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ORIGINAL ARTICLE

Biosorption Of Heavy Metals From Aqueous Solution Using Termite Feathers

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ABSTRACT
Removal of heavy metals from aqueous solutions by termite feather (TF) was investigated. A systematic comparison of biosorption performance for removing Cu(II), Pb(II), Cd(II), Cr(III), Co(II), Ni(II) and Fe(II) ions under different condition was provided. The biosorption capacities of heavy metals followed the order Pb > Cr ≈ Fe > Cu > Co > Ni > Cd. The optimum conditions of adsorption were determined by investigating the initial metal ions concentration, contact time, adsorbent dose, and pH value of aqueous solution. The extent of adsorption of metal ions was investigated using metal concentrations in solution ranging from 20-120 mg/L. The adsorption efficiencies were found to be pH dependent, with maximum metals uptake recorded at pH of 7.
Keywords: termite feather, heavy metals, biosorption, concentration, pH

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INTRODUCTION

Rapid industrialization has resulted in severe environmental and health problems to man. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products[1]. The presence of heavy metal ions is a major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, chlor alkali, radiator manufacturing, smelting, alloy industries and storage batteries industries, etc[2].

Filtration, adsorption, reverse osmosis, solvent extraction, and membrane separation techniques are used for removal of heavy metals in aqueous solutions. Adsorption has been shown to be an economically feasible alternative method for removing heavy metals from wastewater and water supplies[3]. Indeed, adsorption of metal on materials considered as a waste of natural origin is the most important chemical process[4]. This technique can be controlled by physical attraction, the chemical bonds of complexion with surface functional groups, or formation of hydrate on the surface[5]. Biosorption has been employed as an alternative method for removal of toxic metal ions from dilute aqueous solutions and industrial effluents[6]. The biosorption process is technically feasible, eco-friendly and economical, due to the availability of biomaterials and their reusability[7]. Improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of its toxicity, short operation time and no production of secondary pollutants are the advantages of this biological method of heavy metal recovery[6]. Various biomaterials such as algae, bacteria, mosses, plant materials, agricultural wastes and keratin biomaterials (hair, feathers, horn etc) have been found useful for removal of heavy materials from aqueous solutions[8].

As a kind of abundant biological resources, keratin biomaterials can be used as biosorbents for the removal of heavy metal ions from aqueous wastes, either used directly or after properly activation pre-treatment. Such keratin biomaterials have intricate networks of stable, water-insoluble fibers with high surface areas and with abundant functional groups (carboxyl, hydroxyl, amino and sulfonate groups) on their surface which give them such sorbent properties. Keratin is the major component of wool, hair, feather, horn and nail.

EXPERIMENTAL METHODS

Termite feathers (TF) were collected at night immediately after rainfall, washed several times with distilled water and then left to dry at room temperature. The feathers were cut into smaller sizes using a scissors. The smaller sized feathers were used in the biosorption experiments.

All the chemicals used in this work were of analytical grade. Preparation of adsorbate was carried out by preparing 1000 mg/L stock solution of each metal ion which was later diluted to the aqueous feed for each experiment. Sodium hydroxide (0.1M) and nitric acid (0.1M) were alternately used for the pH adjustment of the feed solution prior to commencing the biosorption experiments.

Determination of moisture content

This was done by weighing 5g of TF into a crucible. This was placed in the oven and heated for 4 hours at constant temperature of 105°C. The sample was then removed and put rapidly into a desiccator in order to prevent more moisture uptake from atmosphere. The sample was re-weighed. This procedure was repeated several times until a constant weight was obtained. The difference in the mass constitutes the amount of moisture content of the adsorbent.

$$\frac{W_2 - W_3}{W_2 - W_1} \text{ X } 100$$

W_1 = Weight of crucible W_2 = Initial weight of crucible with sample W_3 = Final weight of crucible with sample

Determination of loss on ignition

The determination of loss of mass on ignition was done by weighing 10g of the adsorbent (TF) and put inside furnace at constant temperature of 600°C for 2 hours. After roasting, the sample was removed and put in a desiccator for cooling. The residual product is then weighed and the difference in mass represented the mass of organic material present in the sample. This operation was repeated four times

pH determination

The determination of pH of the samples was done by weighing 1g each of TF, boiled in a beaker containing 50 cm^3 of distilled water for 5 minutes, the solution was made up to 100 cm^3 with distilled water and cooled at room temperature, the pH of each was measured using a pH meter.

