



Adsorption study: Removal of nickel ions using Kenaf fiber/chitosan biosorbent

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ABSTRACT

Removal of toxic metal contaminants from wastewater has been a cause of major concern. Much attention has recently been focused on various biosorbent materials. The present study aimed to prepare the biosorbent, chitosan/kenaf fiber bio-composite for the removal of toxic heavy metal Nickel(II) ions from the synthetic wastewater. The prepared adsorbent was characterized using FTIR and XRD to study its suitability and confirms the formation of the bio-composite by the chemical versus physical changes. Adsorption was done under batch mode to investigate the parameters such as initial metal ion concentration, contact time, adsorbent dose and pH which affects the adsorption process. The maximum adsorption capacity of chitosan can be estimated to be greater than $70.55 \text{ mg}\cdot\text{g}^{-1}$ for Ni(II) ions and the removal was high at pH 5. The experimental data was modeled using the Langmuir and Freundlich adsorption isotherms and the adsorption kinetics were tested using pseudo-first-order, pseudo-second-order and intraparticle diffusion models. Kinetic studies showed that the adsorption followed pseudo-second-order reaction with regard to the intraparticle diffusion rate. The results were discussed.

Key words: chitosan/kenaf bio-composite, adsorption, nickel(II) ions, isotherms, intraparticle diffusion

INTRODUCTION

Water pollution is the leading worldwide cause of deaths and diseases and it accounts for the deaths of more than 14,000 people daily [1]. When toxic substances enter water bodies naturally or through any human activity, they either get dissolved or lie suspended or deposited on the bed in water [2]. Organic pollutants and inorganic pollutants manifest their toxic effects on the aquatic living community, cause wide range of environmental hazards [3,4]. Among the pollutants, the heavy metal pollutions are in much concern due to its toxicity.

Heavy metals like Copper (Cu), Nickel (Ni) and Zinc (Zn) are essential micronutrients for plants, but in excess all these metals are harmful to humans, animals and plants and not bio-degradable and tend to accumulate in living organisms, causing diseases and disorders; as are the non essential metals, Lead (Pb), Cadmium (Cd) and Mercury (Hg) [5]. These metals may emerge in a variety of wastewaters come from catalysts, electrical apparatus, painting, extractive metallurgy, battery industries, photography, pyrotechnics, etc. [6]. Combustion of fossil fuels produces the greatest contribution of nickel compounds in ambient air [7]. The main use of Ni is in the steel and Ni-Cd batteries, and coins to replace silver.

The accumulation of nickel in the body can lead to lung fibrosis, cardio vascular, kidney diseases and nickel's carcinogenic activity [8]. Nickel allergy in the form of contact dermatitis is the most common and well-known reaction. In the present investigation the toxicities due to Nickel were reviewed and efforts were made to remove them from water.

Common removal technologies of heavy metals are membrane separation, ion exchange, electrodeposition, and chemical precipitation proved to be costly and ineffective, with sludge disposal problems [9], biological treatments, membrane processes [10], advanced oxidation processes and adsorption procedures [11,12], which are the most widely used technologies.

Among them, adsorption effectively removes contaminants in wastewater with high solute loadings and even at dilute concentrations (<100 mg/L). Natural adsorbents for plant and animal waste like peat, banana pith, rice hull, chitosan, waste wool, nut wastes, tree barks, modified cotton and saw dust etc. prove to be economical and effective in removing a variety of contaminants [13,14]. The natural affinity of biological compounds for metallic elements could contribute to the purification of metal loaded wastewater. Thus the biopolymer chitosan was selected in this study to prepare a novel biosorbent by mixing with kenaf fiber for the removal the toxic metal nickel.

Chitosan is composed of both glucosamine and acetylglucosamine units and produced by the alkaline deacetylation of chitin carrying positive charge which is biocompatible and biodegradable are of commercial interest because of their high nitrogen content (6.89%) and their excellent properties as non-toxicity and adsorptive abilities [15-17]. Chitosan is a hydrophilic, natural cationic polymer and an effective ion exchanger, with large number of amino groups responsible for high adsorption property of chitosan [18] and chemically functionalizable. This special structure makes it exhibit chelation with various metal ions pointed out that chitosan combines with metal ions by three forms; Ion exchange, sorption and chelation.

Chitosan and its products are used to remove all kinds of dyes and the adsorption of metal cations such as Pb, Cd, Cu, Ni and oxyanions as well as complex metal ions by chitin and chitosan were investigated [19,20]. Chitosan polyvinyl chloride beads (PVC beads), for the removal of Cu(II) and Ni(II) ion from aqueous medium through adsorption studied by Srinivasa Popuri *et al.*, [9].

Bio-composites are defined as composite materials that combine natural fibers such as sisal, jute, hemp, and kenaf with either biodegradable or non-biodegradable polymers [21]. Natural fibers have many advantages include biodegradability, hygroscopic, low density, high toughness, acceptable specific strength, reduced dermal and respiratory irritation, low cost, and less use on non renewable resources [22,23]. Kenaf is one of the least expensive natural fibers and, known to have the potential as a reinforcing fiber in thermoplastic composites, because of its superior toughness and high aspect ratio in comparison to other fibers [24]. The main constituent of any plant fiber is cellulose the natural homopolymer (polysaccharides), where D-glucopyranose rings are connected to each other with (1,4)-glycosidic linkages. Simple chemical treatments like the alkali treatment leads to an increase in the amount of amorphous cellulose [25] Chitosan/cotton fiber composites were prepared for the removal Pb(II), Ni(II), Cd(II), Cu(II) [26].

Combining the biofibers with a biodegradable and renewable resource based polymer offers additional sustainability benefits. In the present work kenaf fibers are combined with chitosan, due to their superior sustainability profile from the perspective of Industrial ecology used as a biosorbent for uptake of Nickel ions. The prepared adsorbent was characterized using FTIR and XRD to study its suitability for adsorption process. Adsorption was done under batch mode; during adsorption the composite retains the polymer-metal complex. The results were discussed.

