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Utilization of Emu (*Dromaius novaehollandiae*) Feathers for the Adsorption of Lead from Aqueous Solution: Kinetic, Isotherm and Thermodynamic Studies.

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ABSTRACT

The sorption capacity of *Dromaius novaehollandiae* feathers (DNF) was evaluated for adsorption of lead from aqueous solution. The optimum conditions viz. contact time, pH, initial adsorbate concentration, adsorbent dosage and temperature were studied by one variable at a time method in a batch mode. Adsorption equilibrium was established by 70min. The desired pH of the aqueous solution was found to be 4.0 with an initial adsorbate concentration of 20mg/L and an adsorbent dosage of 0.5g. The pseudo first order and pseudo second order models were applied to study the kinetics of sorption process. Kinetic data were best described by pseudo second order model. The fitness of the adsorption data for Langmuir, Freundlich and Temkin isotherm models were investigated and fitted well to the Langmuir and Freundlich isotherm models. Thermodynamic parameters 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. The present data confirms that emu feathers (a poultry waste) could better be used as adsorbent for efficient removal of lead ions from contaminated water.

Keywords: Adsorption, *Dromaius novaehollandiae* feathers, lead, kinetic, isotherm, thermodynamic.

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INTRODUCTION

Clean and fresh water is the basic need for biotic community. The discharge of metal containing effluents into the water bodies leads to contamination of aqueous environment by heavy metals like copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), chromium (Cr), mercury (Hg) etc. Heavy metal pollution has become one of the most serious environmental issues of the century, due to its harmful effects on human health and to both the fauna and the flora. Heavy metals are not degradable, enter into the food chain either from air, soil or water, and accumulate in living organisms causing various disorders and diseases. In particular, lead has been classified as a serious hazardous heavy metal [1], and is released in to the environment from activities like mining, smelting, printing, metal plating, explosive manufacturing, dyeing etc. and industries such as paint, plastics, alloys, batteries, ceramic glass etc. [2]. According to World Health Organization (1984), the permissible level for lead in drinking water is 0.05 mg/L, while in solid and liquid foods, it is 6 mg/ L and 1 mg/L respectively [3]. Even very low concentrations of lead in regular drinking water causes long term effects; it damages kidney, liver, brain, nervous system and reproductive system, while severe exposure leads to sterility, abortion, stillbirths and neonatal deaths [4]. Therefore, removal of lead from the contaminated waters has received much attention in recent years.

The existing conventional processes for the removal of lead from effluents are ion exchange, membrane filtration, electro-dialysis and chemical precipitation. But these methods are expensive or inefficient when the concentrations of metals are low (below 100ppm) and there is generation of large quantities of wastes. The use of low cost materials as potential sorbents for the removal of heavy metals, even when present in low concentrations, is highly warranted. Feathers are the waste generated from the poultry industry. Feathers consist of 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 [5, 6]. Feathers of chick, duck and ostrich are used by researchers for the removal of heavy metals like copper, chromium, zinc, lead, cadmium, nickel and arsenic [7-21]. To the best of our knowledge, emu feathers were not used as an adsorbent for the removal of heavy metals, particularly lead. The objective of the present work therefore, was to investigate the feasibility of lead removal from aqueous solution by DNF and finally understanding the lead adsorption mechanism through Scanning Electron Microscopy (SEM) - Energy dispersive spectroscopy (EDS), Fourier Transform Infra Red spectroscopy (FTIR) & X-Ray Diffraction (XRD).

MATERIALS AND METHODS

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

Standard lead stock solution was prepared by dissolving 1.598 g of $Pb(NO_3)_2$ in 100ml 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 lead 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

The batch adsorption experiments were carried out in 250ml Erlenmeyer flasks containing 0.3g of the adsorbent in 50ml of lead solution (20mg/L) of pH 5 at 30^oC temperature on an orbital shaker (REMI make CIS-24BL) at 180rpm. For optimization of contact time, samples were collected at predefined time intervals (1, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80 and 90 min). For further experiments, contact time was adjusted to the optimum and the experimental results were used for kinetic studies. The effect of pH on adsorption was investigated in a pH 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 lead ion concentrations; the adsorption isotherm models were determined using this experimental data. Similarly, the adsorbent dosage was varied from 150 mg to 550 mg. Finally, temperature was varied between 10⁰C and 50⁰C, and using Van't Hoff equation, the thermodynamic parameters were calculated. Each experiment was repeated twice and the results are given as average values. 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 lead hollow cathode lamp using air acetylene flame at a wavelength of 283 nm. The percentage removal was obtained by using the expression

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

Where C₀ is the initial concentration of stock sample (mg/L), C_e is the final concentration of stock sample after adsorption (mg/L).

