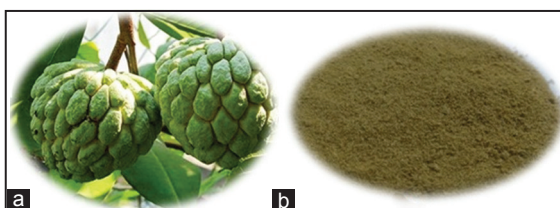

Figure 1: Picture of (a) *Annona squamosa* fruit, (b) Annona bark powder.

These small pieces were dried in the sunlight for 3 days. The dried pieces were ground in a steel mill to get a fine powder, and it was sieved. This powder was again washed with deionized water to eliminate the soluble components present in it. The washed powder was dried in hot air oven at 70°C for 4 h. The final product was named as custard apple bark (CAB) powder.

CAB modification by using CA was done by taking previous method [13]. 200 g of prepared CAB powder was added to 4 L of 0.1 N NaOH and made into a slurry. The slurry was stirred at 300 rpm for 1 h at 23°C. After stirring, the bark powder was decanted onto a 40 mesh sieve and rinsed with double distilled water. The moist bark powder was placed in 4 L of double distilled water and stirred at 300 rpm for 45 min at 23°C to remove excess base. Again the washed powder was taken to 40 mesh sieve, rinsed and added 4 L of double distilled water. This procedure was repeated two more times to ensure removal of excess base from CAB powder. The resulted in bark powder then mixed with CA in a ratio of 1.0 g of bark powder to 7.0 mL of CA. Annona bark powder readily absorbed the acid and this ratio of bark powder to acid was required to ensure the complete absorption of liquid by bark powder. The acid/bark slurry was dried overnight at 50°C. The dried bark powder was placed on Whatman 41 filter paper and washed in a Buchner funnel under vacuum with 150-200 mL of distilled water per gram of the product to remove excess CA. This volume of water was sufficient to remove unreacted CA since no turbidity from lead (II) citrate was observed when the washed bark powder was suspended in 10 mL of water to which 10 mL of 0.1 M lead (II) nitrate was added. The CA treated bark powder was dried at 50°C overnight and sieved to retain the 20±30 mesh fraction. Insertion and cross-linking of carboxylic groups to CAB by the reactions of NaOH and CA increases the uptake capability of positively charged ions [14]. The modified bark powder was named as CAMAB and used in the present study to sequester Ni (II) from wastewater.

2.3. Batch Biosorption Process

The batch adsorption experiments were carried out by adding a fixed amount of the dried sample into a simulated wastewater containing Ni (II) ions at a desirable concentration and pH values. The mixture was shaken in a shaking incubator at an appropriate temperature until the equilibrium was established. The pH of solutions was adjusted by the dilute hydrochloric acid and sodium hydroxide solutions. For investigating the effect of the initial pH of solutions on adsorption, a pH range from 2.0 to 9.0 was selected, and a concentration of 50.0 mg L^{-1} was selected as the initial concentration of Ni (II) solution. The

effect of contact time was determined by varying the contact time form 10 min to 100 min. For equilibrium adsorption experiments at different concentration range from about 10 mg L^{-1} to 150 mg L^{-1} were used, and the mixture was shaken in a shaking incubator for 24 h to ensure the equilibrium to be established. The concentration of nickel in solutions was determined by an atomic adsorption spectrophotometer (Shimadzu Model AA-6300). The adsorption capacity of the adsorbent sample for Ni (II) ions at a given time t or at equilibrium can be derived using the following equation:

$$q_e = (C_0 - C_e) \frac{V}{W} \qquad (1)$$

Where q_e is the amount of Ni (II) adsorbed at time t or at equilibrium (mg g^{-1}), C_0 is the initial Ni (II) concentration (mg L^{-1}), C_e is the Ni (II) concentration at time t or at equilibrium (mg L^{-1}), W is the mass of the adsorbent used (g) and V is the volume (L) of Ni (II) solution used.