Determination of bulk density

The bulk density of each of the samples of TF was determined using Archimedes's principle by weighing a 10 cm^3 measuring cylinder before and after filling with the samples. The measuring cylinder was then dried and the sample was packed inside the measuring cylinder, leveled and weighed. The weight of the sample packed in the measuring cylinder was determined from the difference in weight of the filled and empty measuring cylinder. The volume of water in the container was determined by taking the difference in weight of the empty and water filled measuring cylinder. The bulk density was determined using the equation below.

Bulk density = $\frac{w_2 - w_1}{V}$

W_1 = Weight of empty measuring cylinder W_2 = Weight of cylinder filled with sample V = Volume of cylinder

Biosorption experiment

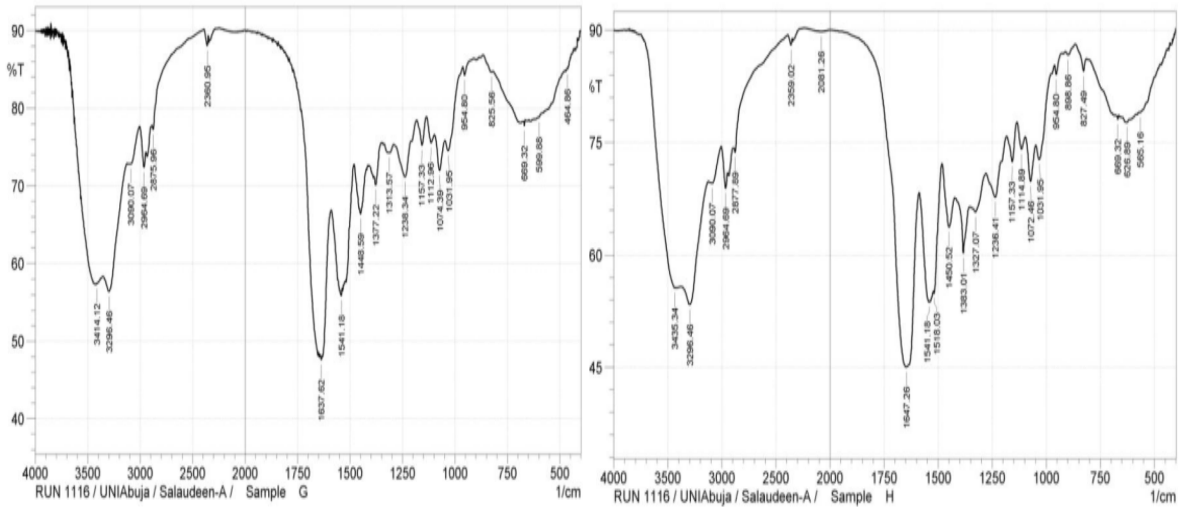
Experiments were carried out by varying the initial adsorbate concentration, contact time, adsorbent dose and pH of solution. The batch adsorption experiments were conducted using 0.05 g of adsorbent with 50 mL of solutions containing heavy metal ions of desired concentrations in 100 mL plastic bottles. The bottles were shaken with the aid of a thermostated stirrer for 5 hours and solutions containing heavy metals were filtered through Whatman filter paper No. 42. The concentration of metal ions in the initial and final solution was determined by atomic absorption spectrophotometer. The amount of heavy metal ions adsorbed, qe (mg/g) and % biosorption were computed by:

q_e (mg/g) = $\frac{(C_I - C_f) \times V}{W}$

% biosorption = $\frac{(C_I - C_f) \times 100}{C_I}$

Where C_i and C_f are the initial and the final concentration of metal ions in the aqueous solution respectively (in mg/L), V is the total volume of the solution (in L) and W is the total amount of biosorbent used (in g).

RESULTS AND DISCUSSION
FTIR CHARACTERIZATION



Full scan spectra of virgin and metal load TF

Figure 1: FTIR spectra of virgin and metal loaded TF

Table 1: TF FTIR spectra bands and assignments

ASSIGNMENTS	**WAVENUMBERS (cm^{-1})**
NH stretching,	3296.46
C-H stretching, $-CH_3$ and $-CH_2-$ asymmetric and symmetric mode	2964.69 & 2875.96
Amide I, 80% C=O stretch and small contribution from NH bend	1637.62
Amide II, C-N stretching/N-H bending	1541.18
Amide III, complex vibration contains N-H bending, C-N stretching, C=O stretching and O=C=N bending	1238.34
Sulphonate, S-O asym. Stretch	1157.33
Sulphonate, S-O sym. Stretch	1031.95
Cystine dioxide ($R-SO_2-S-R$)	1238.34
Cystine monoxide (R-SO-S-R)	1074.39

Table 2: The physico-chemical parameters of the Termite feather(TF)

PARAMETERS	**TF**
pH	8.40
Moisture (%)	6.97
Loss of mass (%)	86.6
Bulk density (g/cm^3)	0.0132

In order to understand how metal ions bind to the biosorbent, it is essential to identify the functional groups of its surface as they could be responsible for such metal binding. So, the virgin and metal loaded TF were discriminated by using Fourier transform infrared (FT-IR) spectroscopy, as can be seen from the infrared spectra collected in Figure 1.

