



Optimization and modeling of physico-chemical factors affecting the removal of copper from aqueous solutions using feathers of *Dromaius novaehollandiae*

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ABSTRACT

To meet the constant challenge of maintaining the wholesomeness of water without pollutants, new biological material viz. feathers of *Dromaius novaehollandiae* (DNF) were used for the removal of copper ions. Batch studies were conducted to evaluate the adsorption capacity of the adsorbent with respect to variations in different parameters like contact time, pH, initial adsorbate concentration, adsorbent dosage and temperature by one variable at a time method. Adsorption equilibrium was found to be established by 70 min. The maximum uptake of copper ions was observed at pH 6.0 with an initial adsorbate concentration of 20mg/L and an adsorbent dosage of 0.5g. The pseudo first order and the pseudo second order models were applied to study the kinetics of the sorption process. The adsorption data were then correlated with the Langmuir, Freundlich and Temkin isotherm models. Thermodynamic parameters were calculated by Van't Hoff equation and indicated that the process was spontaneous, irreversible and endothermic in nature. The adsorbent was characterized before and after adsorption by SEM – EDS, FTIR and XRD.

Key words: Adsorption, *Dromaius novaehollandiae* feathers (DNF), copper, isotherm, kinetic, thermodynamic.

INTRODUCTION

The presence of heavy metals like copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), chromium (Cr), mercury (Hg) and others in aqueous water streams has become a problem due to their harmful effects on human health and to the fauna and flora. Metal cleaning and plating baths, pulp, paper board mills, printed circuit board production, wood pulp production, fertilizer industry etc. are releasing copper into the environment [1]. According to Safe Drinking Water act, copper has a permissible limit of 1.3mg/L in drinking water [2]. Beyond these levels, in human beings it causes stomach upset and ulcers, mental retardation, liver and brain damage and so on [1]. Due to strict environmental regulations and concern about the environment, the safe removal of copper from contaminated water is a significant environmental issue of global concern.

Numerous processes such as sedimentation, ion exchange, membrane filtration, electrochemical processes, chemical precipitation, reverse osmosis and solvent extraction are in use for the removal of heavy metals from effluents. But these methods are expensive or inefficient when the concentrations of metals are low (below 100ppm) and there is generation of large quantities of waste. The use of low cost materials as potential sorbents for the removal of heavy metals is being emphasized, of late, with the advantages of high selectivity for adsorbing metals in low concentrations, recycling of the adsorbent and minimization of the sludge generation.

By poultry processing industries 8.5billion tons of feathers are generated worldwide annually [3]. The composition of feathers is about 91% keratin, 1.3% fat and 7.9% water. Keratin is a self organized protein consisting of 41% α -helix, 38% β -sheet and 21% disordered structures, having a plenty of free carboxyl, hydroxyl and amino groups [4,

5]. Literature review suggests that various researchers used chicken feathers in natural and modified form for the removal of heavy metals like copper, chromium, zinc, lead, cadmium, nickel and arsenic [6- 17]. Currently, emu feathers are disposed off either in landfill, burned or processed (to make a low-grade animal feedstock) which are not ecofriendly. In the present study, the authors studied the adsorptive capacity of emu feathers for the removal of copper ions. To our knowledge emu feathers were not used for the removal of heavy metals. The objectives of the present work were to know the adsorption kinetics, equilibrium isotherms, thermodynamics and finally understand the copper adsorption mechanism through Scanning Electron Microscopy (SEM) - Energy dispersive spectroscopy (EDS), Fourier Transform Infra Red spectroscopy (FTIR) & X-Ray Diffraction (XRD) studies.

EXPERIMENTAL SECTION

Adsorbent

Dromaius novaehollandiae feathers (DNF) were collected from poultry processing facilities of Bapatla, Andhra Pradesh, India. Feathers were washed several times with deionized water to remove dirt particles, dried at room temperature. After drying, the barbs were detached from the shaft and used for the adsorption experiments.

Adsorbate

Stock solution was prepared by dissolving 3.798g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 250ml of deionized water, diluted to 1 liter in a volumetric flask with double distilled water obtained through Millipore ELIX-10 unit. Test solutions were prepared by progressive dilution of stock solution of copper with double distilled water and the pH was adjusted to the appropriate value by using 0.1N HNO_3 or 0.1N NaOH solutions. All chemicals used in the present study were of analytical grade.

Batch adsorption

Experiments for adsorption of copper ions by the DNF (0.3g) were carried out in aqueous solutions (50ml) with initial copper concentration of 20mg/L and pH 5 in 250ml Erlenmeyer flasks; then the flasks were agitated on an orbital shaker (REMI make CIS-24BL) at 180 rpm and 30°C temperature. The time-dependent copper ion concentration in aqueous solutions during removal experiments was measured for 90 min. For further experiments, contact time was adjusted to the optimum. The results of the experimental data were used to determine the rate of adsorption of copper with the pseudo-first-order and pseudo-second-order kinetic models. The pH values of the aqueous adsorbate solution were studied in the range of 2 - 9. With optimum contact time and pH, metal solutions in the initial concentration range of 10 to 100mg/L were used to assess the effect of initial copper ion concentrations. The sorption equilibrium was determined by using Langmuir, Freundlich and Temkin isotherm models. Similarly, the adsorbent dose was varied from 150 mg to 550 mg and finally temperature was varied between 10°C and 50°C. Thermodynamic parameters were calculated using Van't Hoff equation. All the experiments were carried out in duplicate and the average values are reported. At the end of each adsorption process, the adsorbate was filtered out through whatman filter paper and the residual metal concentration was determined by Atomic Absorption Spectrophotometer (Shimadzu make AA-6300) with copper hollow cathode lamp using air acetylene flame at a wavelength of 324.8nm. The percentage removal was obtained by using the expression

$$\text{Percentage removal (\%)} \text{ of metal} = [(C_0 - C_e)/C_0] \times 100 \quad (1)$$

Where C_0 is the initial concentration of stock sample (mg/L), C_e is the final concentration of stock sample after adsorption (mg/L).

Analysis of adsorption mechanism

The morphology and composition of DNF before and after sorption were analyzed by using a scanning electron microscope (SEM, EVO 18 make Carl Zeiss) equipped with an energy dispersive X-ray spectrometer (EDS, Oxford instrument, Inca) analysis. To know the main functional groups present on the adsorbent and their interaction with the metal ions, Fourier transform Infrared (Bruker U.K, ATR) analysis was performed. X-ray diffraction patterns of the adsorbent before and after sorption were obtained using X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406\text{\AA}$). The measurement was in the scanning range of 5-100 at a scanning speed of $>19.685\text{s}^{-1}$. The 2θ angles of the peaks were identified by X'pert High Score software.