2.4. Desorption Studies

Desorption and recovery of Ni (II) from metal loaded CAMAB was carried out by using different concentrations of HCl solution. After determination of metal content in the final solutions by atomic adsorption spectrophotometer, the biosorbent was washed with excess of acid solution and distilled water in order to recover and reuse the adsorbent. The results showed that 0.15 N of HCl solution is enough to get 98.5% recovery of the Ni (II) from the adsorbent.

2.5. Statistical Analysis

The total experiments in the present study were carried out in triplicate (n=3) and data presented are the mean values of three independent experiments. All statistical analysis was done by using Origin pro.7.5 (Origin Lab Corporation).

3. RESULTS AND DISCUSSION

3.1. Characterization of the Biosorbent

3.1.1. FT-IR analysis

FT-IR technique is using as the main tool in the identification of functional groups present in the sample. Figure 2 shows the FT-IR spectrum of CAMAB and Ni (II) treated CAMAB. The spectrum exhibited characteristic cellulose peak in the finger print region of 1200-1000 cm^{-1}. The peaks at 2919-2890 cm^{-1} and 2820-2798 cm^{-1} represent the symmetric and asymmetric C-H stretch respectively. With the comparison of CAMAB to CAB, a strong peak was appeared in the spectrum at 1742 cm^{-1} that indicates the ester group formed by the reaction of the alcohol group present in the cellulose and CA. The adsorptions around 2500-3500 cm^{-1} indicates the presence of free carboxylic –OH groups and free –OH groups. After adsorption the peaks are shifted and indicated that the metal ions were bound to the hydroxyl groups, carboxylic groups and other electron donating groups. Mainly the shifting of peak at 1742 cm^{-1} confirmed that the metal ions were bound to the free carboxylic groups (Figure 3).

3.1.2. X-ray diffraction

Figure 4 shows the XRD image of CAMAB. The image has small tiny peaks at 2θ values of 17°, 23°, 31° which indicates the amorphous phase. No other peaks are observed which represents the crystalline nature. The insertion of acid chains on to the CAB may disturb the bonding in CAB and results in the amorphous [15].

3.1.3. Scanning electron microscopy

In order to elucidate the textural properties of CAMAB, it was examined by Scanning electron microscopic analysis. From a photograph of Figure 5 it is evident that the surface of CAMAB consists of several pores and irregular cages, which are considered to be responsible for adsorption of nickel ions onto
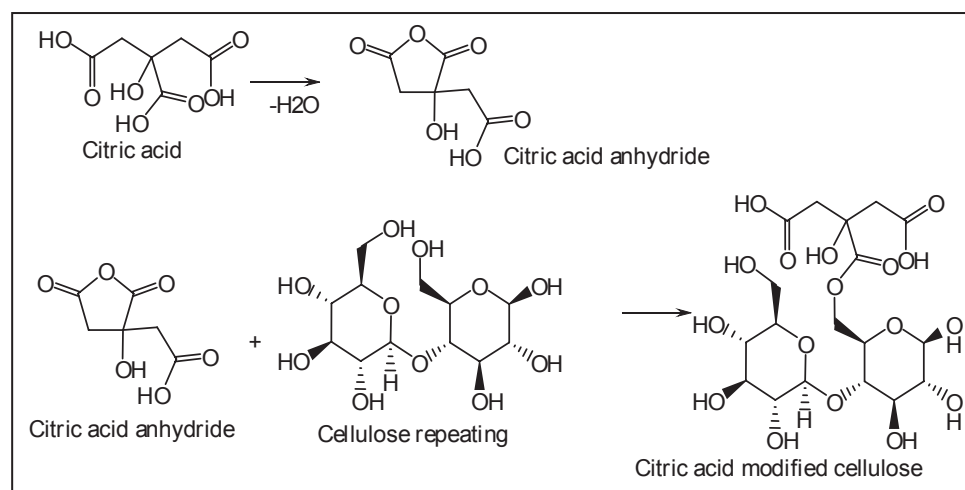

Figure 2: Proposed reaction between citric acid and cellulose in custard apple bark (CAB) to produce citric acid-modified CAB.

the sample. Prior to the observation, the sample was coated with electric conductive gold film.