The wavenumbers and approximate assignments of the vibrational modes for the FT-I R spectra are listed in Table 1.

BIOSORPTION ANALYSIS

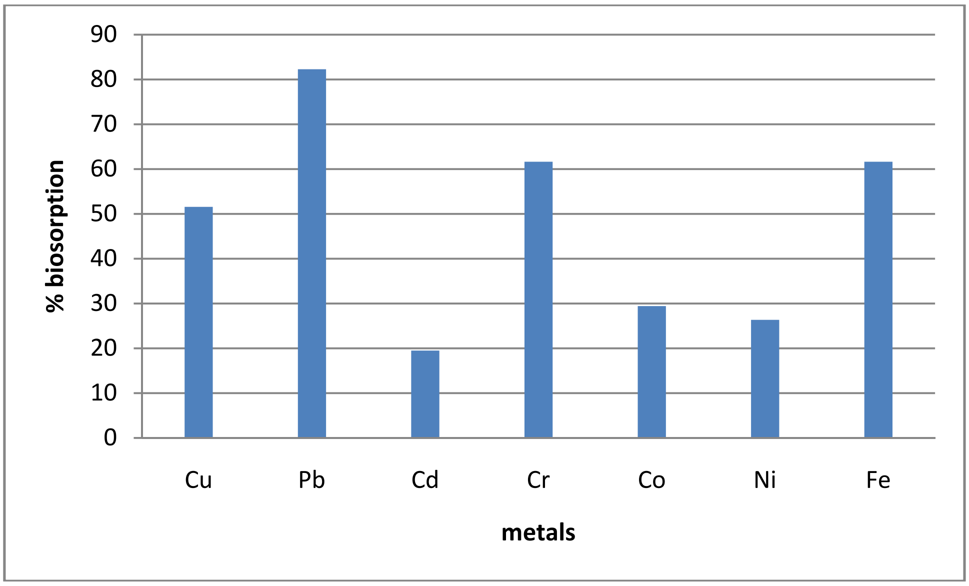


Figure 2: Biosorption of Cu(II), Pb(II), Cd(II), Cr(III), Co(II), Ni(II) and Fe(II) by TF from multiple-metal aqueous system.

The TF was evaluated as biosorbent for the removal of heavy metals from multiple-metal aqueous solution containing seven metal ions of Co(II), Cd(II), Ni(II), Fe(II), Cu(II), Cr(III) and Pb(II). The results are shown in figure 2. From the result, TF showed different biosorption capacity for the different metal ions. In general, Pb(II), Cr(III), Cu(II) and Fe(II) were the most sorbed with a trend in the order of Pb > Cr ≈ Fe > Cu > Co > Ni > Cd. This can be explained by the different affinity of metal ions for the metal binding donor atoms present in the biosorbent. Finally, four metal ions including Pb(II), Cr(III), Cu(II) and Cd were selected for further studies under different experimental conditions.