RESULTS AND DISCUSSION

Effect of contact time

The duration of time required for heavy metal concentration to reach a constant value during adsorption is defined as the equilibrium. The percent biosorption of copper increased rapidly up to 70 min reaching 84% (Fig. 1), due to the availability of adequate vacant surface binding sites especially amino, hydroxyl and carboxyl groups present on the

feather keratin protein. Beyond 70 min, the % of adsorption remained constant (indicating the attainment of equilibrium conditions) due to repulsive forces between the molecules of the solid and the bulk phases; consequently, the remaining vacant binding sites failed to bind with the metals [18]. The reported contact time for adsorption of copper is 8h [7] using chick feathers and 48h [19] in the case of duck feathers.

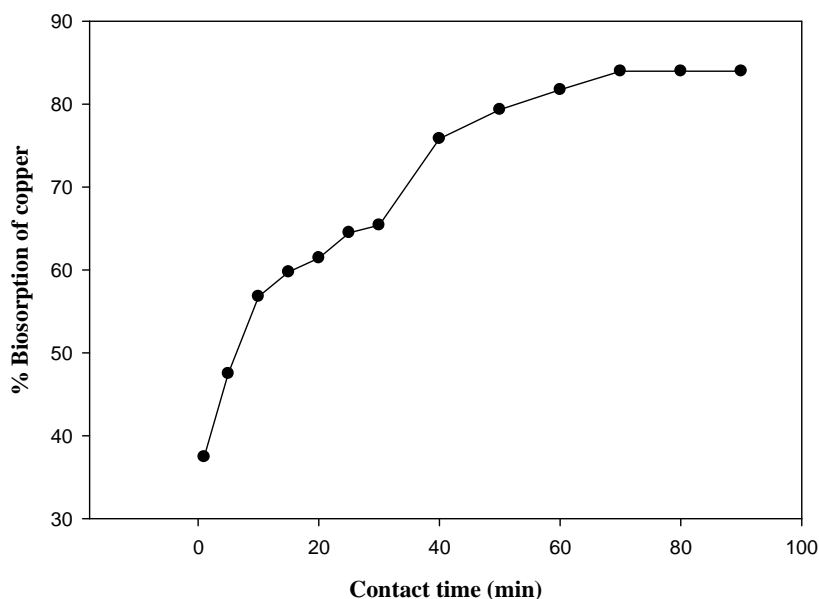


Fig. 1. Effect of contact time on % biosorption of copper

The kinetics of adsorption of copper was found out using the pseudo - first order and the pseudo - second order models. The pseudo – first order equation is

$$\log (q_e - q_t) = \log q_e - K_1/2.303 (t) \quad (2)$$

where q_e and q_t are the amount of metal adsorbed at equilibrium and at time t ; K_1 is the rate constant of pseudo – first order (min^{-1}).

The pseudo – second order equation is $t/q_t = 1/K_2 q_{\text{max}}^2 + 1/q_{\text{max}} (t)$ (3)

where K_2 (min^{-1}) is the pseudo - second order rate constant and q_{max} is the adsorption capacity. The pseudo - first and the pseudo - second order kinetic plots are given in Fig. 2a and 2b respectively. This suggests that the adsorption of copper by DNF preferably follows the pseudo- second order model. The confirmation of pseudo - second order kinetics indicates that in the adsorption process, both the adsorbent and the adsorbate concentrations are involved in the rate determining step.

Table 1. Parameter values calculated using the pseudo-first order and pseudo-second order models for adsorption of copper with DNF

Pseudo- first order model			Pseudo- second order model		
q_e	K_1	R^2	q_e	K_2	R^2
1.7664	0.0479	0.9576	2.9931	0.0506	0.9926

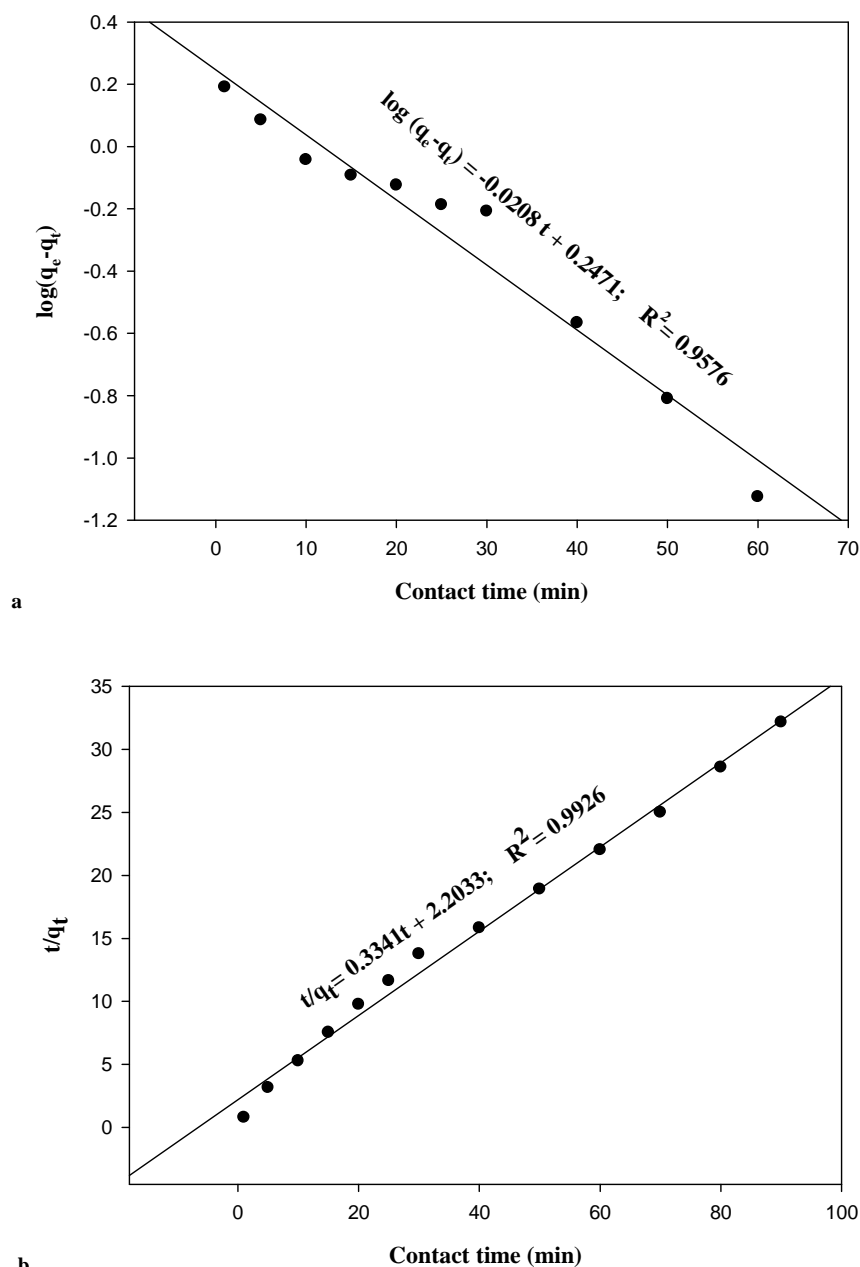


Fig. 2 Kinetics for adsorption of copper using DNF a. Pseudo – first order b. Pseudo – second order kinetics