Characterization of adsorbent

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

RESULTS AND DISCUSSION

Effect of contact time

The equilibrium contact time was determined by plotting the % biosorption of lead against contact time as shown in Fig.1. During the first 5min, the % of adsorption was 55.4, then steadily increased up to 85.2% by 70 min due to the availability of 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, presumably due to repulsive forces between the solute molecules of the solid and the bulk phases; consequently, the remaining vacant binding sites failed to bind with the metals [22]. The reported contact time for adsorption of lead is 8h [19] using ostrich feathers and 90 min [20] in the case of chick feathers.

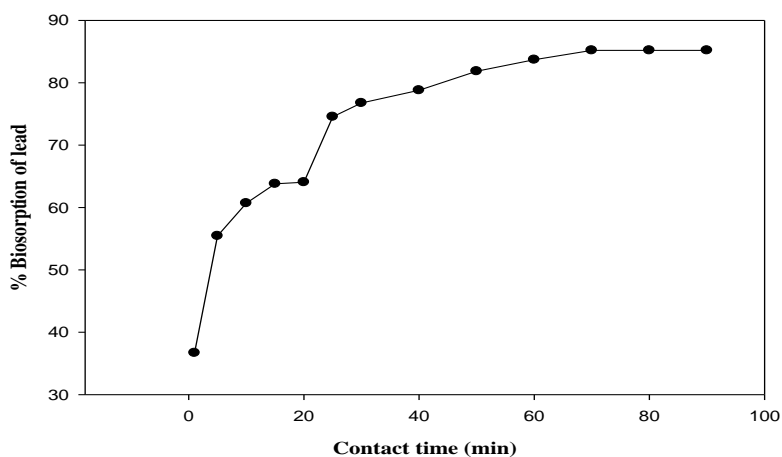


Figure 1: Effect of contact time on % biosorption of lead

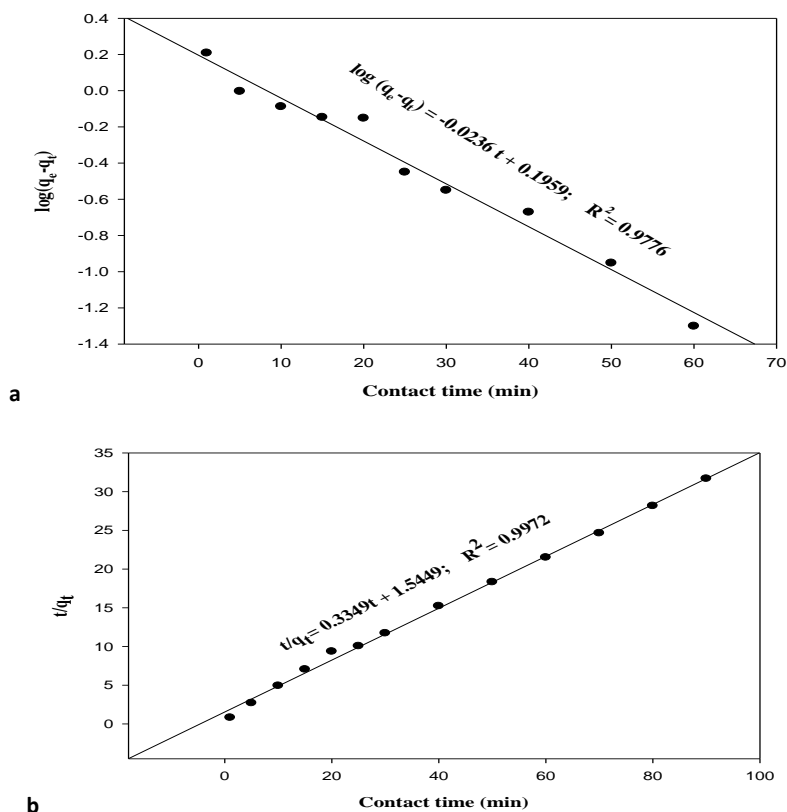


Figure 2: Kinetic models for adsorption of lead using DNF a. Pseudo – first order b. Pseudo – second order

Table 1: Pseudo-first order and pseudo-second order model equations and respective parameter values

Kinetic model	Equation	Parameters
Pseudo- first order model	$\log (q_e - q_t) = \log q_e - K_1/2.303 (t)$	$q_e = 1.57$
		$K_1 = 0.0543$
		$R^2 = 0.9776$
Pseudo- second order model	$t/q_t = 1/K_2 q_{max}^2 + 1/q_{max} (t)$	$q_e = 2.9859$
		$K_2 = 0.0726$
		$R^2 = 0.9972$

The kinetics of adsorption of lead was worked out using the pseudo - first order and the pseudo - second order models, and are given in Figures 2a and 2b respectively. The kinetic parameter values and their regression coefficients are given in Table 1. The adsorption of lead by DNF preferably follows the pseudo-second order model which is the rate-limiting step. The confirmation of pseudo - second order kinetics indicates formation of chemisorptive bonds involving either sharing or exchange of electrons between the adsorbent and the adsorbate.