EFFECT OF pH

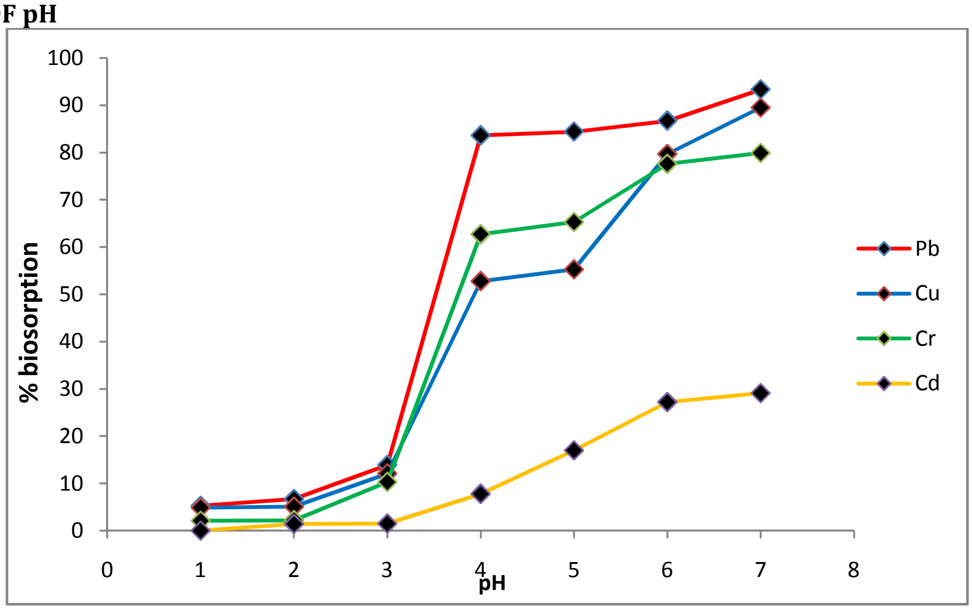


Figure 3: Effect of initial pH on biosorption of Cr(III), Cu(II), Pb(II) and Cd(II) by TF

The pH of solution has a significant impact on metal uptake since it determines the surface charge of adsorbent, solubility of the metal ion, concentration of counter ions on functional groups of the biomass and the degree of ionization and speciation of adsorbate[9]. As usual, batch biosorption experiments are carried out in the pH range of 1.0 to 6.0 (because metal precipitation occurs above this range) in a multiple-metal system, though pH 7.0 was used in this work. The highest percentage biosorption were obtained at pH 7.0 and the overall removal capacity of all metals decreased to a minimum value at pH 1.0. The sorption rate of the four sorbents increased rapidly in this pH range of 3.0 – 4.0 and then increased less rapidly to a peak value at 7.0.

EFFECT OF BIOSORBENT DOSAGE

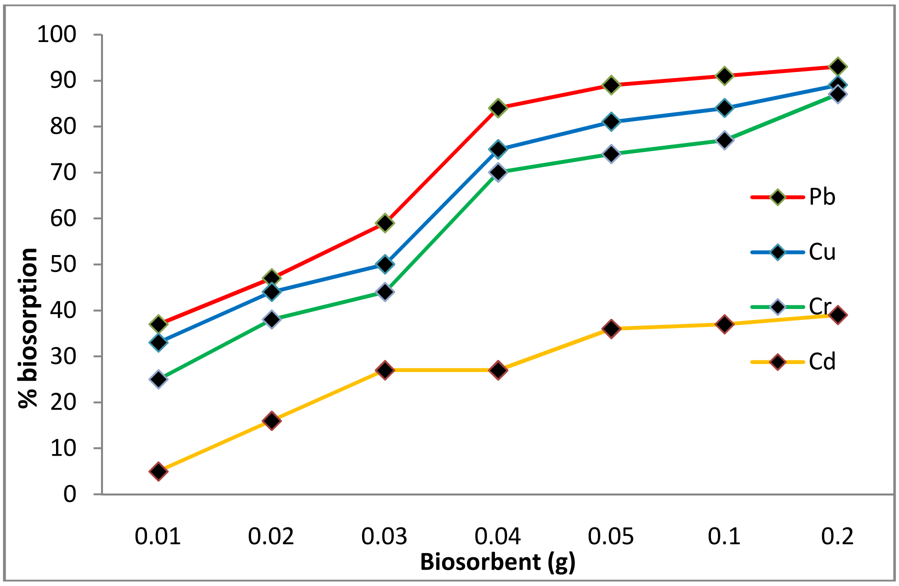


Figure 4: Effect of change in biosorbent mass on the biosorption of Cr(III), Cu(II), Pb(II) and Cd(II) by TF

The effect of the mass of adsorbent on adsorption of heavy metals was studied by changing the mass of the biosorbent dosage from 0.01 to 0.2 g. The percentage adsorption capacity increased with increase in adsorbent dosage. This can be attributed to the decrease in the number of sorbate ions concentration per active site available for sorption on the surface.