Effect of pH on adsorption

Adsorption is influenced by pH; it influences the adsorbent surface charge, the degree of ionization and speciation of the adsorbate as well. The % adsorption of copper increased as the pH was increased from 2 to 6 and decreased beyond the pH value 6. Maximum % removal of copper was 84.65% at pH 6 (Fig. 3) and this is in agreement with the earlier research reports [8]. The increase in % removal when pH was increased from 2 to 5 could be due to decrease in competition between hydrogen ions and copper metal for appropriate sites on the adsorbent surface and also decrease in positive charge on the adsorbent. The increase in adsorption at pH 6 could be attributed to the weak inhibitory effect of H^+ ions and consequent replacement of the H^+ ions bound to the adsorbent by the copper ions.

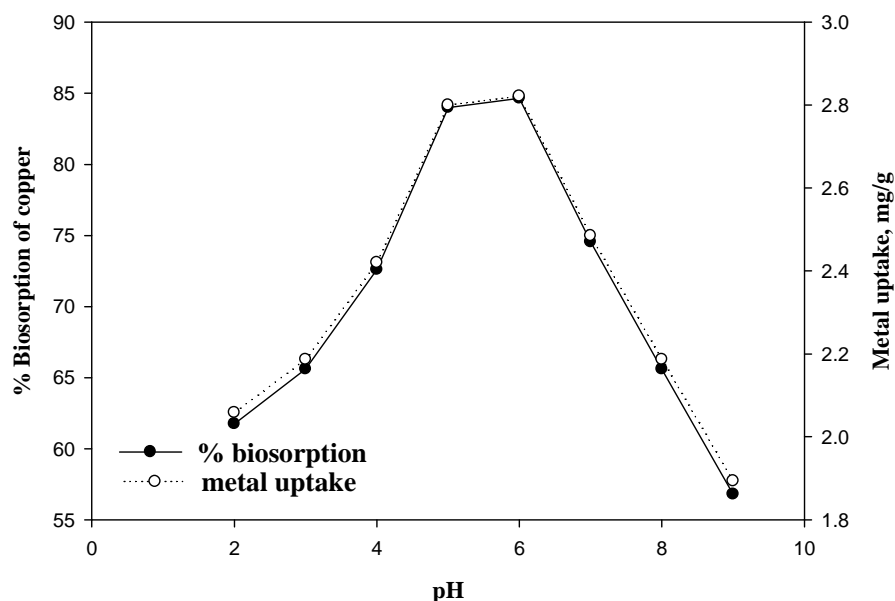


Fig. 3. Effect of pH on % biosorption of copper

Effect of initial metal ion concentration

The maximum percentage removal of copper observed was 84.65% when the initial copper concentration was 20mg/L (Fig. 4). The percent adsorption of copper increased from 83.9% to 84.65% with decrease in initial adsorbate concentration from 10mg/L to 20mg/L. This is due to the increase in adsorbate concentration to a fixed number of available active sites on the adsorbent [20]. The metal uptake increased with increase in metal concentration from 10 mg L⁻¹ to 100 mg L⁻¹.

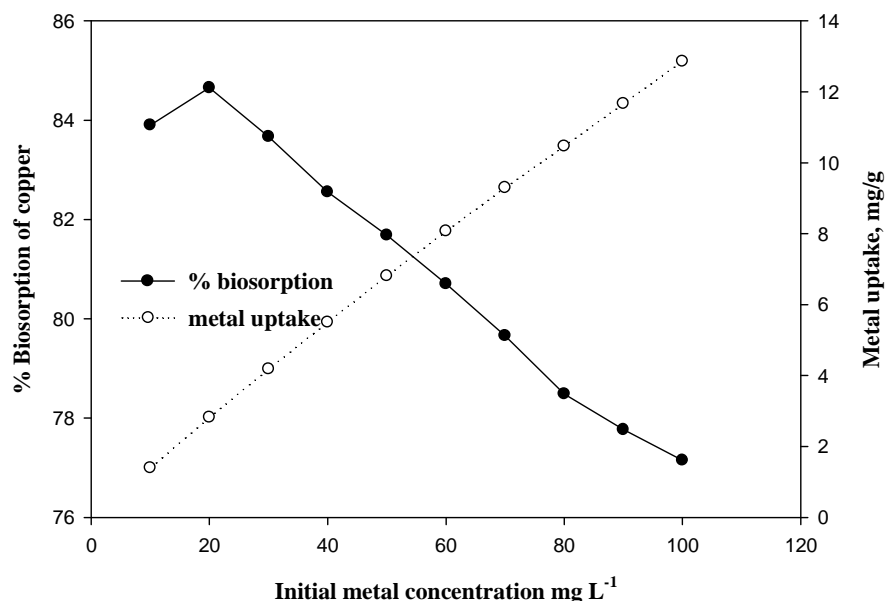


Fig. 4. Variations in the initial metal concentration Vs. % biosorption of copper

Langmuir, Freundlich and Temkin isotherm models were used to know the equilibrium isotherms. The isotherm constants were obtained by non-linear regression methods and are presented in Table 2. Langmuir isotherm, the most widely used model, is given as

$$(c_e/q_e) = 1/(bq_m) + c_e/q_m \quad (4)$$

Langmuir isotherm drawn for our data (Fig. 5a) indicates strong binding of copper ions on to the surface of the adsorbent. Freundlich isotherm, applied in the cases of low and intermediate concentration ranges, is given as

$$q_e = K_f C_e^n \quad (5)$$

where K_f and n are adsorption capacity and intensity respectively. Freundlich equation can be linearized in logarithmic form as

$$\log q_e = \log K_f + n \log C_e \quad (6)$$

With the experimental data represented in Fig. 5b, the adsorption appears to be favored over the entire concentration range. Temkin isotherm equation describes the behavior of many adsorption systems on the heterogeneous surface. The linear form of the equation is

$$q_e = (RT/b_T) \ln (A_T) + (RT/b_T) \ln (c_e) \quad (7)$$

The experimental data were analyzed according to the equation and depicted in Fig. 5c. Based on the regression correlation coefficient R^2 , the Langmuir and the Freundlich isotherms were inferred to be the best fitted models followed by the Temkin model.