Effect of pH on adsorption

The pH is one of the important parameters in controlling uptake of metal ions from aqueous solution. It influences the adsorbent surface charge, the degree of ionization and speciation of the adsorbate as well. The % adsorption of lead increased significantly as pH increased from 2 to 4 and decreased beyond the pH value 4. Maximum % removal of lead was 85.7% at pH 4 (Fig. 3) and this is in agreement with the earlier research reports [20, 23]. At pH lower than 4, the % of adsorption was low due to high concentration of hydrogen ions and the mobility of hydrogen ions is higher (36.25X108m2s-1V-1) than all cations [24]. Hence, hydrogen ions reach to the surface of the adsorbent first than the other cations. At pH 4, electrostatic repulsion decreases due to reduction of positive charge on sorption sites, thus resulting in enhanced metal

adsorption. Further increase in pH decreases adsorption which could probably be due to increased concentration of hydroxyl ions that apparently form complexes with lead ions.

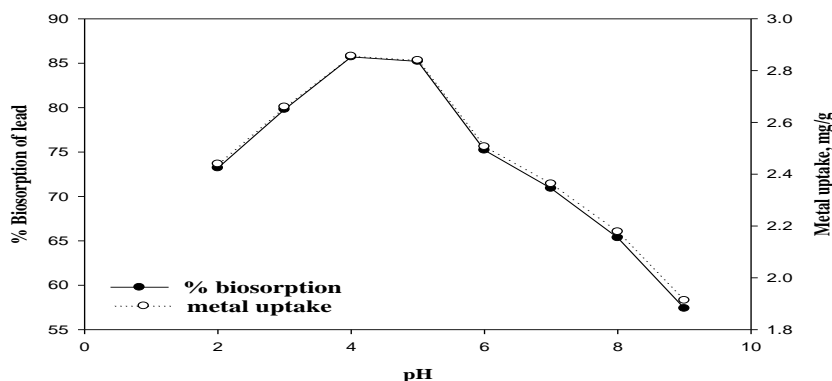


Figure 3: Effect of pH on % biosorption of lead

Effect of initial metal ion concentration

The maximum percentage removal of lead observed was 85.7% when the initial lead concentration was 20mg/L (Fig. 4). The percent adsorption of lead increased from 85.1% to 85.7% with an increase in initial adsorbate concentration from 10mg/L to 20mg/L. This can be attributed to the increase in adsorbate concentration to a fixed number of available active sites on the adsorbent [25].

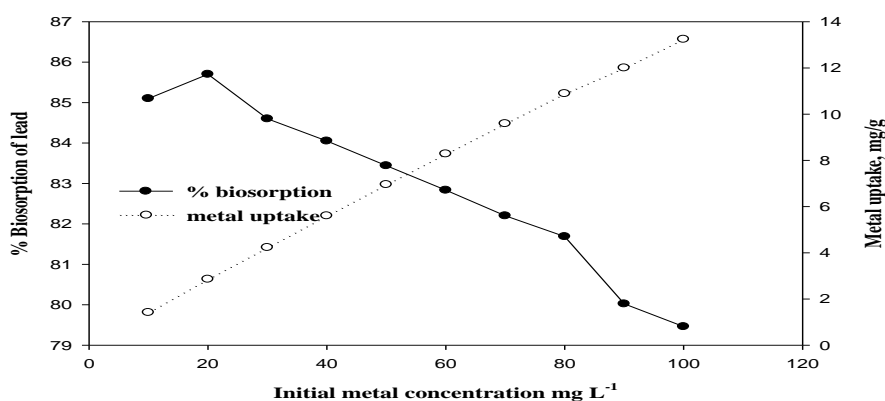


Figure 4: Variation of initial metal concentration Vs. % biosorption of lead

Langmuir, Freundlich and Temkin isotherm models were used to know the equilibrium isotherms and are shown in Fig. 5a-c. The isothermal constants were obtained by non-linear regression methods and are presented in Table 2. Based on the regression correlation coefficient R², the Langmuir and the Freundlich isotherms were inferred to be the best fitted models followed by the Temkin model.

Table 2: Isothermal models and their constants for the Langmuir, Freundlich and Temkin Models

Isotherm model	Equation	Parameters
Langmuir model	$(c_e/q_e) = 1/(bq_m) + c_e/q_m$	$q_{max} = 35.2112$
		$R_L = 0.09279$
		$R^2 = 0.9803$
Freundlich model	$\log q_e = \log K_f + n \log C_e$	$n = 0.8408$
		$k_f = 1.1256$
		$R^2 = 0.9933$
Temkin model	$q_e = (RT/b_T) \ln (A_T) + (RT/b_T) \ln (c_e)$	$A_T = 546.8668$
		$B_T = 0.6636$
		$R^2 = 0.9492$