EXPERIMENTAL SECTION

Materials

Chitosan with 92% of deacetylated were purchased from India Sea Foods, Cochin, Kerala. Kenaf (*Hibiscus cannabinus*) fiber from Vibrant Nature, Chennai. All other chemical were used are of Analytical grade.

Preparation of chitosan/kenaf fiber biocomposite

10g of chitosan was dissolved in 150 ml of acetic acid (8%) at room temperature and stirred for 30 minutes using a vertical mechanical stirrer until viscous, transparent and homogeneous gel of chitosan was obtained. Kenaf

(*Hibiscus cannabinus*) fiber was mercerized using 10% sodium hydroxide solution with mild agitation and washed with water and dried. Fibers of required size were prepared by cutting the kenaf fiber using surgical knife. The prepared chitosan gel was poured into petri dish and the required amount of kenaf fiber was spread over the gel for the formation of chitosan/kenaf fiber biocomposite. Then the biocomposite was allowed to dry in room temperature. The film formed was used for further analysis.

Characterization

FTIR studies

Fourier Transform Infra Red spectra of chitosan, kenaf fiber composites were recorded in the frequency range of 400 – 4000 cm^{-1} using Thermo Nicolet AVATAR 330 spectrophotometer. The samples were pressed into pellets with KBr.

X – ray diffraction studies

X – ray diffractograms of powdered samples were obtained using a X - ray powder diffractometer (XRD – SHIMADZU XD – D1) with Ni – filter, Cu K_{α} radiation source. The relative intensity was recorded in the scattering range 2θ of 10° – 90° .

Batch experimental studies

Study of the metal ion retention properties of the chitosan/kenaf composites were carried out using a batch equilibrium procedure. Solutions containing Ni(II) ions were prepared in distilled water. Batch experimental studies were carried out with 1g of adsorbent in 100 mL of Ni(II) solution of desired concentration at an optimum pH 5 in conical flasks. The flasks were agitated on an orbit mechanical shaker at 190 rpm for a known period of time at room temperature. After attaining equilibrium, adsorbent was separated by filtration using Whatman filter paper and the aqueous-phase concentration of metal was determined with atomic absorption spectrophotometer (Varian AAA 220 FS).

RESULTS AND DISCUSSION

FTIR studies

The FTIR spectrum of pure chitosan (**Figure 1**) showed a strong absorption band at 3454.75 cm^{-1} due to OH and amine N-H symmetrical stretching vibrations. A peak at 2923.08 cm^{-1} was due to symmetric $-\text{CH}_2$ stretching vibration attributed to pyranose ring. A peak at 1156 cm^{-1} was assigned to the structure of saccharide. The sharp peak at 1384.01 cm^{-1} was assigned to CH_3 in amide group [27]. The broad peak at 1021.37 cm^{-1} and 1098.72 cm^{-1} indicate the C-O stretching vibration in chitosan and peaks at 1628.87 and 1540.02 cm^{-1} were due to $-\text{C}=\text{O}$ stretching (amide I) and NH bending (amide II). The absorption bands at 1151.84 cm^{-1} (anti symmetric stretching of the C-O-C bridge) 1098.72 and 1021.37 cm^{-1} (skeletal vibration involving the C-O stretching) are characteristics of chitosan polysaccharide structure. The spectral features of pure chitosan were in agreement with previous results [28].

The FT-IR spectrum of the CS/KF composite showed a prominent peak at 3450.43 cm^{-1} corresponding to $-\text{OH}$ stretching, $-\text{NH}$ stretching, Intermolecular hydrogen bonding strong polymerization of chitosan/fiber. Peak at 2923.64 cm^{-1} correspond to aliphatic C-H stretching [32]. The peaks at 1626.27 cm^{-1} , 1320.36 cm^{-1} , 1221.30 cm^{-1} , 1093.19 cm^{-1} , 988.40 cm^{-1} and 670.50 cm^{-1} were due to amide I band, C-O stretching, C-O-C linkage, C-N stretching, N-H wagging and O-H out of plane bending vibrations respectively [29-31].