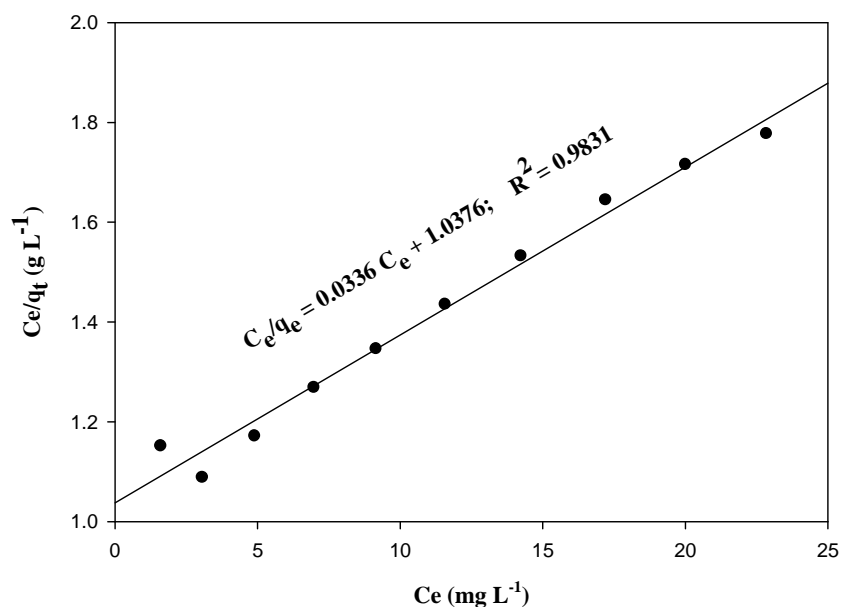


Fig. 5a Langmuir isotherm for adsorption of copper using DNF

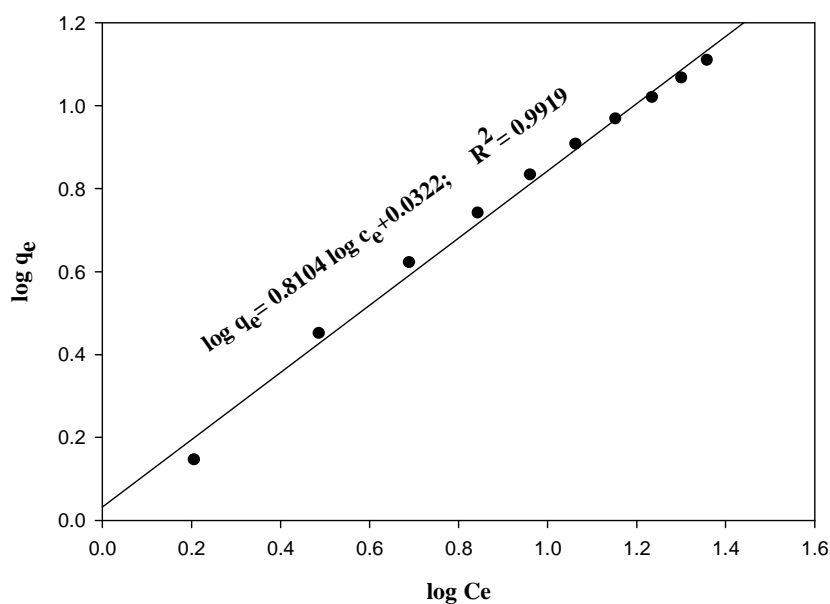


Fig. 5b Freundlich isotherm for adsorption of copper using DNF

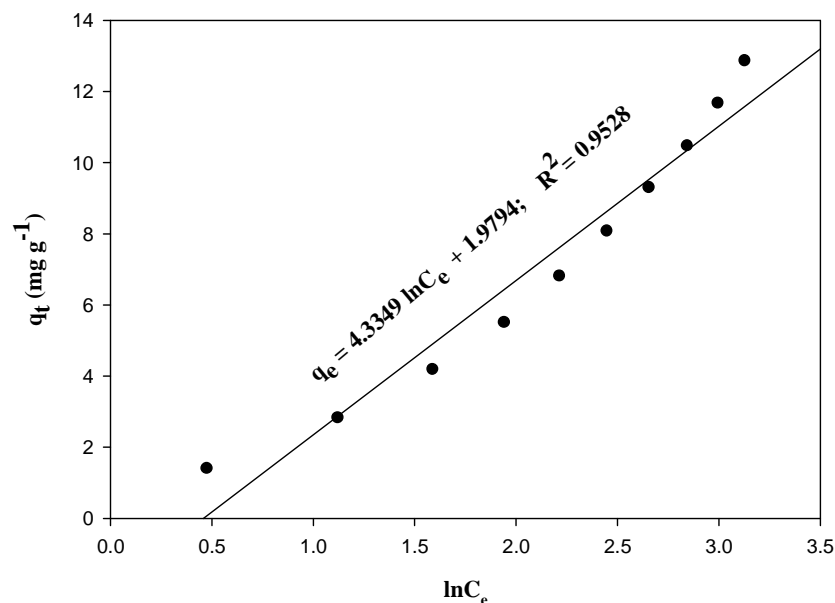


Fig. 5c. Temkin isotherm for adsorption of copper using DNF

Table 2. Isothermal constants for the Langmuir, Freundlich and Temkin models

Langmuir	Freundlich	Temkin
$q_{\max} = 29.76 \text{ mg/g}$	$n = 0.8104$	$A_T = 0.6334$
$R_L = 0.9035$	$K_f = 1.0769 \text{ mg/g}$	$b_T = 581.1303$

Effect of adsorbent dosage

The percentage removal of copper by DNF at different adsorbent doses is presented in Fig. 6. Experimental studies were carried out at 30°C temperature with an initial metal concentration of 20mg/L at pH 6. The removal of copper increased rapidly from 75.95% to 85.105% with an increase in adsorbent dose from 3 to 10g/L, due to the increased surface area of the adsorbent and the number of binding sites. For a fixed initial metal concentration, the equilibrium has reached at 10g/L; further increase in the adsorbent dosage effected no significant change in the adsorption [21].