EFFECT OF TIME

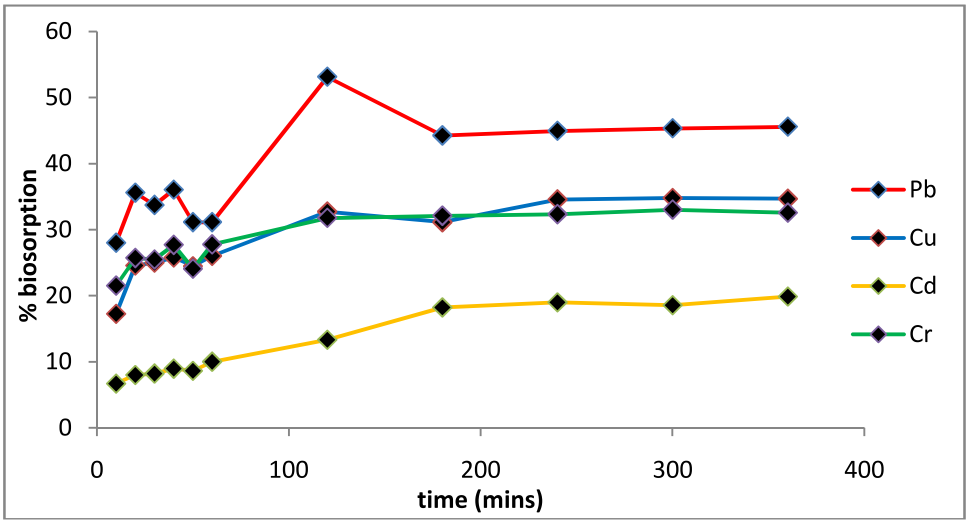


Figure 5: Effect of contact time on the biosorption of Cr(III), Cu(II), Pb(II) and Cd(II) by TF

The effect of contact time is important for designing batch biosorption studies. The result of this effect is presented in Fig. 5 which shows that the optimum time for biosorption is less than 200 minutes. It is observed that further increase in time did not cause any increase in the biosorption of the metal ions because at such optimum time, there is saturation of the active sites on the biomass.

EFFECT OF CONCENTRATION

The initial metal ion concentration greatly influenced the equilibrium metal uptake and adsorption yield as shown in Figure 6. An increase in initial concentration increased the amount of ions adsorbed (mg/g). When the initial metal ions concentration was varied from 20 to 120 mg/l, the adsorption capacity of TF increased significantly for Cr(III), Cu(II) and Pb(II) and slightly for Cd(II). The increase in adsorption capacity of adsorbents with the increase in metal ion concentration is probably due to higher interaction between metal ions and adsorbent surface.

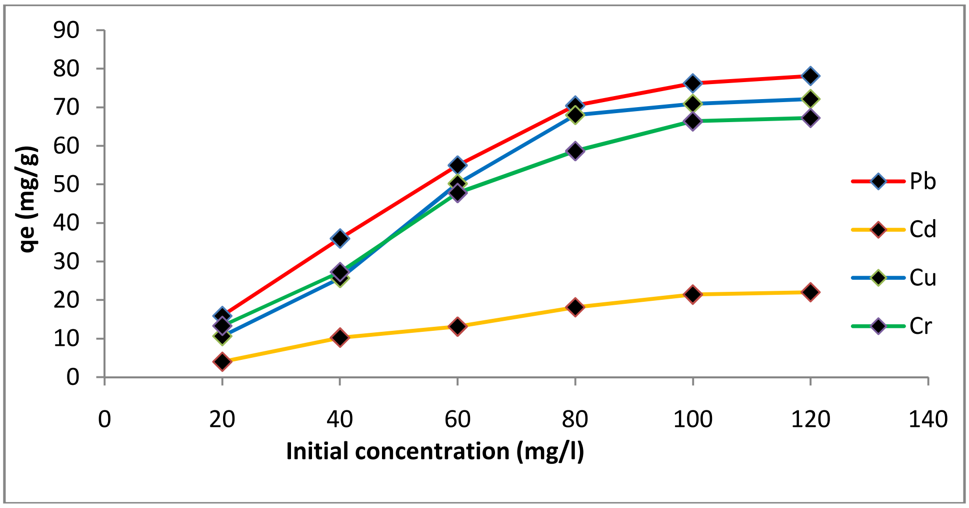


Figure 6: Effect of initial metal concentration on the biosorption percentage of Cr(III), Cu(II), Pb(II) and Cd(II) by TF

DESORPTION AND RE USE STUDIES

Table 3: The elution of adsorbed Pb(II) by EDTA and HNO_3 solutions

SORBENT	CF
% METAL ADSORBED	84
% ELUTION EFFCIENCY (0.1 M EDTA)	67
% ELUTION EFFCIENCY (0.1 M HNO_3)	69

Desorption results for Pb(II) loaded TF biomaterials with EDTA and HNO_3 solutions as eluents are given in table 3. As seen from the table, elution effiency of HNO_3 solution is higher than that of EDTA.

CONCLUSION

Termite feather have been used successfully for the removal of metals from aqueous solutions. The FTIR analysis reveals that carbonyl, hydroxyl, amino and sulphur containing groups as the major functional groups that act as biosoption sites. Biosorption percentage is affected by various parameters such as the pH of the initial aqueous solution, the biosorbent dosage and contact time. The pH is found to be a critical parameter in the biosorption processes, with pH being 7.0 being the optimum pH in all the cases.

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