
Biosorption of Heavy Metals (Cd^{2+} , Cr^{3+} , Cu^{2+} , Ni^{2+} , Pb^{2+} And Zn^{2+}) From Aqueous Solution onto Activated Carbon Prepared From Chicken Feather

By

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ABSTRACT

Heavy metals present in waste waters which are released into the environment by various industries have become a serious problem. This research focuses on the use of Activated Carbon from Chicken Feathers (ACCF) in the removal of Cd^{2+} , Cr^{3+} , Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} ions from aqueous solution. Scanning Electron Microscope (SEM) and Fourier Transform Infrared (FTIR) analysis was carried out on ACCF before and after biosorption. SEM analysis reveal the surface morphology of the biosorbents while FTIR analysis reveal the functional groups present which will aid adsorption. The optimisation of operational factors such as biosorbent concentration and initial metal ion concentration were investigated at physiological temperature. The optimum initial metal ions concentration and biosorbent concentration were therefore determined. The experimental data obtained for Cd^{2+} , Cr^{3+} , Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} sorption were treated using Langmuir, Freundlich and Temkin isotherms and the data fitted well into the langmuir isotherm model for $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Pb}(\text{II})$. Also the data obtained fitted well into Freundlich and Tempkin isotherm models for $\text{Cd}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Pb}(\text{II})$. This study demonstrates the efficiency and effectiveness of ACCF as biosorbent for the removal of Cd^{2+} , Cr^{3+} , Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} from aqueous solution.

INTRODUCTION

Various methods exist for the removal of toxic metal ions from aqueous solutions, such as ion exchange, chemical precipitation, adsorption, etc (Sari and Tuzen, 2009). Among these methods, adsorption onto activated carbon is by far the most versatile and widely used process because of its capability of adsorbing a broad range of different types of adsorbates efficiently (Ghodbane *et al.*, 2008; Vimala and Das, 2009; Pehlivan *et al.*, 2008; Nwabanne and Igbokwe, 2008).

The process of adsorption is widely used as an effective physical method of separation in order to remove or reduce the concentration of a wide range of dissolved pollutants (organic or inorganic) in an effluent (Mohammed-Khah and Ansari, 2009).

Oftentimes metals, including cadmium, chromium, copper, lead, mercury, nickel, selenium, silver and zinc, are released into the environment in quantities that may be hazardous and pose a risk to human health (Ireland and Dillon, 1991).

Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders (Gupta and Rastogi, 2009). For instance, Cadmium causes serious

renal damage, anemia, hypertension and itai-itai. The reduction of pollutants to an acceptable level is necessary when toxic metals are present in aquatic system.

Biosorption is a process that uses biological materials to remove heavy metals from solution through adsorption. The mechanism responsible for biosorption, although understood to a limited extent, may be one or a combination of ion exchange, complexation, coordination, adsorption, electrostatic interaction, chelation and microprecipitation (Veglio and Beolchini, 1997; Wang and Chen, 2006).

Nowadays the use of plant and animal products and by-products as sorbents has become popular for many researchers in the field of environmental chemistry. These materials can be used, either directly or after activation, in the adsorption processes (Osman *et al.*, 2014).

MATERIALS AND METHODS

Collection of chicken feathers.

Chicken feathers were obtained from several poultry processing facilities across Zaria metropolis in Kaduna state, Nigeria. They were stored in a clean polyethene bag prior to analysis.

Sample Preparation

Preparation of biosorbent (chicken feather)

Some of the materials attached to the feathers were removed through several washings with distilled water and detergent. It was later left in the open air for several days to get rid of odors.

Preparation of activated carbon from chicken feathers

The chicken feathers were impregnated with H_3PO_4 in 1:1 weight ratio, and carbonized inside steel cups with a small hole inserted on the lids for venting gases produced during the carbonization process. This step was carried out in order to restrict the formation of tar and in this way a carbonized product with a well-developed porosity may be obtained in a single operation. The cups were heated in a muffle furnace set at 400 °C and this temperature was maintained for 1 hour, then left to cool to ambient temperature. The collected solid product was then characterized (Osman, Mansour and Nahla, 2014).

Reagents

In this study, stock solutions of cadmium, chromium, copper, nickel, lead and zinc (1000 mg/ l) were prepared by dissolving appropriate amounts of Cadmium nitrate butahydrate ($CdN_2O_6 \cdot 4H_2O$), Copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$), Chromium sulphate hexahydrate ($Cr_2S_3O_{12} \cdot 6H_2O$), Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), Lead nitrate (PbN_2O_6), and Zinc nitrate hexahydrate ($ZnN_2O_6 \cdot 6H_2O$) in deionized water and then the desired concentrations were provided by diluting the stock solution. Stock solutions of nitric acid and NaOH 0.1N were also prepared.