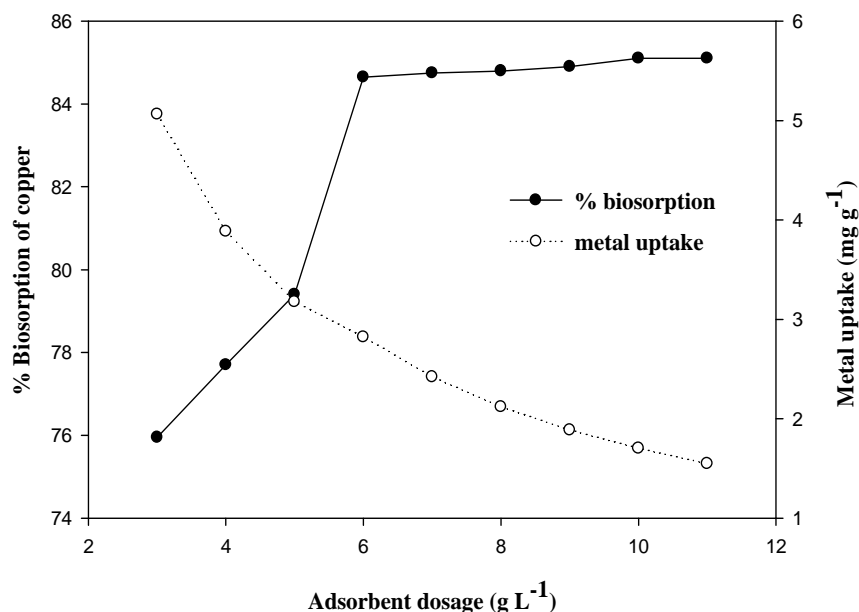


Fig. 6. Dependency of % biosorption of copper on adsorbent dosage

Effect of temperature

The effect of changes in the temperature on the copper uptake is shown in Fig. 7. Copper uptake marginally increased from 83.65% to 85.105% for DNF with increasing temperature from 283 °K to 303 °K indicating that the adsorption of copper on to the adsorbent is an endothermic process. When the temperature was lower than 30°C,

copper uptake increased with increase in temperature, but when the temperature was above 30°C, the increase in uptake was marginal.

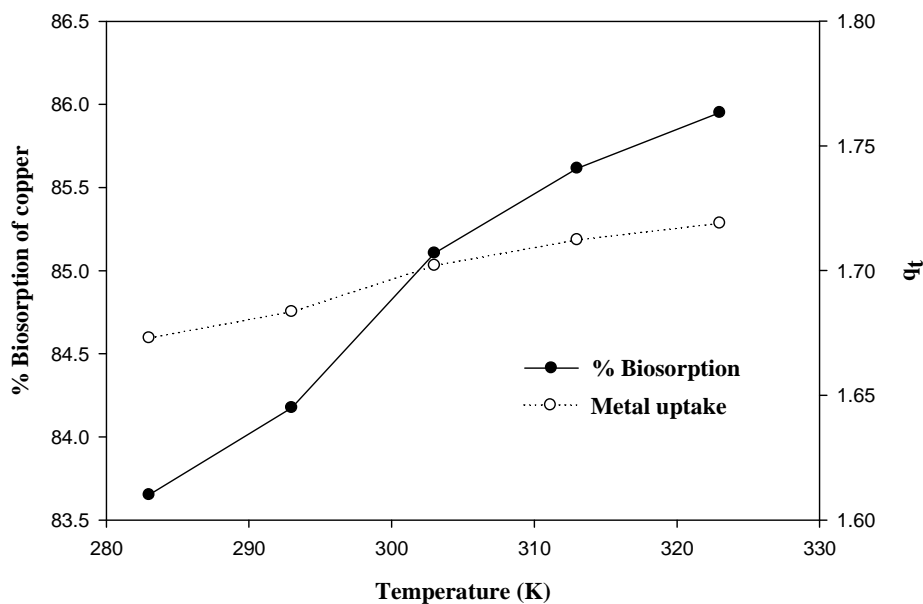


Fig. 7. Dependency of % biosorption of copper on temperature

To investigate the nature of adsorption, the three thermodynamic parameters, enthalpy (ΔH°), entropy (ΔS°) and Gibbs free energy (ΔG°), were estimated. The following Van't Hoff equation was used to evaluate thermodynamic parameters:

$$\log (q_e/c_e) = \Delta H/2.303RT + \Delta S/2.303R \quad (8)$$

Van't Hoff plot is represented in Fig. 8. The experimental ΔH° value of 3.5805 kJ mol⁻¹ indicates that the adsorption process was endothermic in nature and there was a possible strong bonding between the metal ion and the adsorbent. As ΔS° (7.0672 kJ mol K⁻¹) was more than zero, the adsorption process appears to be irreversible. The Gibbs free energy (-2137.7811 kJ mol⁻¹) is negative, suggesting the spontaneous nature of the adsorption process. The free energy change (ΔG°) increased with increase in temperature (10°C - 50°C), possibly due to activation of more sites on the surface of the adsorbent [1].