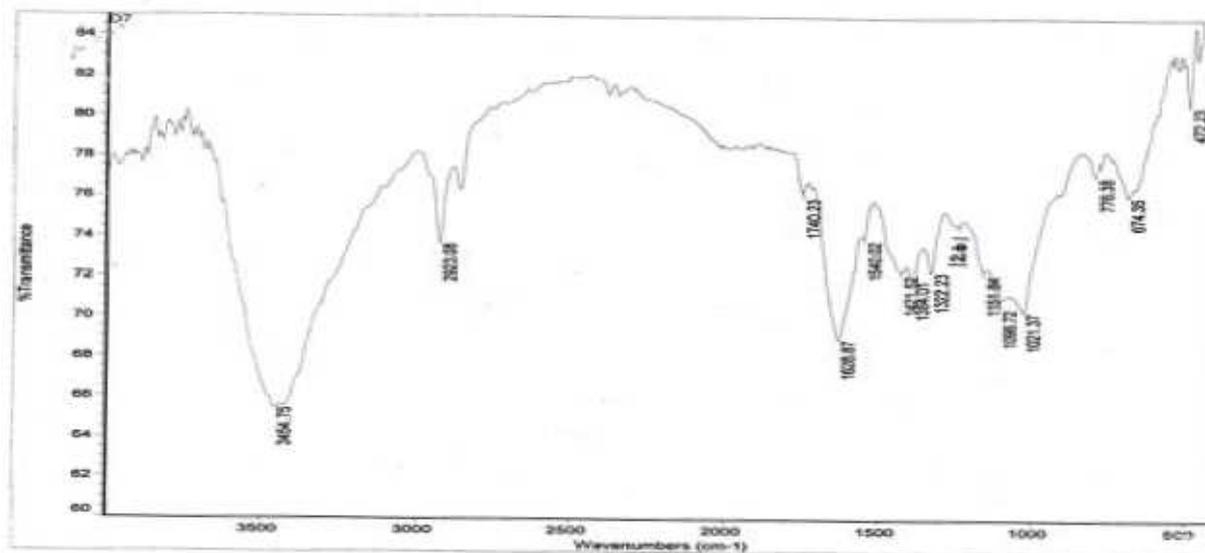


Figure-1: FT-IR Spectrum of Chitosan

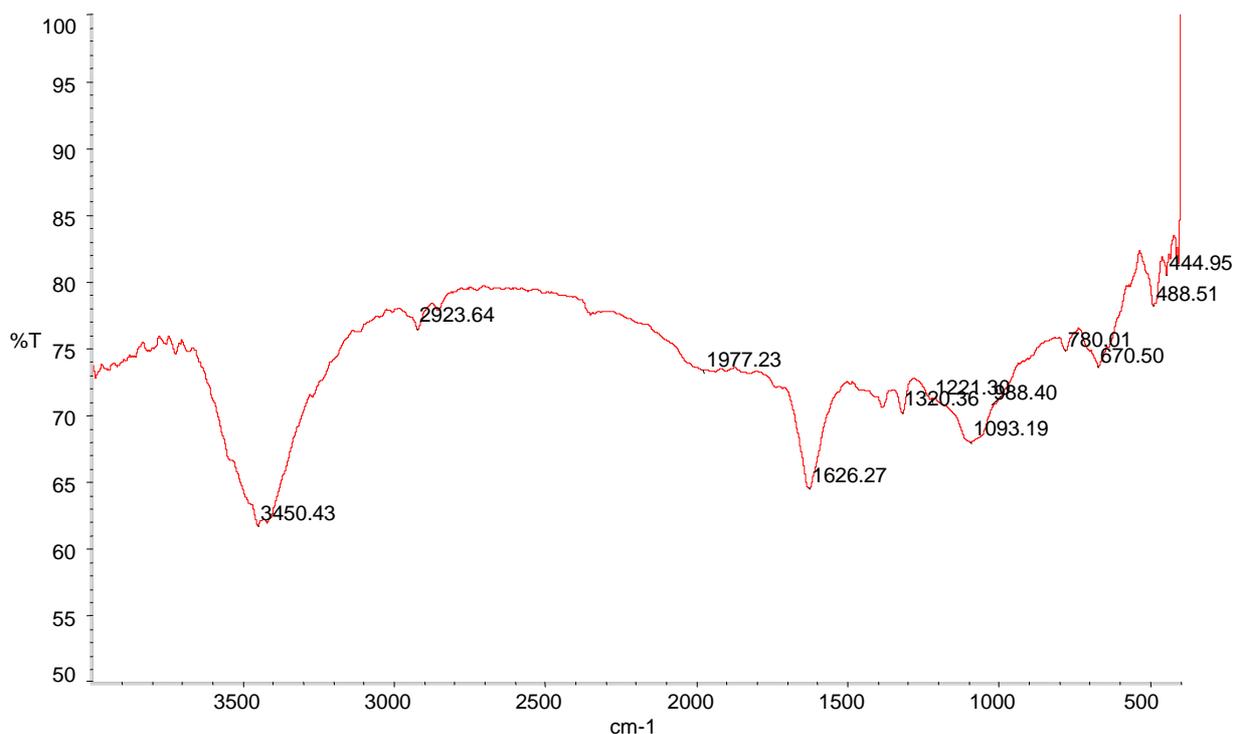


Figure-2: FT-IR Spectrum of CS/KF composite (10:3)

From the results obtained in the region around 3400 cm^{-1} , it can be said that the addition of kenaf fiber into chitosan has significantly influenced the properties of chitosan through the formation of hydrogen bonding which increases the intermolecular forces exist between chitosan and kenaf fiber.

X – ray diffraction studies

The X – ray diffraction patterns of the pure chitosan and composite of chitosan/kenaf showed in the figure 3. On comparing the XRD pattern of biocomposite with pure chitosan, the reduction in the crystallinity was observed in

the case of chitosan composites. After making the composites, two crystalline peaks 21.96 and 40.56 (2θ) were observed [33,34]. The calculated crystallinity index (CI) values of the composite is 21.6%, for the sample. The more amorphous nature of that composite is essential for the adsorption of heavy metal.

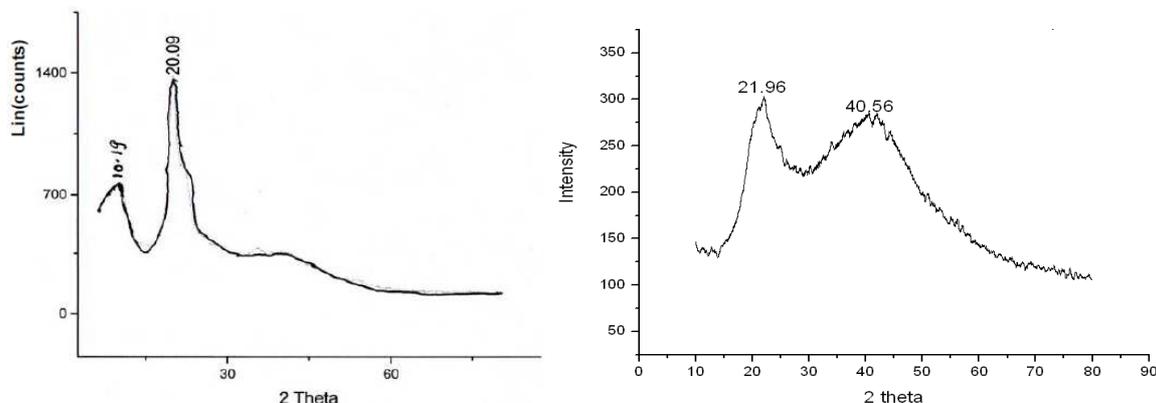


Figure 3: XRD pattern of (a) chitosan; (b) CS/KF composite

Batch adsorption studies

Effect of adsorbent dose

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent dosage (figure 4) was studied on Ni(II) ion removal from aqueous solutions by varying the amount of CS/KF composite from 0.5 to 3.0 g/L, while keeping other parameters (pH and contact time) constant. It is observed that removal efficiency of the adsorbent generally improved by increasing its dosage. This is expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites for the ions. The maximum percentage removal of Ni (II) it was 81% at the dosage of 3 g. This result also suggested that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions in the solution remain constant even with further addition of the dose of adsorbent [35,36].