3.2. Effect of pH on Removal of Nickel

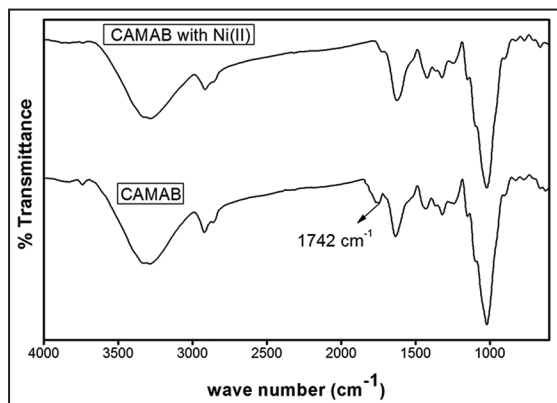pH is one of the most important parameters in the adsorption process. The dependence of the

Figure 3: Fourier transmission infrared spectra of citric acid-modified custard apple bark (CAMAB) and CAMAB with Ni (II).
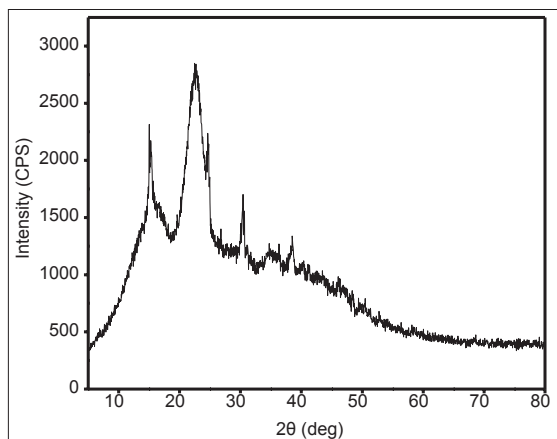

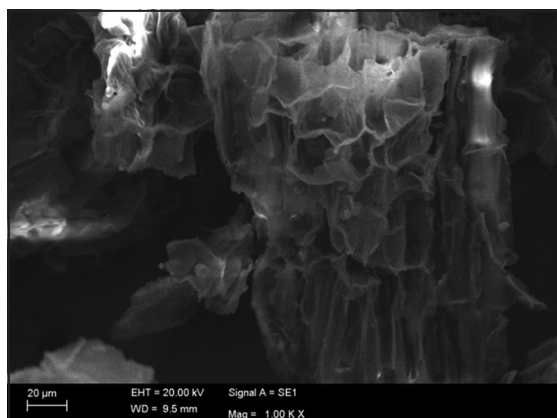**Figure 4:** Powder X-ray diffractometer spectra of citric acid-modified custard apple bark.

Figure 5: Scanning electron microscopic image of citric acid-modified custard apple bark.

adsorption process mainly on pH is because of (A) the competitive effect of the H^+ ions and (B) the fact, that the pH affects the ionization of the functional groups on the surface of the adsorbent [16]. We found that the pH of the system had a remarkable effect on nickel biosorption on CAMAB as shown in Figure 6. The adsorption of the metal onto the adsorbent is mainly due to the driving forces, and it could be the electrostatic interactions [17]. Figure 6 showed the results that correlate the biosorption of Ni (II) would be pH-dependent, i.e. with the increase of pH, the uptake of nickel by sample tended to increase and a sharp increase in Q_{max} was observed in between pH 3 and 6. A plateau was reached at about pH 6. This indicated that the optimum pH value for Ni (II) biosorption by adsorbent would be around 6. It is well known that both the cell surface binding sites and the availability of metal in solution are related to pH. At low pH values the adsorbent surface binding sites don't allow the other cations to bind because the surface binding sites were already protonized. As increase in the pH, the negative charge on adsorbent surface binding sites will lead to bind more cations [18].