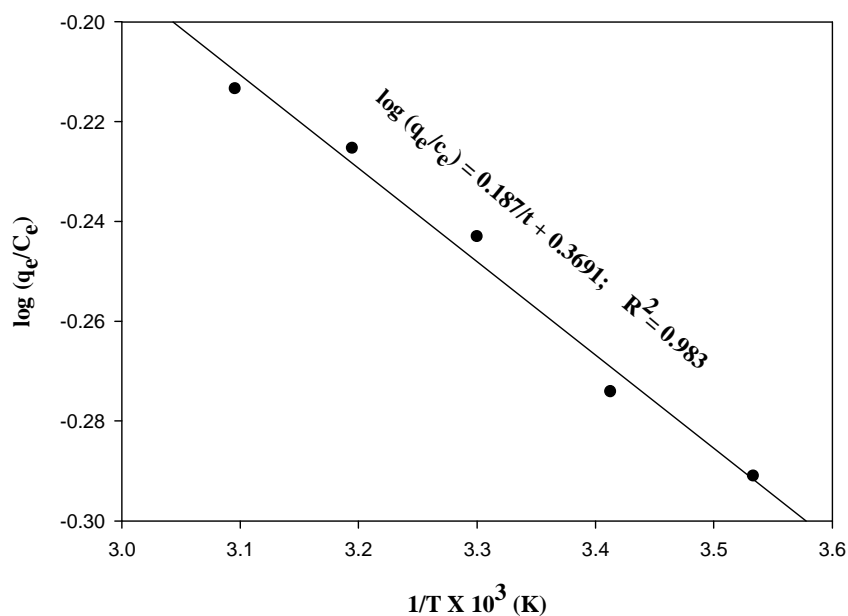
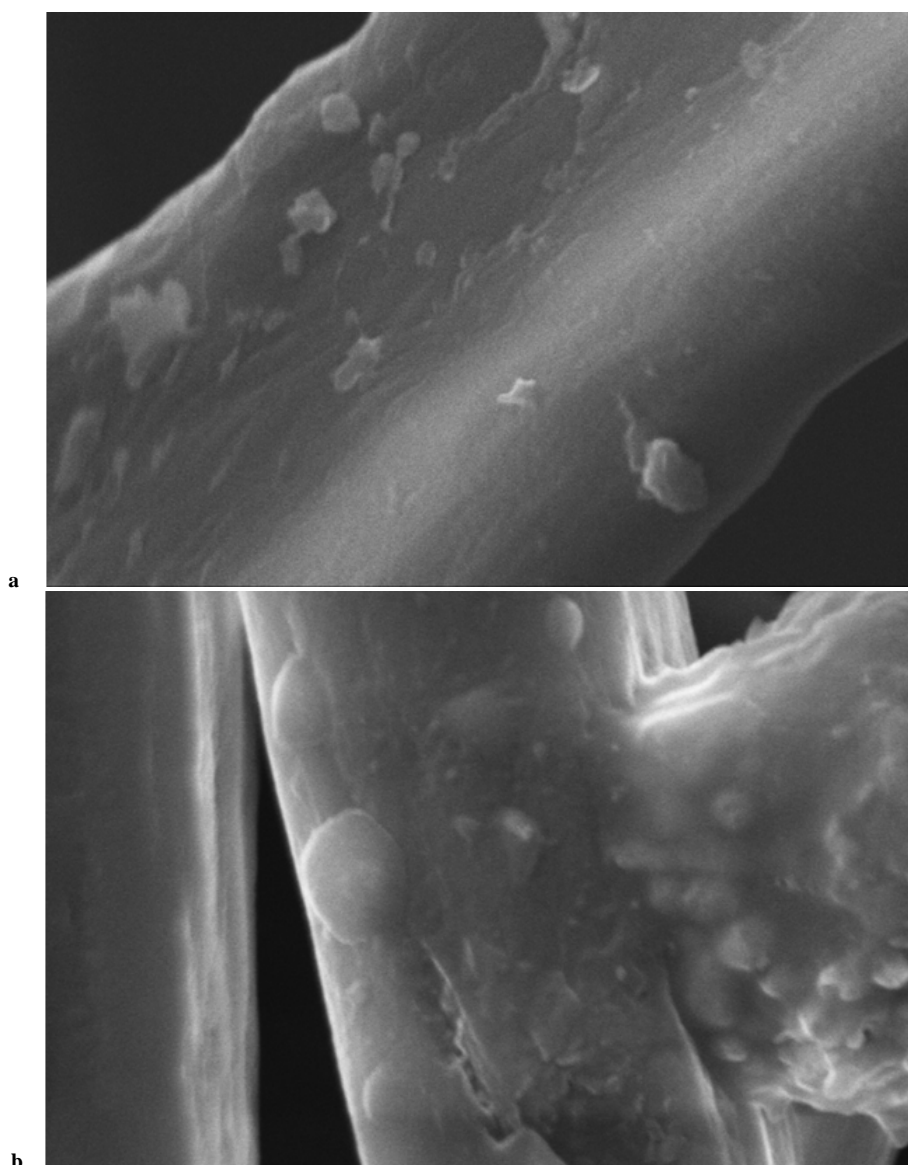


Fig. 8. Van't Hoff plot for adsorption of copper using DNF

The reported maximum adsorption capacities (q_{\max}) of natural chick feathers, chick feathers which were treated with alkaline solution and anionic surfactant for adsorption of copper were 11.811mg/g (0.186mmol/g), 24.82mg/g (0.391mmol/g) and 18.7325mg/g (0.295mmol/g) respectively [6], revealing that emu feathers (DNF) with a q_{\max} of 29.76 mg/g (0.472295mmol/g) are more effective and efficient for the adsorption of copper.

SEM - EDS analysis

The surface morphology of the adsorbent (DNF) analyzed using SEM before and after adsorption of copper are presented in Fig. 9a and b respectively. Feather morphology was clear before adsorption, while after adsorption of copper, the formation copper precipitates on the surface could be visualized from the glossy thick appearance. The major constituent of feather is keratin protein, in addition to sulphur, and metals like Cr, Mn, Fe, Zn, Ni, As, Al, Se etc. (evident from EDS analysis before biosorption) (Fig. 10a). After adsorption of copper (Fig. 10b), the EDS analysis showed the presence of copper ions with a concomitant decrease in the percentage of some positively charged metal ions like Cr, Mn, Ni and Fe suggesting that the adsorption of copper may also include the ion-exchange mechanism. In addition, presence of sulphur before adsorption indicates the occurrence of sulphur containing aminoacids like cysteine, and its absence after adsorption indicates the binding of copper to sulphur.



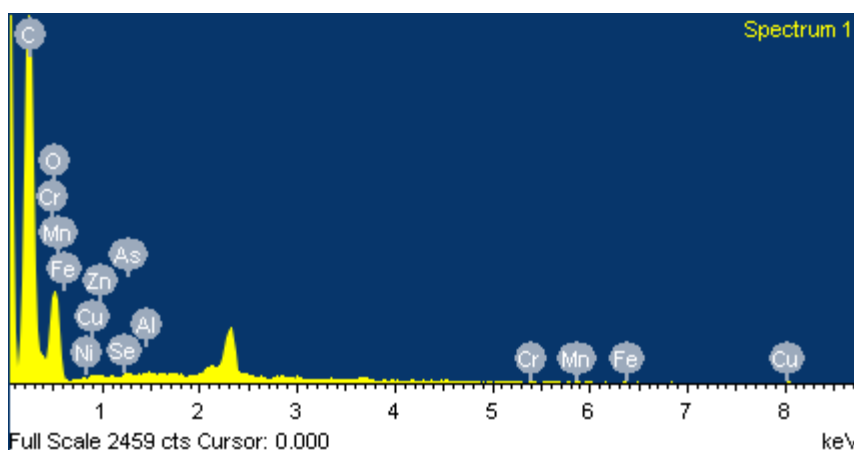
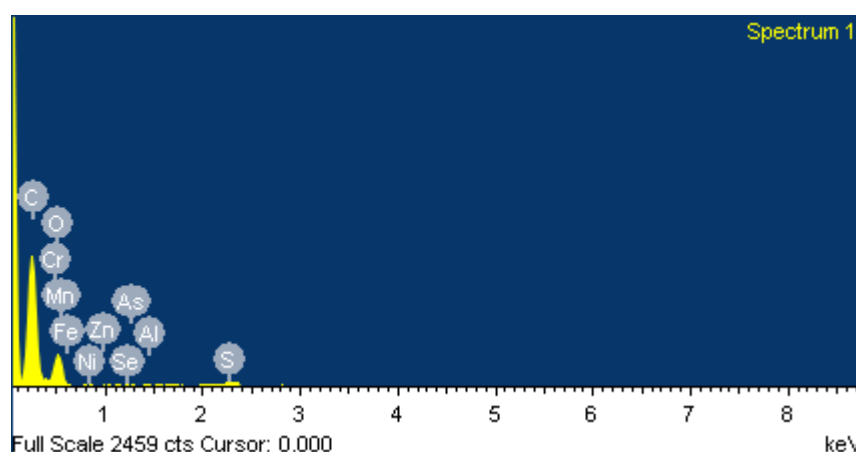