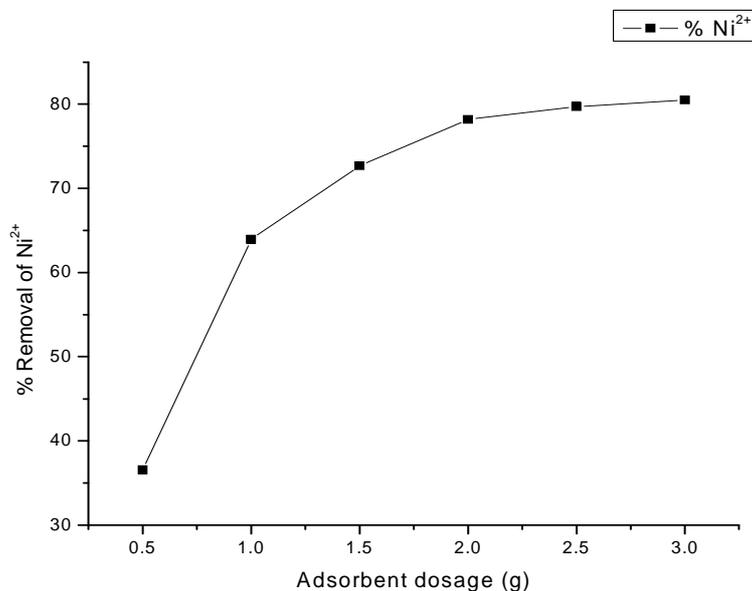


Figure 4: Effect of adsorbent dose on removal of Nickel by chitosan/kenaf fiber composite

Effect of pH

The metal sorption and percentage removal from the aqueous solution are strongly affected by the pH of the solution [37] and was studied by performing equilibrium sorption tests at different pH values. Adjustments to pH were made with $0.1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH or $0.1 \text{ mol}\cdot\text{dm}^{-3}$ HCl. During these tests the metal concentration ($200 \text{ mg}\cdot\text{l}^{-1}$), the amount of chitosan/kenaf composite (1g), the stirring speed ($190 \text{ rpm}\cdot\text{min}^{-1}$) and the temperature (30°C) were kept constant. Sample solutions of Nickel were taken in the measuring flasks the pH was adjusted from 4 to 8. Flasks were agitated on orbital shaker (top loaded) for one hour results (figure 5) shows that there was a change in the percentage removal of Nickel over the range of 4 to 8. The Nickel uptake increased with increasing pH to the maximum at pH 5, and then decreased with higher pH value. The optimum adsorption onto CS/KF composite was observed at pH 5, 89% for Nickel. After this at higher pH the adsorption decreased.

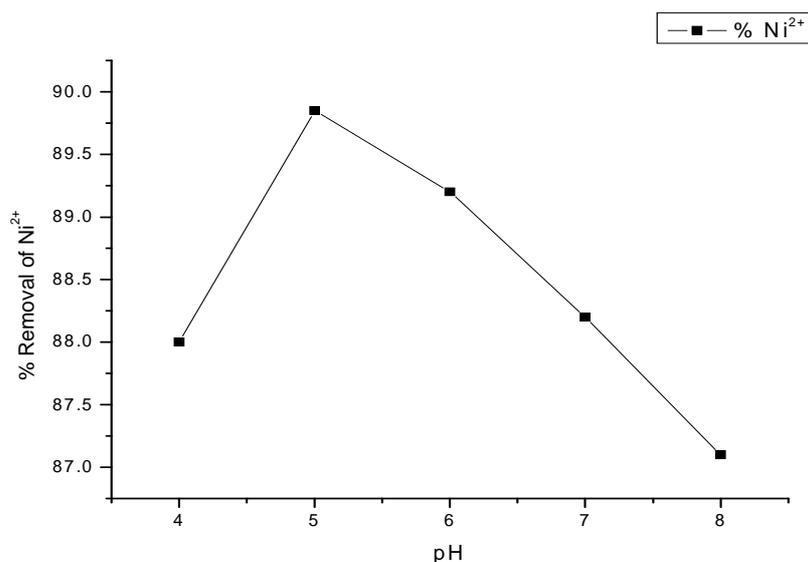


Figure 5: Effect of pH on removal of Nickel by chitosan/kenaf fiber composite

Effect of contact time

Uptake of the ion Nickel with increasing contact time by the chitosan/kenaf fiber composite was studied the efficiency increased with increase in time of contact, due to the availability of more time for metal ions to make an attractive complex with the composite. Initial removal occurs immediately as soon as the metal and composite came into contact and after some time further increase in contact time did not increase the uptake due to decrease of the easily available active sites for the binding of metal ions, and the equilibrium was reached. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system [38].

The kinetic curve for Ni^{2+} ions showed that the adsorption onto the CS/KF fiber composite was initially rapid, and reached equilibrium after approximately 3 hrs given in figure 6. Initially, a large number of vacant surface sites were available for adsorption; the adsorption rate was very fast, thus it rapidly increased the amount of adsorbates accumulated on the composite surface mainly within the first hour of adsorption. The equilibrium was attained due to the limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of the composite [39].