Experimental plan

This study investigates some factors such as the initial metal ion concentration (20, 40, 60, 80 and 100 mg/l) and the amount of adsorbent (0.2, 0.4, 0.6, 0.8 and 1g) using batch adsorption

technique with contact time and pH kept constant at 60 minutes and 7 respectively. The nitric acid and NaOH 0.1N were used to adjust the pH of the solution.

The amount of metal ion adsorbed at equilibrium q_e (mg/g) was calculated by Equation:

$$q_e = \frac{V(C_i - C_f)}{S}$$

q_e = Metal ion uptake capacity (mgg-1),

C_i = Initial concentration of metal in solution (ppm),

C_f = Final concentration of metal in solution (ppm),

S = weight of biosorbent (g), and V = Solution volume (cm³).

The difference between the initial metal ion concentration and final metal ion concentration was assumed to be bound to the biosorbent.

The Biosorption efficiency, A %, of the metal ion was calculated from:

$$A\% = \frac{C_o - C_e}{C_o} \times 100$$

Where C_o and C_e are the initial and equilibrium metal ion concentrations (ppm), respectively (Ding *et al.*, 2012).

RESULTS AND DISCUSSION

Effect of Adsorbent Dose

The effect of initial biosorbent dosage was investigated, since it can determine the biosorption capacity under given operating conditions. The number of available sites and exchanging ions for adsorption depends upon the amount of adsorbent in the biosorption process. The experiment was done under conditions of constant pH of 7, initial concentration of 60mg/l, contact time of 60 minutes and variable adsorbent doses (0.2g, 0.4g, 0.6g 0.8g and 1g). The trend of adsorption at various dosages is shown in figure 1 and table 1. It can be observed that the rate of Cd (II), Cr (III), Cu (II), Ni (II), Pb (II) and Zn (II) removal was found to increase with increasing concentration of adsorbent while keeping other parameters constant. At very low adsorbent concentration, the adsorbent surface became saturated with the metal ions and the residual metal ion concentration in the solution was large. The increase in percentage metal ion adsorption with increase in biosorbent concentration can be attributed to increase in binding sites. This can be explained since more active sites of sorbent were exposed when the sorbent dose was increased.

Declining Cd (II), Cr (III), Cu (II), Ni (II), Pb (II) and Zn (II) ion percentage removal occurred after equilibrium had reached. The optimum adsorbent dose for Cd (II), Cr (III), Cu (II), Ni (II), Pb (II) and Zn (II) ion removal using ACCF was 0.8g, 0.8g, 0.6g, 1g, 0.8g and 0.4g respectively with their corresponding percentage removal as 92.248%, 92.457%, 99.358%, 89.897%, 99.458% and 92.707%. A sharp decrease in adsorption observed after optimum biosorbent dose was reached may be due to aggregation of adsorption sites resulting in decrease in total adsorbent surface area of particles available to adsorbates and an increase in diffusion path length. The optimum dosage is very important for economic reasons if it will be applied in real scale wastewater treatment process.

Table 1: Adsorption data of ACCF for Cd (II), Cr (III), Cu (II), Ni (II), Pb (II) and Zn (II) removal in solution with different adsorbent dose

	Cd	Cr	Cu	Ni	Pb	Zn
0.2	87.360	66.487	97.415	68.952	95.212	91.268
0.4	87.913	69.377	99.177	80.935	95.525	92.707
0.6	90.155	87.127	99.358	84.188	96.217	91.398
0.8	92.248	95.360	99.267	87.967	99.458	89.043
1	90.522	92.457	99.215	89.897	97.565	89.057