Fig. 10. EDS micrograph of DNF a. Native b. After adsorption of copper

Adsorption mechanism through FTIR spectral analysis

The adsorption mechanism was investigated using FTIR analysis of native and metal loaded DNF in the range of $400\text{-}4000\text{cm}^{-1}$ (Fig. 11a and 11b). FTIR spectra showed marked differences before and after adsorption of copper. Broadly, the spectrum could be divided into 2 distinct regions viz. $1390 - 1627\text{ cm}^{-1}$ and $3065 - 3677\text{ cm}^{-1}$ wherein there are significant variations in the absorption patterns and the groups assigned for biosorption.

After interaction with the copper ions, it was identified that the sharp band at 3447 cm^{-1} shifted to 3458 cm^{-1} mainly due to hydrogen bonded N-H stretching vibrations. In the secondary structure of the protein, the peptide N-H groups form hydrogen bonds with amide C=O groups. The bands at $3381, 3263, 3197\text{ cm}^{-1}$, assigned to O-H & N-H inter hydrogen bonds' vibration, shifted to $3353, 3268, 3178\text{ cm}^{-1}$ respectively, indicating disruption of hydrogen bonds due to the binding of copper metal ions. Amide I, 80% C=O stretching and small contribution from NH bend - shifted from 1637 (assigned to the β -sheet structure) to 1627 cm^{-1} and widened; it also indicates the disruption of β -sheet and the binding of copper metal ions [22]. The peak at 1516 which corresponds to the Amide II, 60% C-N stretch plus 40% N-H in plane bend, disappeared after metal uptake. Moreover, the adsorption intensity for N-H bending vibration at 1541 cm^{-1} shifted to 1538 cm^{-1} and decreased after copper uptake. This observation is supported by an extreme change in absorption intensity for C-N stretching vibrations at $1457, 1424\text{ cm}^{-1}$ to $1455, 1392\text{ cm}^{-1}$ respectively. Accordingly, the observed changes in absorption intensity and the wave number of functional groups strongly suggest the occurrence of complexation between N and O atoms on the adsorbent binding sites and the copper ions. The FTIR analysis suggests that the maximum adsorption of copper by the DNF is due to the availability of more number of N and O atoms.