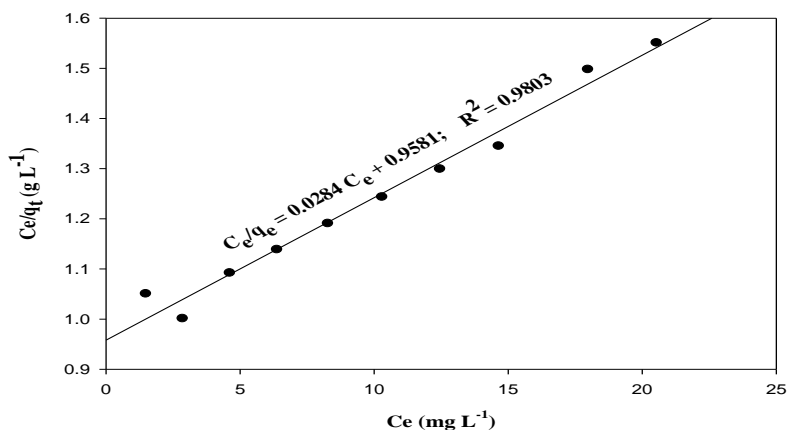


Figure 5a: Langmuir isotherm for adsorption of lead using DNF

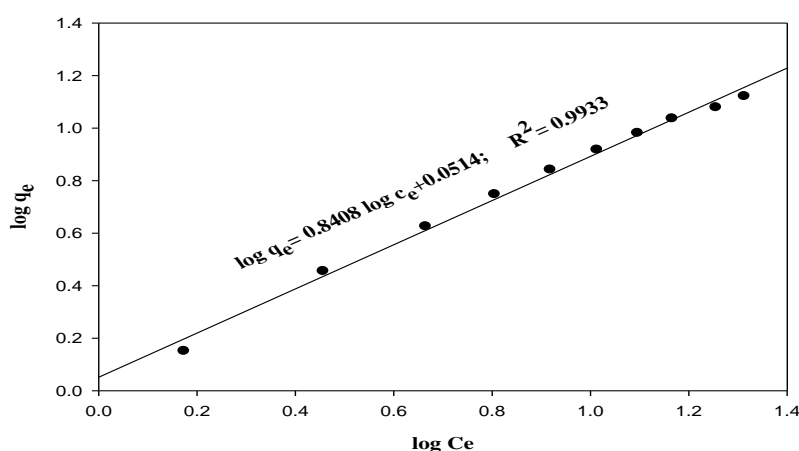


Figure 5b: Freundlich isotherm for adsorption of lead using DNF

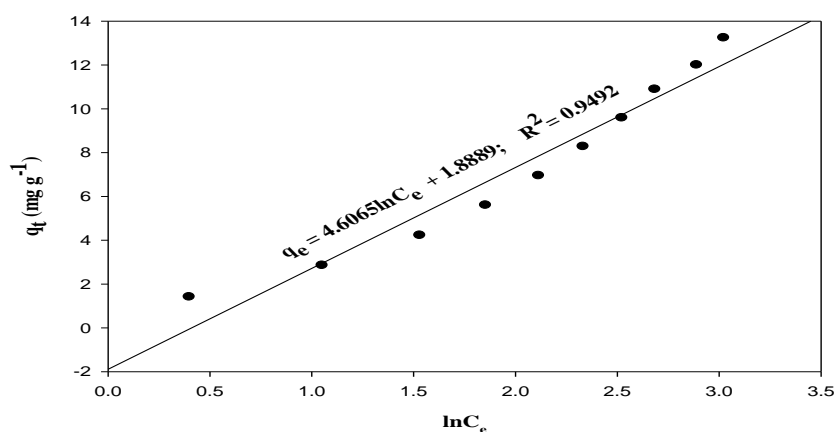


Figure 5c: Temkin isotherm for adsorption of lead using DNF

Effect of adsorbent dosage

The percentage removal of lead 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 4. The removal of lead increased rapidly from 77.425% to 88.7% with an increase in adsorbent dose from 3 to 10g/L, due to the increase in the number of binding sites. For the fixed initial metal concentration, equilibrium was attained at 10g/L, and no further increase with the increase in adsorbent dosage was obtained [26, 27].