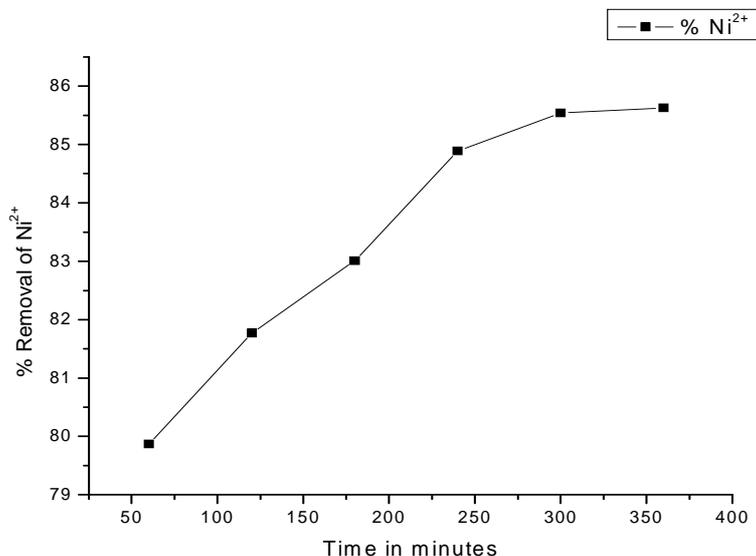


Figure 6: Effect of contact time on removal of Nickel by chitosan/kenaf fiber composite

Adsorption isotherm

The sorption of nickel ions was carried out by varying the parameters such as adsorbent dose, contact time, pH and initial metal ion concentration. The sorption data can be interpreted to describe the distribution of metal ion between the biomaterial and the liquid phase. The utilization of various isotherm models rests solely on the adequacy between the experimentally observed tendencies and the shape of the mathematical laws associated with these models. These models can be used to design and optimize an operating procedure [40].

Langmuir, [41] and Freundlich, [42] sorption models are commonly used to fit experimental data when solute uptake occurs by a monolayer and multilayer sorption. These models were tested in the present work. This modeling permits us to determine the maximum capacity of removal of adsorbate. The quality of the isotherm fit to the experimental data is typically assessed based on the magnitude of the correlation coefficient for the regression; i.e. the isotherm giving an R^2 value closest to unity is deemed to provide the best fit.

Langmuir Isotherm

The Langmuir equation (Eq. (1)), which is valid for monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies, is expressed as:

$$C_{\text{ads}} = (K_L C_{\text{eq}}) / (1 + b C_{\text{eq}}) \quad (3)$$

In this study the following linearised form of the Langmuir isotherm was used.

$$C_{\text{eq}} / C_{\text{ads}} = b C_{\text{eq}} / K_L + 1 / K_L \quad (4)$$

and

$$C_{\text{max}} = K_L / b \quad (5)$$

where:

C_{ads} = amount of metal ion adsorbed ($\text{mg} \cdot \text{g}^{-1}$)

C_{eq} = equilibrium concentration of metal ion in solution ($\text{mg} \cdot \text{dm}^{-3}$)

K_L = Langmuir constant ($\text{dm}^3 \cdot \text{g}^{-1}$)

b = Langmuir constant ($\text{dm}^3 \cdot \text{mg}^{-1}$)

C_{max} = maximum metal ion to adsorb onto 1 g chitosan ($\text{mg} \cdot \text{g}^{-1}$)

The constant b in the Langmuir equation is related to the energy or the net enthalpy of the sorption process. The constant K_L can be used to determine the enthalpy of adsorption. A plot of C_{eq}/C_{ads} vs. C_{eq} yielded a straight line confirming the applicability of the Langmuir adsorption isotherm (figure 7).

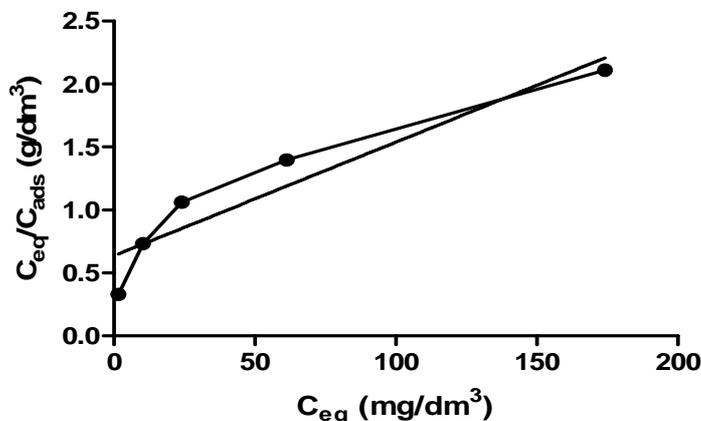


Figure – 7: Langmuir plot for the adsorption of Ni(II) ion onto CS/KF composite

The plot of C_e/q_e against C_e for the experimental data of Nickel ion adsorption onto the CS/KF fiber composite can be fitted to the Langmuir isotherm model very well. From the slope and the intercept, the values of C_{max} and K_L can be estimated. Langmuir isotherms constants for Nickel are given in Table 1. The Linear Langmuir plot indicates the formation of monolayer coverage of adsorbate on the surface of adsorbent.

Table 1: Adsorption isotherm constant, C_{max} and correlation coefficients

Metal ions	Langmuir constants			
	K_L (dm ³ /g)	b (dm ³ /mg)	C_{max} (mg/g)	R^2
Ni(II)	0.6364	0.009021	70.55	0.8916

C_{max} value was found to be 70.55 mg/g and the R^2 value was close to 1, showing the good correlations with the Langmuir equation under the concentration studies.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L is used to predict if an adsorption system is “favourable” or “unfavourable” [43]. The separation factor, R_L is defined by:

$$R_L = \frac{1}{1 + bC_f} \quad (12)$$

where C_f is the final Cu(II) and Ni(II) concentration (mg/dm³) and b is the Langmuir adsorption equilibrium constant (dm³/mg). The values of R_L calculated for different Ni(II) concentration are given in Table 2. If the R_L values are in the range of $0 < R_L < 1$, it indicated that the adsorption of Ni(II) onto CS/KF fiber composite was favourable adsorbent. The Langmuir isotherm model assumed that the adsorbed layer was one molecule in thickness and that all adsorption sites had equal energies and enthalpies of adsorption given in Table 2

Table 2: R_L values based on Langmuir adsorption

Metal ion	Initial concentration C_0 (mg/dm ³)	Final concentration C_f (mg/dm ³)	R_L values
Ni (II)	1000	174.2	0.7259
	500	61.26	0.8828
	250	24	0.9506
	150	10.24	0.9783
	50	1.6	0.9965

Freundlich Isotherm

A brief empirical equation often used to represent adsorption data is called the Freundlich equation. The Freundlich isotherm describes physical adsorption from liquids. The exponent $1/n$ is an index of the diversity of free energies associated with the adsorption of the solute by multiple components of a heterogeneous adsorbent.