3.3. Effect of Adsorbent Dose

Dose is an important parameter for the determination of the biosorption capacity of CAMAB. The effect of CAMAB dose on the percentage removal of nickel (II) increases very sharply with the increase in CAMAB dose but beyond 0.4 g, the percentage removal reaches almost a constant value and this may be due to a reduction in the concentration gradient. The maximum biosorption efficiency of nickel (II) ion onto CAMAB was found to be 98.96% at the dose of 0.4 g. The increase in removal efficiency of nickel (II) ions from aqueous solutions can be attributed to the increased number of sites and exchangeable sites available for adsorption (Figures 7and 8).
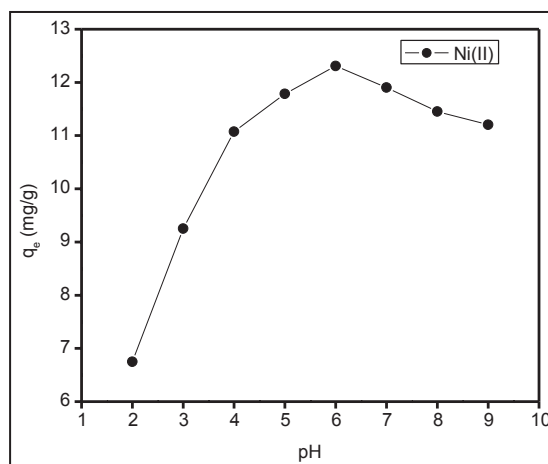

Figure 6: Effect of initial pH on the removal of Ni (II) on citric acid-modified custard apple bark.
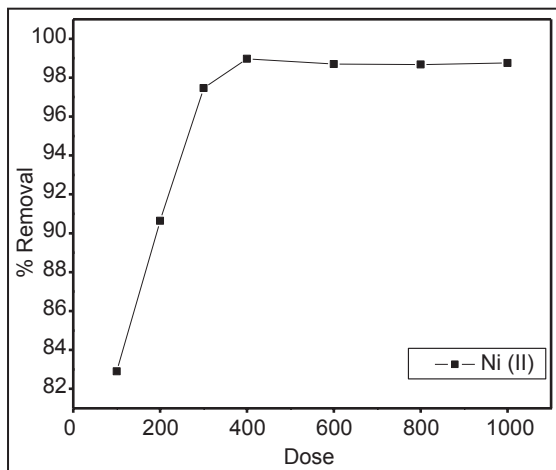
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Figure 7: Effect of dose on the removal of Ni (II) on citric acid-modified custard apple bark.
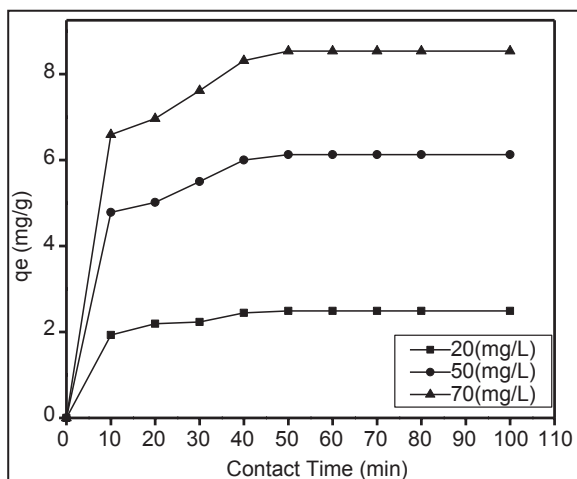

Figure 8: Effect of contact time on the removal of Ni (II) on citric acid-modified custard apple bark.

3.4. Effect of Contact Time

The experiment was performed by using fixed amount (0.4 g) of adsorbent, with different Ni (II) metal ion concentrations (20 mg L^{-1}, 50 mg L^{-1}, 70 mg L^{-1}) in the time range of 10-100 min at pH=6.0. Metal solutions were taken from the thermostatic shaker at the desired intervals (from 10 min to 100 min) and subsequently centrifuged for 10 min. The heavy metal concentration in the supernatant was analysed by flame atomic absorption spectroscopy.