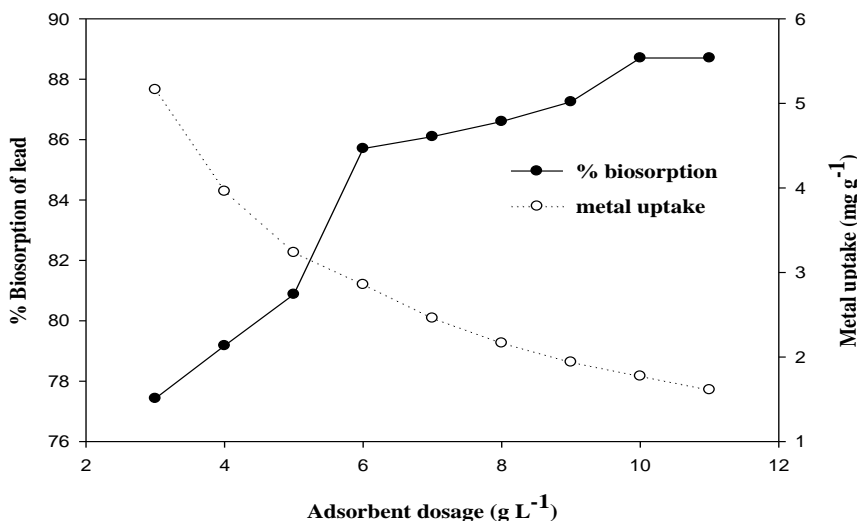


Figure 6: Dependency of % biosorption of lead on adsorbent dosage

Effect of temperature

The effect of changes in the temperature on the lead uptake is shown in Fig. 7. With increasing temperature from 283^oK to 303^oK, lead uptake marginally increased from 86.6% to 88.7%, indicating that the adsorption of lead on to the adsorbent is an endothermic process. Lead uptake increased with increase in temperature, when the temperature was lower than 30^oC; but the increase in metal uptake was marginal with the temperatures above 30^oC.

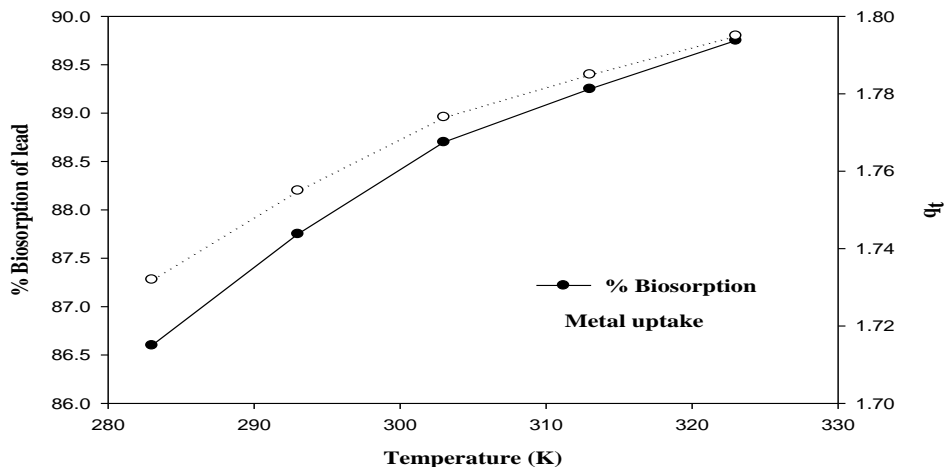


Figure 7: Dependency of % biosorption of lead on temperature

The following Van't Hoff equation was used to evaluate the three thermodynamic parameters viz. enthalpy (ΔH°), entropy (ΔS°) and Gibbs free energy (ΔG°):

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

Van't Hoff plot is represented in Fig. 8. The experimental ΔH° value of 5.7671 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° (16.8609 kJ mol K⁻¹) was more than zero, the adsorption process appears to be irreversible. The Gibbs free energy (-5103.0856 kJ mol⁻¹) is negative, suggesting the spontaneous nature of the adsorption process. The free energy change (ΔG°) increased with the increase in temperature (10^oC - 50^oC), possibly due to activation of more sites on the surface of the adsorbent [28].

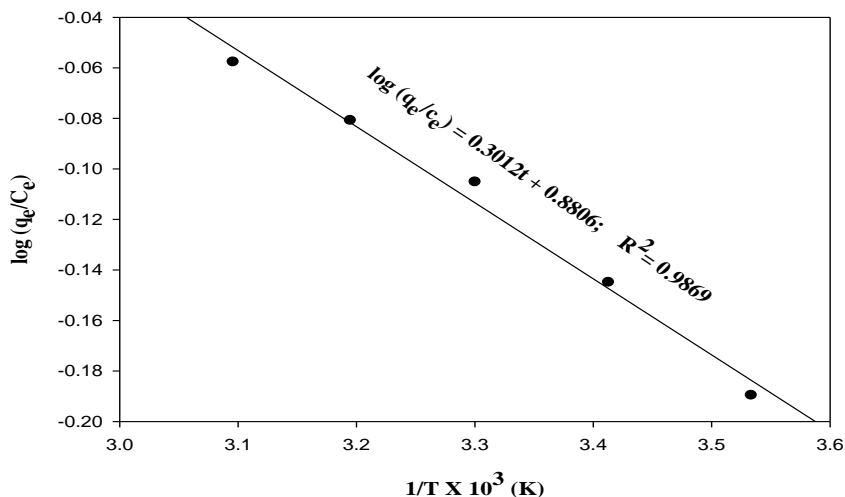


Figure 8: Van't Hoff plot for adsorption of lead using DNF

The reported maximum adsorption capacities (q_{max}) for adsorption of lead with the natural chick feathers, chick feathers treated with an alkaline solution, and those treated with anionic surfactant were 0.0260 mmol/g (5.382 mg/g), 0.047 mmol/g (9.729 mg/g) and 0.005 mmol/g (1.14995mg/g) respectively [9, 11, 20], revealing that the emu feathers (DNF) with a q_{max} of 0.1701 mmol/g (35.2112 mg/g) are more effective and efficient for the adsorption of lead.