The good fit of Freundlich isotherm to an adsorption system means there is almost no limit to the amount adsorbed and there is a multilayer adsorption. The applicability of the Freundlich equation to a particular case was tested by plotting $\log C_{\text{ads}}$ vs. $\log C_{\text{eq}}$ from the logarithmic form of Equation 7 (figure 8).

The Freundlich equation (Eq. 6) which was used to describe heterogeneous surface energies was expressed as:

$$C_{\text{ads}} = K_f C_{\text{eq}}^{1/n} \quad (6)$$

In this study the following linearised form of the Freundlich equation was used.

$$\log C_{\text{ads}} = \log K_f + 1/n \log C_{\text{eq}} \quad (7)$$

where;

C_{ads} = amount of metal ion adsorbed ($\text{mg}\cdot\text{g}^{-1}$)

C_{eq} = equilibrium concentration in solution ($\text{mg}\cdot\text{dm}^{-3}$)

$1/n$ = Freundlich constant ($\text{mg}\cdot\text{g}^{-1}$)

K_f = Freundlich constant ($\text{g}\cdot\text{dm}^{-3}$)

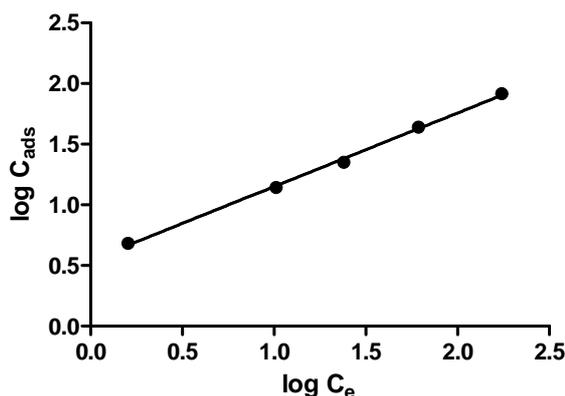


Figure –8: Freundlich plot for the adsorption of Nickel onto CS/KF composite

Table 3: Freundlich isotherm constants for the adsorption of Ni(II) onto CS/KF composites

Metal ion	Freundlich constants		
	K_f	N	R^2
Ni (II)	3.5011	1.6464	0.9983

It is evident that the values of $1/n$ and K_f , which are rough measurements of the adsorption intensity and adsorption capacity of the adsorbent, have been determined by the least-square fit and were found to be for Nickel the values are 0.5611 to 0.6536 $\text{mg}\cdot\text{g}^{-1}$ and 0.4750 to 0.6133 $\text{g}\cdot\text{dm}^{-3}$. The R^2 values are found to be 0.9983, which showed the best fit. The $1/n$ value suggested that the adsorption forces of Ni (II) acting on the surface of the chitosan/ kenaf composite was stronger.

Kinetic parameters

In order to examine the controlling mechanism of the adsorption process such as mass transfer and chemical reaction, kinetic models were used to test the experimental data. The kinetics of metal ion adsorption on the CS/KF composite was determined with three different kinetic models, i.e., the pseudo-first and pseudo-second order and the intra-particle diffusion model.

The pseudo-first order equation of Lagergren (Eq. 8) is one of the most widely used equations, being the first rate equation developed for sorption in liquid/solid systems [44].

$$\text{Log } (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (8)$$

where q_e and q_t are the amounts of ion metallic adsorbed at equilibrium (mmol/g) and at time t , respectively, and k_1 is the rate constant of pseudo-first order sorption (g/mmol min). The slopes and intercepts of plots of $\log (q_e - q_t)$ versus t (Figure 9) were used to determine the pseudo-first order rate constant k_1 and q_e , the values obtained were presented in Table 4.

The adsorption data were also treated according to the pseudo-second-order kinetics (Eq. 9) because it was shown to be more likely to predict the behavior over the whole range of adsorption being based on the assumption that the rate-determining step may be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and sorbate [45].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where k_2 is the rate constant of pseudo-second order sorption (g/mmol.min). The values of q_e and k_2 were obtained from the slope and intercept of the straight line obtained by plotting t/q_t against t (Figure 10).

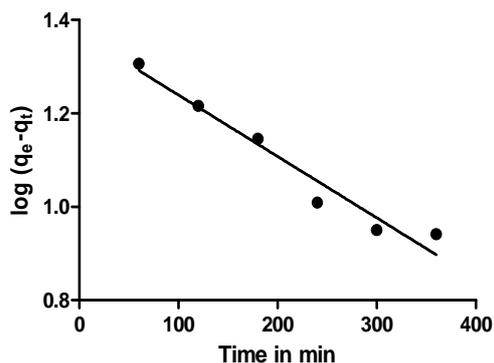


Figure -9: Pseudo-first-order kinetics for Nickel

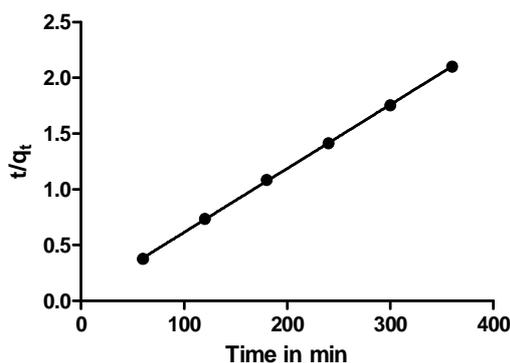


Figure -10: Pseudo-second-order kinetics for Nickel

Table 4: Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models for Ni(II) sorption by CS/KF

Metal ion	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	q _e (mg/g)	k ₁ (min ⁻¹)	R ²	q _e (mg/g)	k ₂ (g mg ⁻¹ min ⁻¹)	R ²
Ni (II)	1043.3	0.001314	0.9555	10.67	0.005724	0.9999

The results obtained from pseudo-first-order kinetics demonstrated that the experimental q_e (mg. g⁻¹) values did not agree well with the calculated values obtained from the linear plots. The correlation coefficient, R² of pseudo first order kinetics for Ni(II) is 0.9555. This confirmed that it is not appropriate to use the Lagergren first order kinetic model to predict the adsorption kinetics for Ni(II) onto CS/KF composite for the entire sorption period.