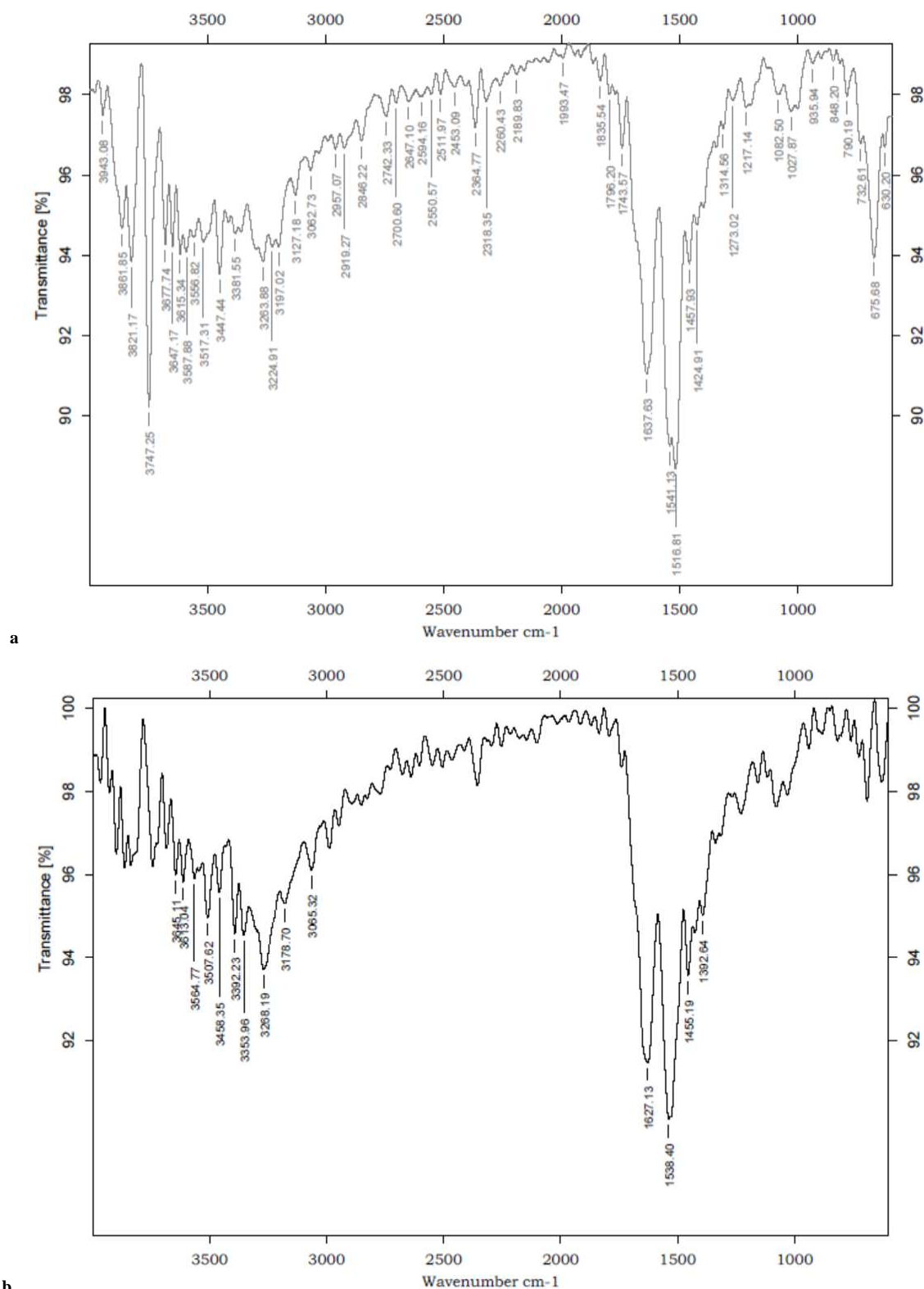


Fig. 11 FTIR spectra of DNF a. Native b. After adsorption of copper

X-ray diffraction (XRD) analysis

The DNF X-ray diffractogram (as shown in Fig. 12a) exhibited crystalline nature and showed peaks at 2θ positions nearer to 10° and 19° . The downward curvature at 10° shows the α -helix configuration of the keratin and a wide band at 19° is indexed for the β -sheet of keratin protein secondary structure [23]. There are noticeable differences in the XRD pattern of DNF after adsorption of copper (as shown in Fig. 12b). Mild shift in the 2θ positions especially in the range of 10° to 20° indicates the disruption of both the α -helix and the β -sheet. Formation of an extra peak at 2θ position of 24° (JCPDS copper: 04-0836) indicate the presence of copper and the disappearance of peak at 2θ

position 43° in copper treated adsorbent, as also evidenced by SEM analysis, are suggestive of the adsorption of copper. This could be due to the electron pair sharing between copper metal and the carboxyl/hydroxyl/carbonyl/amino groups in DNF.

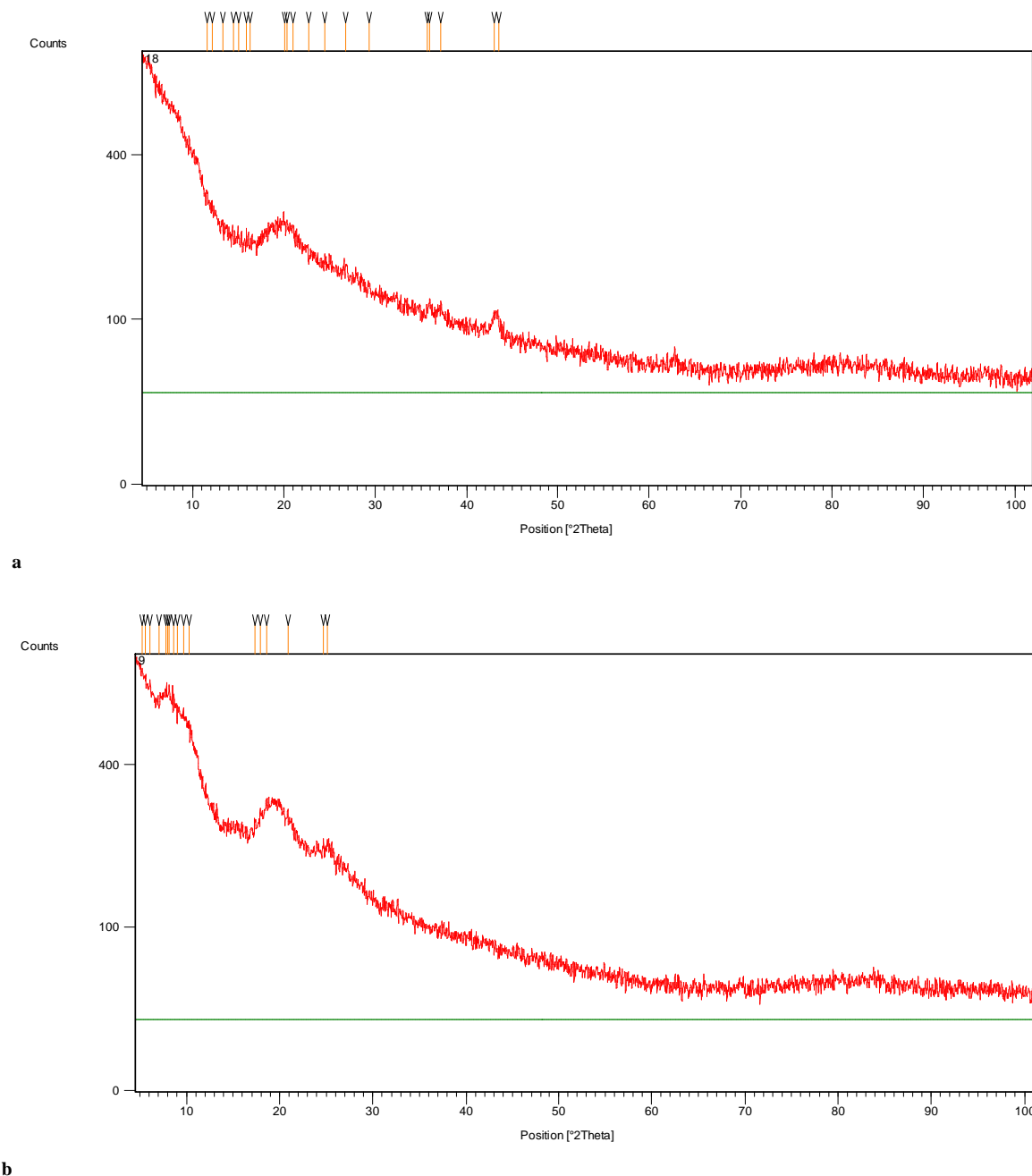


Fig. 12. XRD of DNF a. Native b. After adsorption of copper

CONCLUSION

Equilibrium was attained at 70 min of contact time due to the presence of more and/or active functional groups. The metal uptake increased with an increase in the initial concentration of the adsorbate. The removal of copper increased rapidly with increasing adsorbent dosage initially and attained equilibrium at 10 g/L. Percentage removal of copper from aqueous solution increased significantly with increase in pH from 4 to 6; thereafter, increase in pH decreased the percentage removal. From Langmuir isotherm model, the maximum uptake capacity of 29.76 mg of copper per gram of the adsorbent was obtained at a temperature of 30°C . The results of the present study demonstrate that DNF could be considered as an adsorbent for safe, effective and economic treatment of the industrial waste water containing copper.

Acknowledgements

Ratna Kumari expresses her sincere thanks to the Management and the Principal of Bapatla Engineering College, Bapatla, India for providing the laboratory facilities.

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