SEM - EDS analysis

Using SEM, surface morphology of the adsorbent (DNF) was analyzed before and after adsorption of lead and presented in Figures 9a and b respectively. Before adsorption, the feather morphology was smooth and clear while after adsorption of lead, it became rough. The major constituent of feathers is keratin, present in association with metals Cr, Mn, Fe, Zn, Ni, As, Al, Se, S etc. as is evident from EDS analysis before biosorption (Fig. 10a). After adsorption of lead (Fig. 10b), the EDS analysis showed the binding of lead ions to S; this indicated that cysteine amino acid of keratin played an active role. Further, the absence of As and Al suggest that the adsorption of lead may also include the ion- exchange mechanism.

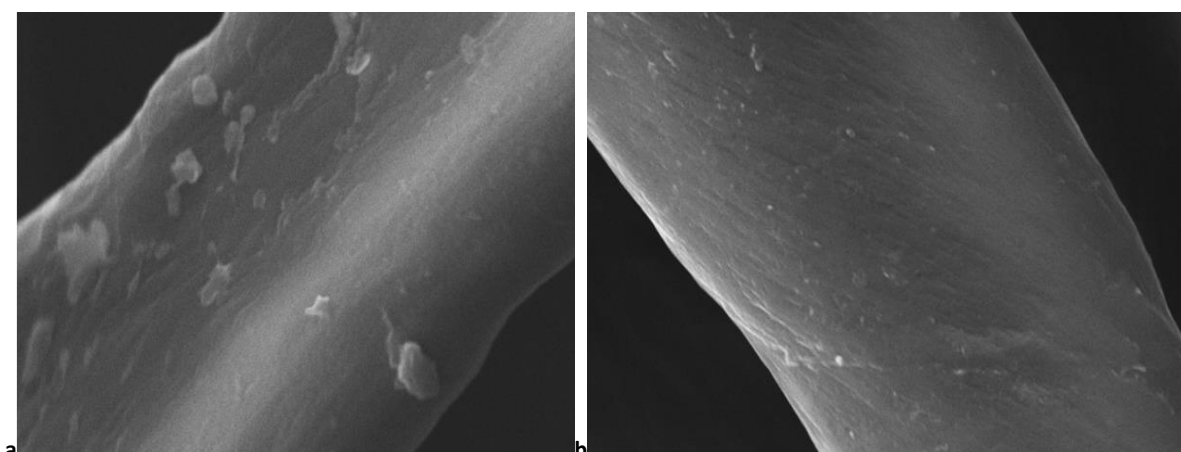


Figure 9: SEM micrograph of DNF a. Native b. After adsorption of lead

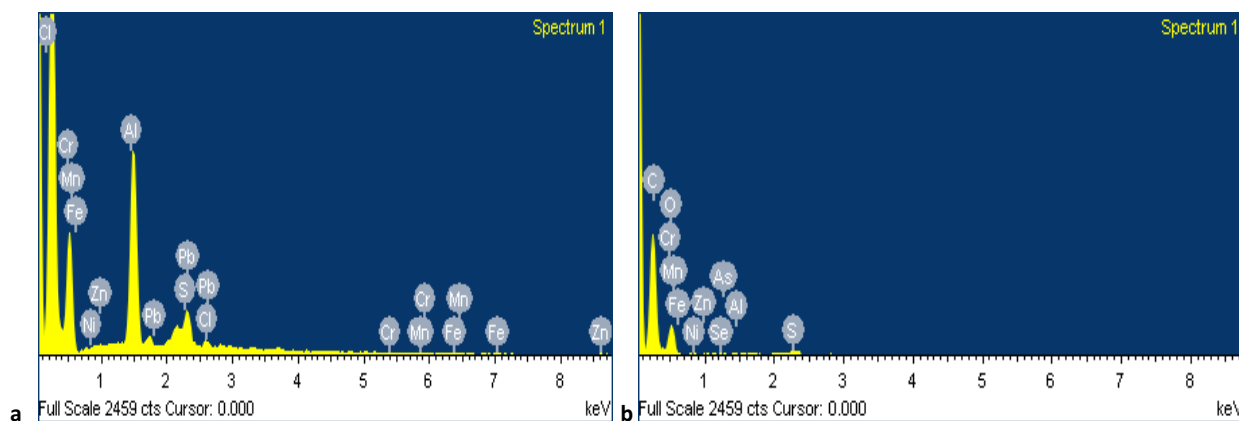


Figure 10: EDS micrograph of DNF a. Native b. After adsorption of lead

Adsorption mechanism through FTIR spectral analysis

The adsorption mechanism was investigated using FTIR analysis of native and metal loaded DNF in the range of 400-4000cm⁻¹ (Figures 11a and b). FTIR spectra showed marked differences before and after adsorption of lead. Broadly, the spectrum could be divided into 2 distinct regions viz. 1423 – 1743 cm⁻¹ and 3565 -3747 cm⁻¹ wherein there are significant variations in the absorption patterns and the groups assigned for biosorption.