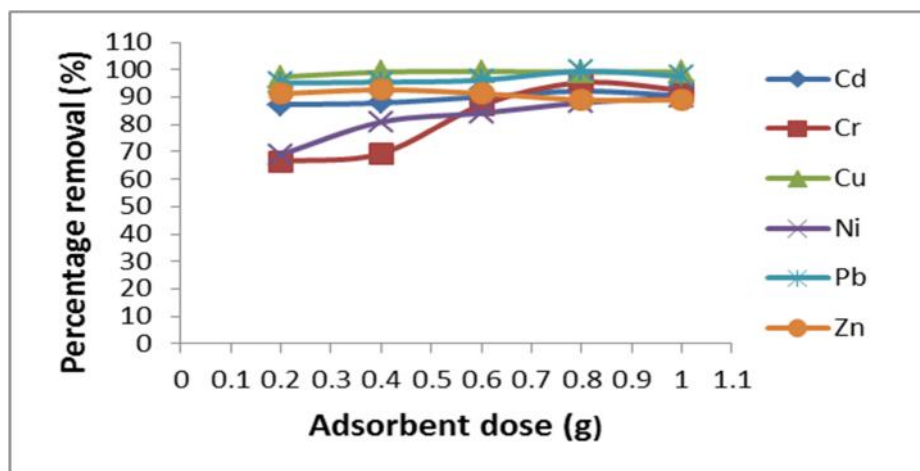


Figure 1: Effect of adsorbent dose on adsorbate removal by ACCF

Effect of Initial Concentration

Results from figure 2 and table 2 showed that the removal efficiencies of Cd (II), Cr (III), Cu (II), Ni (II) and Pb (II) by ACCF decreased as the initial concentration was increased from 20mg/L to 100mg/L. This is because for a fixed dose of the biomass the total available binding sites are limited, thus an increase in initial concentration from 20mg/L resulted in the exhaustion of the available binding site on the biosorbent. These results are consistent with the results obtained by Peric *et al.*, 2004. However, the removal efficiency of Zn (II) by ACCF was observed to increase as the initial adsorbate concentration was increased from 20mg/L to 60mg/L. This is due to the availability of binding sites on the biosorbent. The maximum Zn (II) ion removal occurred at initial concentration of 100mg/L with percentage sorption of 95.705 %.

Table 2: Adsorption data of ACCF for Cd (II), Cr (III), Cu (II), Ni (II), Pb (II) and Zn (II) removal in solution with different initial concentrations

	Cd	Cr	Cu	Ni	Pb	Zn
20	92.615	59.415	99.310	96.715	98.860	90.745
40	90.743	17.807	98.075	94.308	96.475	92.048
60	89.515	26.343	96.143	90.322	92.382	93.738
80	91.125	39.116	96.820	89.421	95.315	90.029
100	91.233	23.003	93.650	84.323	92.221	95.705

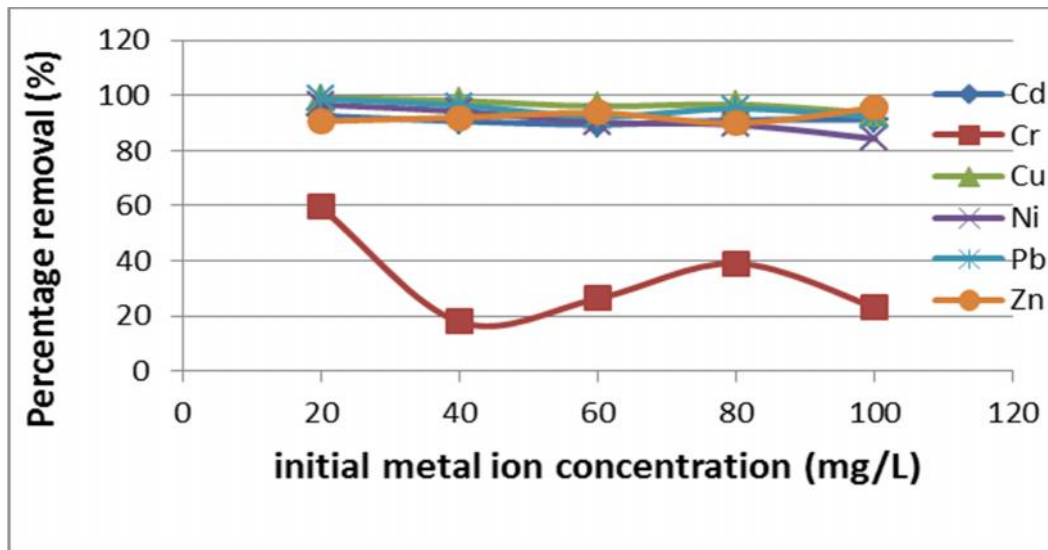


Figure 2: Effect of initial concentration on adsorbate removal by ACCF

SEM images

The SEM images of ACCF before and after adsorption are given in figures 3 and 4 respectively. The images show tiny pores on ACCF before adsorption occurred. However, these pores disappeared after the adsorption process thus showing the adsorption of metal ions on the surface of the activated carbon (ACCF) and indicating that these pores have been occupied by the heavy metal ions.