3.5. Adsorption Kinetic Study

A few kinetic models have been employed to describe the adsorption kinetics [19]. Among these models pseudo first order and pseudo-second order kinetic models are familiar in demonstrating the biosorption history. Kinetic studies were carried out with 50 mL of Ni (II) solution (20 mg L^{-1}, 50 mg L^{-1}, 70 mg L^{-1}) at room temperature (27°C) in contact with the biomass (0.4 g) and a pH of 6.0. Samples of the Ni

(II) solution were removed at different time intervals (10-100 min) and metal concentration was measured. The metal uptake was calculated by using kinetic equations. The mathematical equation for Lagergren, pseudo-first-order kinetics model, is expressed as follows [20]:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{2}$$

Where q_e (mg g^{-1}) is the adsorption capacity at equilibrium and q_t (mg g^{-1}) is the adsorption capacity at time t. K_1 is the rate constant of the pseudo first-order adsorption (min^{-1}). Integrating Eq. (2) for the boundary conditions t=0-t and q_t=0-q_t gives:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{K_1}{2.303}t \tag{3}$$

The rearrangement of equation (3) gives the following linear form:

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

The adsorption kinetic may be described by the pseudo-second-order model [21]. The differential equation is generally given as follows:

$$\frac{dq_t}{dt} = K_1(q_e - q_t)^2 \tag{5}$$

Where K_2 (g mg^{-1} min^{-1}) is the second-order rate constant of adsorption. Integrating Eq. (5) for the boundary conditions q_t=0-q_t at t=0-t is simplified and can be rearranged to obtain linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}(t) \tag{6}$$

The second-order rate constants were used to calculate the initial sorption rate, given by the following equation [22]:

$$h = K_2 q_e^2 \tag{7}$$

If the second-order kinetics is applicable, then the plot of t/q_t versus t should show a linear relationship. Pseudo-second order kinetics model for the biosorption of Ni (II) at different concentrations is given in Figure 9. It is evident that pseudo-second order model explains better Ni (II) sorption with good correlation coefficients and q_e values obtained from this model are close with the experimental values (Table 1).

Being the best theoretical model, the intraparticle diffusion model is employed to describe the adsorption process. The rates of sorption are usually measured by determining the change in concentrations of sorbate with the sorbent as a function of the square root of time. Hence, the intra particle diffusion can be expressed by the following equation [23].

$$q_t = K_{dif}t^{1/2} + C \tag{8}$$

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Table 1: Kinetic parameters for the removal of Ni (II) using CAMAB.

Initial concentration (mg L^{-1})	q$_e$ exp (mg g^{-1})	Pseudo first order			Pseudo second order		
		q$_e$ cal (mg g^{-1})	K$_1$×10^{-2} (min^{-1})	R^2	q$_e$ cal (mg g^{-1})	K$_2$×10^{-2} (g mg^{-1} min^{-1})	R^2
20	2.4912	1.3914	0.0745	0.9241	2.5999	0.11358	0.9995
50	6.1269	3.9870	0.0766	0.9214	6.4403	0.03922	0.9992
70	8.5330	5.1849	0.0705	0.9309	8.9903	0.02672	0.9992

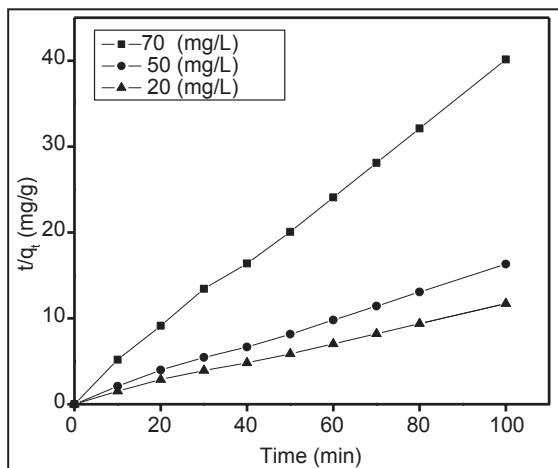CAMAB = Citric acid-modified custard apple bark

Figure 9: Pseudo-second-order kinetic model for Ni (II) onto citric acid-modified custard apple bark.