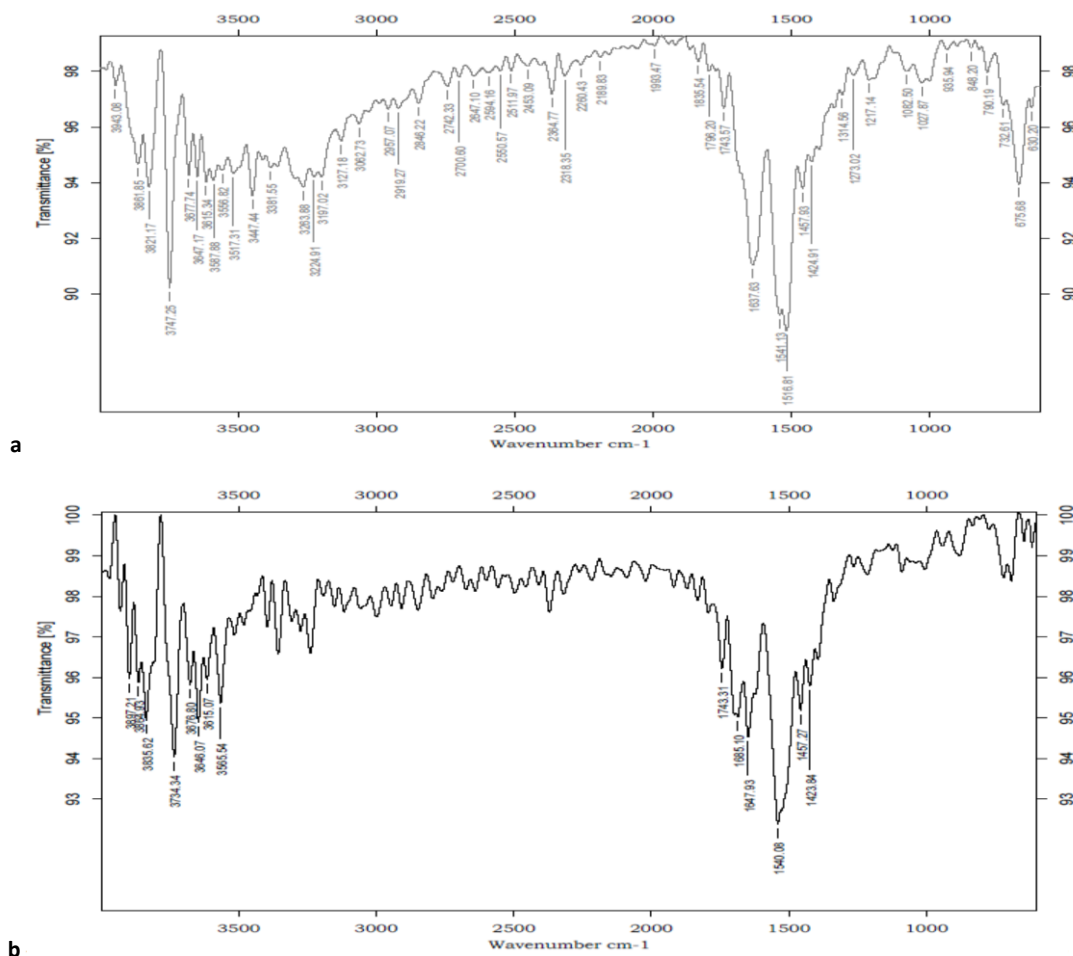


Figure 11: FTIR spectra of DNF a. Native b. After adsorption of lead

After interaction with the lead ions, it was identified that the sharp band at 3747 shifted to 3734cm⁻¹, in addition, the bands at 3647, 3556 cm⁻¹ shifted to 3646cm⁻¹, 3565cm⁻¹ respectively as sharper bands, 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. Shift of this band indicates disruption of hydrogen bonds due to binding of lead metal ions. Amide I, 80% C=O stretching and small contribution from NH bend shifted from 1637 (assigned to the β -sheet structure) [29] to 1647 cm^{-1} and became sharper, it also indicated the disruption of β -sheet and the binding of lead metal ions. 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 a sharp band at 1540 cm^{-1} . This observation is supported by an extreme change in absorption intensity for C-N stretching vibrations at 1424 cm^{-1} to 1423 cm^{-1} . Accordingly, the observed changes in adsorption 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 lead ions. The FTIR analysis suggests that the maximum adsorption of lead by the DNF is due to the availability of more number of N and O atoms