On the contrary, the correlation coefficient, R² for the second order kinetic model were almost equal to unity for all Nickel concentrations indicating the applicability of the model. It has appeared that the system under study is more appropriately described by pseudo second order kinetics which was based on the assumption that the rate limiting step may be chemisorptions involving valency forces through sharing and exchange of electrons.

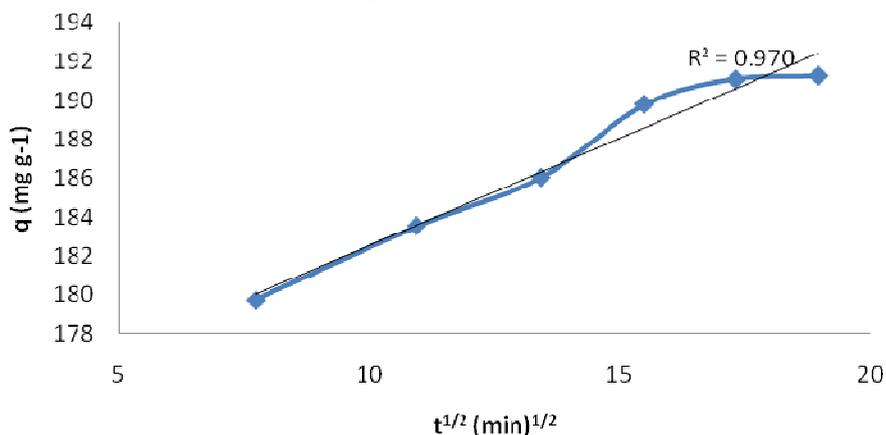
Intraparticle diffusion

The results were also analyzed in terms of intraparticle diffusion model to investigate whether the intraparticle diffusion is the rate controlling step in adsorption of Ni(II) on CS/KF composites. The model proposed by Weber and Morris, [46] can be written as,

$$q_t = k_{id}t^{1/2} + C \quad (10)$$

where K_{id} (mg g⁻¹ min^{-1/2}) is the rate constant of intraparticle diffusion. The Weber–Morris plots for adsorption of Ni(II) given in Figure 11. If the intraparticle diffusion is the sole rate determining step, the plots of q_t vs. t^{1/2} should be linear and pass through the origin. The plots in the figure 11 are multilinear with three distinct regions indicating three different kinetic mechanisms.

For intraparticle diffusion plots, the first, sharper region was the instantaneous adsorption or external surface adsorption. The second region was the gradual adsorption stage where intraparticle diffusion is the rate limiting. In some cases, the third region existed, which was the final equilibrium stage where intraparticle diffusion started to slow down due to the extremely low adsorbate concentrations left in the solutions [47]. As seen from Figure 11 the plots were not linear over the whole time range, implying that more than one process affected the adsorption.

**Figure –11: Weber – Morris plots for adsorption of Ni(II) ion on CS/KF composite**

CONCLUSION

This study shows that the chitosan/kenaf fiber bio-composite could be used as an efficient biosorbent with good metal-binding capacity for the removal of nickel ions from aqueous solutions. The effects of adsorbent dosage, contact time and pH of the medium on adsorption efficiency of chitosan/kenaf fiber bio-composite studied. The maximum adsorption occurred at the optimum pH of 5. The data were in good agreement with Freundlich isotherms

than Langmuir isotherm. According to regression coefficient the Freundlich adsorption isotherm was more fitted for nickel than Langmuir. The adsorption kinetics followed the pseudo-second-order equation for system studied. This adsorbent can be a good candidate for adsorption of not only nickel ions but also other heavy metal ions in wastewater stream. Adsorption capacity for Ni(II) is comparable to literature values (70.55 mg^{-1}).