Where C (mg g^{-1}) is the intercept and K$_{dif}$ is the intra particle diffusion rate constant (in mg g$^{-1 \ \text{min}-½}$). According to equation (8), a plot of q$_t$ versus t$^{0.5}$ should be a straight line with a slope k$_{id}$ and intercept C when adsorption mechanism follows the intra-particle diffusion process.

But, in Figure 10 the plots are multi linear with three distinct regions. The first, second and third portions of plots may be considered as an external surface adsorption stage, gradual adsorption stage, final equilibrium stage respectively. So if the data exhibit multi linear plots, then the adsorption process may be influenced by two or more steps [24]. The k$_{dif}$ values were obtained from the slope of the linear portions of the curve of different initial concentrations and shown in Table 2. Among the results obtained from pseudo-first order, pseudo-second order, intraparticle diffusion models, the experiment followed pseudo-second order model with its great correlation co-efficient values.

3.6. Adsorption Isotherms

Adsorption isotherms give information about the surface properties and performance of the biosorbents [25]. The equilibrium data of Ni (II) biosorption by CAMAB at room temperature have been fitted using four biosorption isotherm models, namely Langmuir, Freundlich, Temkin and Dubnin–Radushkevich (D-R). The general isotherm plots

Table 2: Intra-particle diffusion model parameters for the removal of Ni (II) by CAMAB.

Initial concentration (mg L^{-1})	K$_{id}$ (mg g^{-1} min$^{-½}$)	C (mg g^{-1})	R^2
20	0.08122	1.80546	0.891
50	0.21857	4.27512	0.89715
70	0.31509	5.85994	0.90228

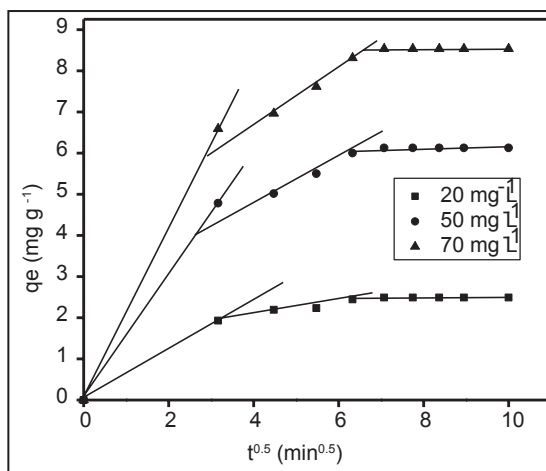CAMAB = Citric acid-modified custard apple bark

Figure 10: Intraparticle diffusion kinetics for adsorption of Ni (II) onto citric acid-modified custard apple bark.

for batch biosorption of Ni (II) and related isotherm constants calculated are shown in Figure 11 and Table 3 respectively.

According to the Langmuir model a biosorbent surface contains a finite number of identical biosorption sites and it describes the monolayer biosorption at specific sites within the biosorbent [26,27]. The non-linear form of the Langmuir equation can be written as followed in the equation (9):

$$q_e = \frac{q_{max}K_dC_e}{(1+K_dC_e)}$$
(9)

Where q$_e$ is the biosorption capacity at equilibrium (mg g^{-1}), q$_{max}$ is the maximum nickel specific uptake
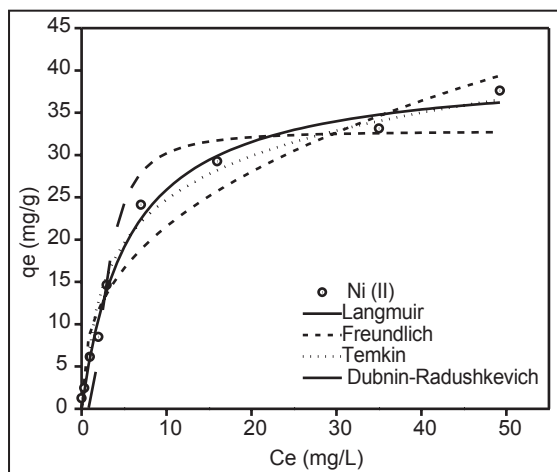
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Figure 11: Biosorption isotherms of Ni (II) onto citric acid-modified custard apple bark.