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 its β -sheet of keratin protein secondary structure [30]. There are noticeable differences in the XRD pattern of DNF after adsorption of lead (as shown in Fig. 12b). Mild shift in the 2θ positions especially in the range of 10° to 20° indicates disruption of both the α -helix and the β -sheet. X-ray diffractogram analysis (as shown in Figure 12(b)) showed the peaks at 13.2° , 14.4° , 20° , 22.72° , 24.46° , 35.67° , 43.03° and 43.47° (JCPDS Pb_3O_4 : 65-7195), a peak at 29.3° (JCPDS Pb_2O : 75-0201), which are indicative of the presence of lead oxide, while the peak at 2θ position of 21° (JCPDS $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$: 13-0131) indicates the formation of lead carbonate hydroxide with hydroxyl and carboxyl groups present on the feather. This could be due to the electron pair sharing between the metal lead and the carboxyl/ hydroxyl/ carbonyl/ amino groups in DNF.

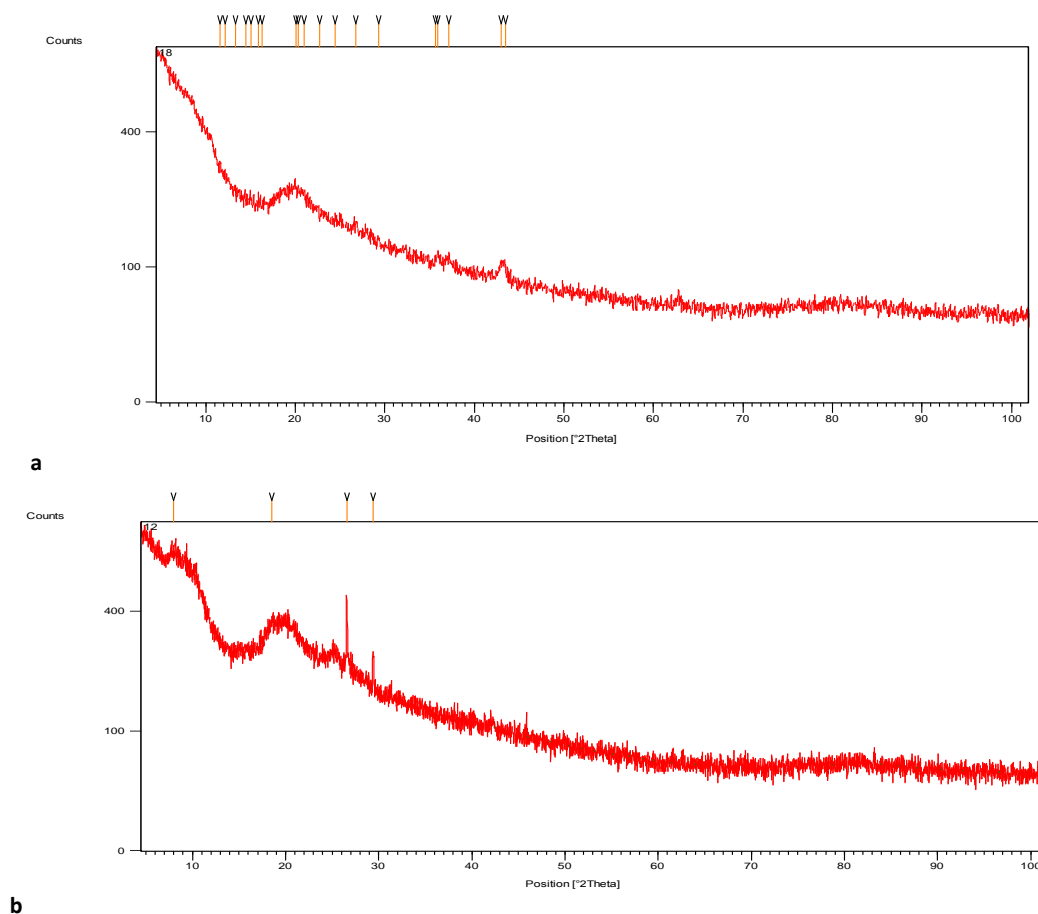


Figure 12: XRD of DNF a. Native b. After adsorption of lead

CONCLUSIONS

Equilibrium was attained at 70min of contact time due to the presence of more and/or active functional groups. The metal uptake of lead increased with increase in the initial concentration of the adsorbate. The removal of lead increased rapidly with increasing adsorbent dosage initially and attained equilibrium at 10 g/L. Percentage removal of lead from aqueous solution increased significantly with increase in pH from 2 to 4; thereafter, increase in pH decreased the percentage removal. From Langmuir isotherm model, the maximum uptake capacity of 35.2112 mg of lead 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 for the safe, effective and economic treatment of the industrial waste water containing lead.

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