REFERENCES

- [1] West Larry. World Water Day: A Billion People Worldwide Lack Safe Drinking Water. **2006**. About. http://environment.about.com/od/environmental_events/a/waterdayqa.htm
- [2] J Harris; D Miller; F Dw. *Health Physics*, **2008**, 95(2), 203–212.
- [3] GS Sodhi. *Fundamental Concepts of Environmental Chemistry*, 5th Edition, **2011**.
- [4] G Allen Burton; Jr. Robert Pitt. *Stormwater Effects Handbook: A Toolbox for Watershed Managers, Scientists, and Engineers*, CRC/Lewis Publishers, New York, **2001**; ISBN 0-87371-924-7, Chapter 2.
- [5] RD Reeves; AJM Baker. Metal accumulating plants, in: I. Raskin, B.D. Ensley (Eds.), *Phytoremediation of Toxic Metals-using Plants to Clean up the Environment*, John Wiley & Sons, **2000**; 193–229.
- [6] J Yoon; X Cao; Q Zhou; LQ Ma. *Sci. Total Environ.*, **2006**, 368, 456–464.
- [7] E Merian; M Anke; M Ihnat; M Stoeppler. *Metals and their compounds in the environment: occurrence*, in: *Analysis and Biological Relevance*, John Wiley and Sons, New York, **2004**.
- [8] F Sunderman; Jr. A Aitio; L Morgan; T Norseth. *Tox. Ind. Health.*, **1986**, 2(1), 17-78.
- [9] SR Popuri; Y Vijaya; VM Boddu; K Abburi. *Bioresource Technology*, **2009**, 100, 194-199.
- [10] CI Pearce; JR Lloyd; JT Guthrie. *Dyes Pigments*, **2003**, 58, 179-196.
- [11] F AL-Momani; E Touraud; JR Degorce-dumas; J Roussy; O Thomas. *J. of Photochem. & Photobiology*, **2002**, 153(1-3), 191-197.
- [12] S Al-Asheh; FA Banat; L Abu-Aitah. *Sep Purif Technol.*, **2003**, 33, 1–10.
- [13] A Septhum; A Rattanaphani; JB Bremner; V Rattanaphani. *Journal of Hazardous Materials*, **2007**, 148, 185.
- [14] M Jayarajan; R Arunachalam; G Annadurai. *Asian Journal of Applied Sciences*, **2011**, 4, 263-270.
- [15] RAA Muzzarelli; C Muzzarelli. *Adv Polym Sci.*, **2005**, 186, 151–209.
- [16] G Crini; PM Badot. *Prog Polym Sci.*, **2008**, 33, 399–447.
- [17] PK Dutta; S Tripathi; GK Mehrotra; J Dutta. *Food Chem.*, **2009**, 114, 1173–1182.
- [18] PN Sudha. *Chitin, Chitosan, Oligosaccharides and Their Derivatives*, Ed. SeKwon Kim, CRC Press, **2010**; 561-585.
- [19] WH Cheung; YS Szeto; G McKay. *Bioresour. Technol.*, **2007**, 98, 2897-2904.
- [20] Z Beke; C Ozveri; Y Seki; K Yurdakoc. *J. Hazard. Mater.*, **2008**, 154, 254-264.
- [21] MJ Johna; S Thomas. *Carbohydr Polym.*, **2008**, 71, 343–64.
- [22] AK Mohanty; M Misra; G Hinrichsen. *Macromol Mater Eng.*, **2000**, 276–277, 1–24.
- [23] HS Yang; HJ Kim; BJ Park; TS Hwang. *Compos Struct.*, **2007**, 77, 45–55.
- [24] AJ Bolton. *Mater Technol.*, **1994**, 9, 12.
- [25] G Bogoeva Gaceva; M Avella; M Malinconico; A Buzarovska; A Grozdanov; G Gentile. *Polymer Composites*, **2007**, 28, 98-107.
- [26] GY Zhang; RJ Qu; CM Sun; CN Ji; H Chen; CH Wang. *Journal of Applied Polymer Science*, **2008**, 110, 2321–2327.
- [27] Joon-Pyo Jeun; Young-Kyou; Young-Chang Nho; Phil-Hyun; Kang. *Journal of industrial and Engineering chemistry*, **2009**, 15, 430-433.
- [28] YX Xu; KM Kim; MA Hanna; D Nag. *Industrial Crops and Products*, **2005**, 21, 185–192.
- [29] J Biagiotti; D Puglia; L Torre; JM Kenny; A Arbelaiz; G Cantero; C Marieta; R Llano-Ponte; I Mondragon. A systematic investigation on the influence of the chemical treatment of natural fibers on the properties of their polymer matrix composites, *Polymer Composites*, John Wiley and Sons Inc, USA, **2004**; Volume 25, No. 5, 470 - 479.
- [30] P Ganan; J Cruz; S Garbizu; A Arbelaiz; I Mondragon. *J Appl Polym Sci.*, **2004**, 94, 1489–95.
- [31] Long Chen; Chang-yu Tang; Nan-ying Ning; Chao-yu Wang; Qiang Fu; Qin; Zhang. *Chinese Journal of Polymer Science*, **2009**, 27(5), 739–746.
- [32] CC Wang; LC Juang; TC Hsu; CK Lee; JF Lee; FC Huang. *Journal of Colloid and Interface Science*, **2004**, 273, 80–86.
- [33] J Nunthanid; S Puttipipatkachorn; K Yamamoto; GE Peck. *Drug Dev. Ind. Pharm.*, **2001**, 27, 143–157.
- [34] PC Srinivasa; MN Ramesh; KR Kumar; RN Tharanathan. *Journal of Food Engineering*, **2004**, 63, 79–85.
- [35] B Omar; Said; B Marline; Shalmor; JN Egila. *Bioresource Technology*, **1993**, 43, 63-65.

-
- [36] Cybelle Morales; Chi-Chuan Kan; Maria Lourdes; Chelo Pascua; Meng-Wei Wan. *Carbohydrate Polymers*, **2011**, 83(2), 697-704.
- [37] CM Zvinowanda; JO Okonkwo; PN Shabalala; NM Agyei. *Int. J. Environ. Sci. Tech.*, **2009**, 6(3), 425-434.
- [38] S Gueu; B Yao; K Adouby; G Ado. *Int. J. Environ. Sci. Tech.*, **2007**, 4, 11-17.
- [39] M Monier; DM Ayad; AA Sarhan. *J. Hazard. Mater.*, **2010**, 176, 348-355.
- [40] TC Yang; RR Zall. *Ind. Eng. Chem. Prod. Res. Dev.*, **1984**, 23, 168-172.
- [41] I Langmuir. *Journal of American Chemical Society*, **1918**, 40, 1361-1402.
- [42] H Freundlich. *Colloid and Capillary Chemistry*, Methuen, London, **1926**; 114-122.
- [43] WSW Ngah; A Musa. *Journal of Applied Polymer Science*, **1998**, 69, 2305-2310.
- [44] KV Kumar; S Sivanesan. *Process Biochem.*, **2006**, 41, 1198-1202.
- [45] Z Chen; W Ma; M Han. *Journal of Hazardous Materials*, **2008**, 155(1-2), 327-333.
- [46] WJ Weber; JC Morris. *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.*, **1963**, 89, 31-60.
- [47] WH Cheung; YS Szeto; G McKay. *Bioresour. Technol.*, **2007**, 98, 2897-2904.