Table 3: Isotherm parameters of Ni (II) biosorption on CAMAB at various initial concentrations.

Isotherm model	Values
Langmuir	
Q_{max} (mg g^{-1})	40.29
b (L mg^{-1})	0.1802
R^2	0.9908
χ^2	2.0093
Freundlich	
K_f (mg g^{-1})	9.04
n	2.6472
R^2	0.9494
χ^2	11.1081
Dubinin-Radushkevich	
Q_m (mg g^{-1})	4.26
K	2.8176
R^2	0.9738
χ^2	5.7426
E	8.4036
Temkin	
b	4.2514
K	2.8176

CAMAB = Citric acid-modified custard apple bark

(mg g^{-1}), and K_d represents the equilibrium constant of the biosorption reaction. The dimensionless constant referred to as separation factor or equilibrium parameter R_L helps in expressing the essential features of Langmuir isotherm model. The equation is as follows (10)

$$R_L = \frac{1}{1 + \left(1 + K_d C_0\right)}$$ (10)

Where: C_0=initial concentration

K_d=constant related to the energy of adsorption (Langmuir Constant). R_L value indicates the nature of the adsorption process. Adsorption process is unfavorable if R_L>1, linear if R_L=1, favorable if 0<R_L<1 and irreversible if R_L=0 [28]. From the data calculated in Table 3, the R_L is >0 but <1 indicating that Langmuir isotherm is favorable.

According to Freundlich model biosorption takes place at specific heterogeneous surfaces and the equation of this model is represented as [29]:

$$q_e = K_f C_e^{1/n}$$ (11)

Where K_f (mg g^{-1}) and n are the Freundlich constants related to the sorption capacity of the adsorbent and the energy of adsorption respectively, C_e indicates the equilibrium concentration of adsorbate (mg L^{-1}), qe is the amount of adsorbate adsorbed per gram of the adsorbent at equilibrium (mg g^{-1}). Therefore, a plot of C_e Vs q_e for the adsorption of Ni (II) on CAMAB (Figure 11) was employed to generate the intercept value of K_f and the slope of 1/n. The D-R model was also applied to estimate the porosity, free energy and the characteristics of adsorbents [30] onto non-homogeneous surface or constant adsorption potential. The D-R model has been commonly applied in the following Eqs. (12 and 13)

$$q_e = Q_m \, \bar{e}xp\left(-K\left[RT\ln\left(1+\frac{1}{C_e}\right)\right]^2\right)$$ (12)

$$q_e = Q_m \, \bar{e}xp\left(-K\varepsilon^2\right)$$ (13)

Where Q_m is the maximum amount of the metal ion that could be sorbed onto unit weight of sorbent (mg g^{-1}), ε is the Polanyi potential which is equal to RT ln (1+1/C_e), where R and T are the universal gas constant (kJ mol^{-1} K^{-1}) and the absolute temperature (K), respectively. The K in eqns (12) and (13) is related to the mean free energy of sorption per mole of the sorbate when it is transferred to the surface of the solid from infinity in the solution and this energy can be computed using the following relationship.

$$E = \frac{1}{\sqrt{2K}}$$ (14)

The Temkin isotherm tells the information about the heat of sorption. This equation derived from the assumption that the fall in the heat of sorption is linear rather than logarithmic. This is supported by the fact that the decrease in the heat of adsorption is due to the adsorbent-adsorbate interactions and that the

adsorption is characterized by a uniform distribution of the binding energies, up to the maximum binding energy [31]. This isotherm is represented by the following equation [32].

$$q_e = \frac{RT}{b} \ln\left(K_T C_e\right) = B_1 \ln\left(K_T C_e\right) \qquad (15)$$

where $B_1 = RT/b$ is a constant which is related to the heat of adsorption, R is the universal gas constant (J mol^{-1} K^{-1}), T is the temperature (K), b is the variation of adsorption energy (J mol^{-1}) and K_T is the equilibrium binding constant (L mg^{-1}) corresponding to the maximum binding energy. A plot of q_e versus ln C_e gives isotherm constants B_1 and K_T from the slope and the intercept, respectively.

The values of correlation coefficients (R^2) of all four adsorption models shown in Table 3 indicate that the Langmuir isotherm model exhibit a better fit to the equilibrium data than Freundlich, Temkin and D-R adsorption isotherms. Therefore, the biosorption process of Ni (II) by CAMAB can be interpreted as monolayer adsorption.

4. COMPARISON OF CAMAB WITH OTHER BIOSORBENTS

The maximum adsorption capacity (Q_{max}) of different adsorbents was shown in Table 4. This can explain the adsorption capacities of different adsorbents [33-39]. The results indicate that CAMAB is a potential adsorbent in the removal of Ni (II) from the waste water.

5. DESORPTION STUDIES

Desorption studies were useful to identify the nature of the biosorption process and to recover the metal from sorbent. Moreover, it also will help to regenerate the sorbents reuse to adsorb metal ions, and to develop the successful sorption process. In the present study, HCl was taken in different concentrations ranging from 0.01 N to 0.25 N. It was found that desorption

Table 4: Comparison of Q_{max} values of different adsorbents in the removal of Ni (II) metal ions.

Adsorbent	Q_{max}	References
Irish peat moss	14.5	[33]
Almond husk	37.1	[34]
Black carrot	6.51	[35]
Orange peels	6.8	[36]
Sugar beet pulp	10.74	[37]
Rice hulls	5.75	[38]
Modified pine tree	20.5	[39]
CAMAB	40.29	Present study

CAMAB = Citric acid-modified custard apple bark

increased initially while moving from 0.01 N to 0.15 N and it became almost stable. The maximum percentage recovery of nickel was 98.5% for CAMAB with 0.15 M HCl solution and it is shown in Figure 12. In each cycle, the biosorbent was filtered and repeatedly washed with deionized water after each desorption to eliminate the excess of acid. The biosorbent was washed with water before each measurement. Interestingly, the biomass was able to sustain its biosorption capacity and remained rigid even after repeated exposure to acidic conditions. This property of CAMAB may be utilized by small scale commercial units to remove Ni (II) from their discharging effluents in an economical and efficient way.

6. CONCLUSION

From the findings of this research, it was concluded that the CAMAB powder is a versatile, novel and eco-friendly adsorbent which can be used successfully for the removal of Ni (II) ions from aqueous medium. The results obtained from the above studies showed that the removal of maximum nickel ions by CAMAB was observed at pH 6.0. Equilibrium adsorption showed that the biosorption process followed Langmuir adsorption isotherm model better than Freundlich, and D-R isotherm models, which indicates that monolayer adsorption exists under the experimental conditions employed. The kinetics studies indicated that nickel removal followed pseudo-second-order rate equation. This study demonstrated that CAMAB could be used as an effective biosorbent for the removal of Ni (II) ions from wastewater.
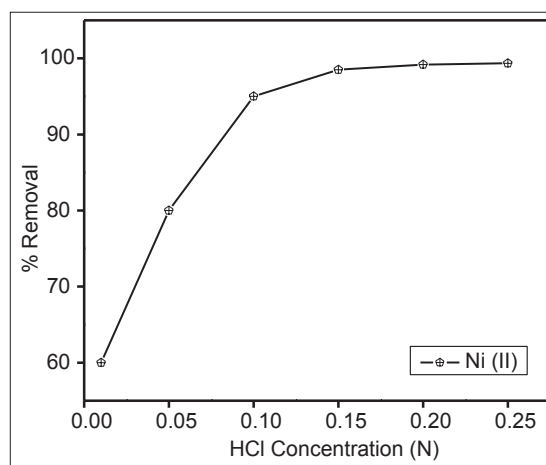
7. ACKNOWLEDGMENTS

Figure 12: Effect of HCl concentration on the desorption of Ni (II) from citric acid-modified custard apple bark.

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