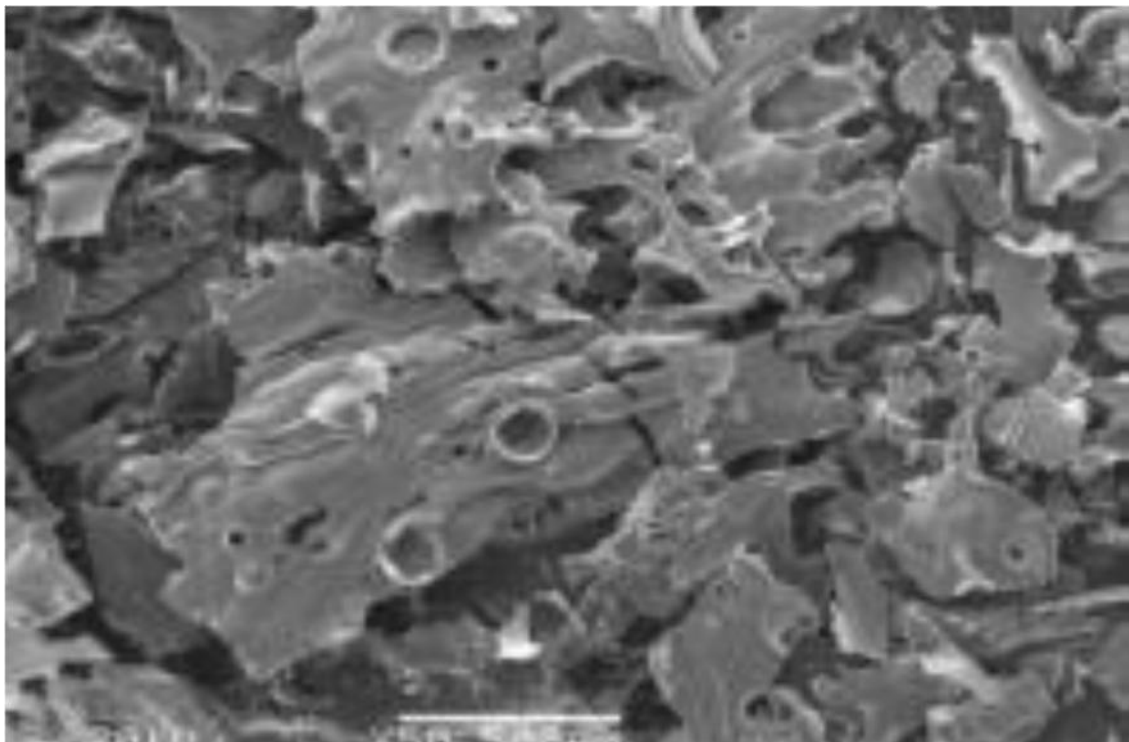


Figure 3: SEM micrograph of biosorbent (ACCF) before adsorption process

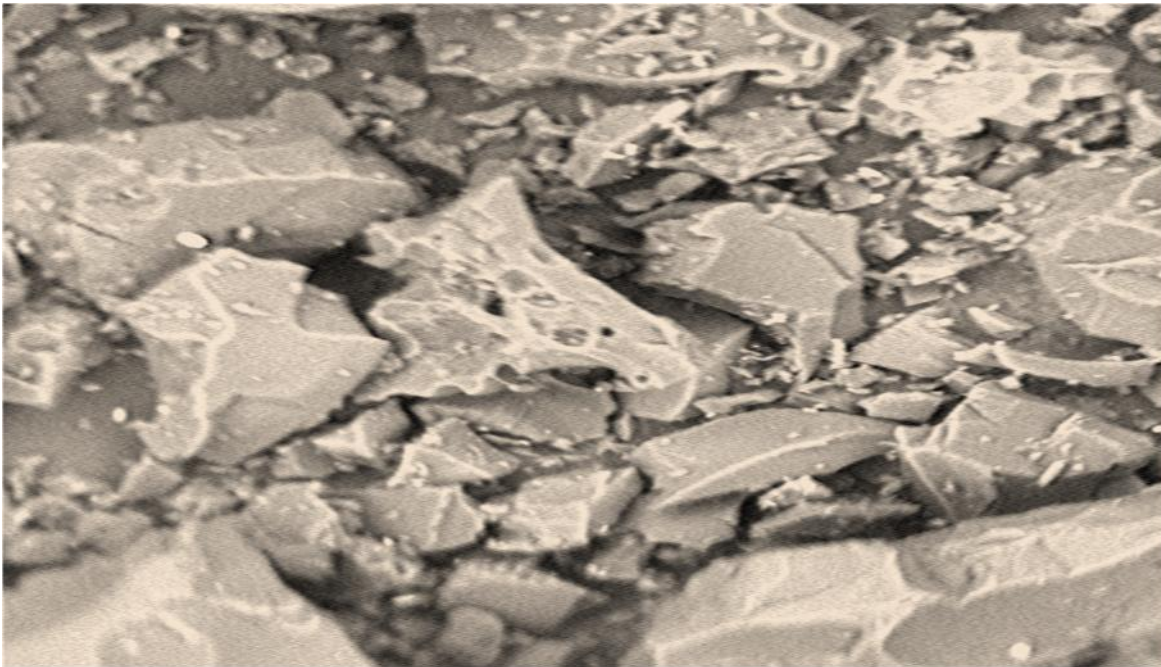


Figure 4: SEM micrograph of biosorbent (ACCF) after adsorption process

Fourier Transform Infrared Spectroscopy (FTIR) of ACCF

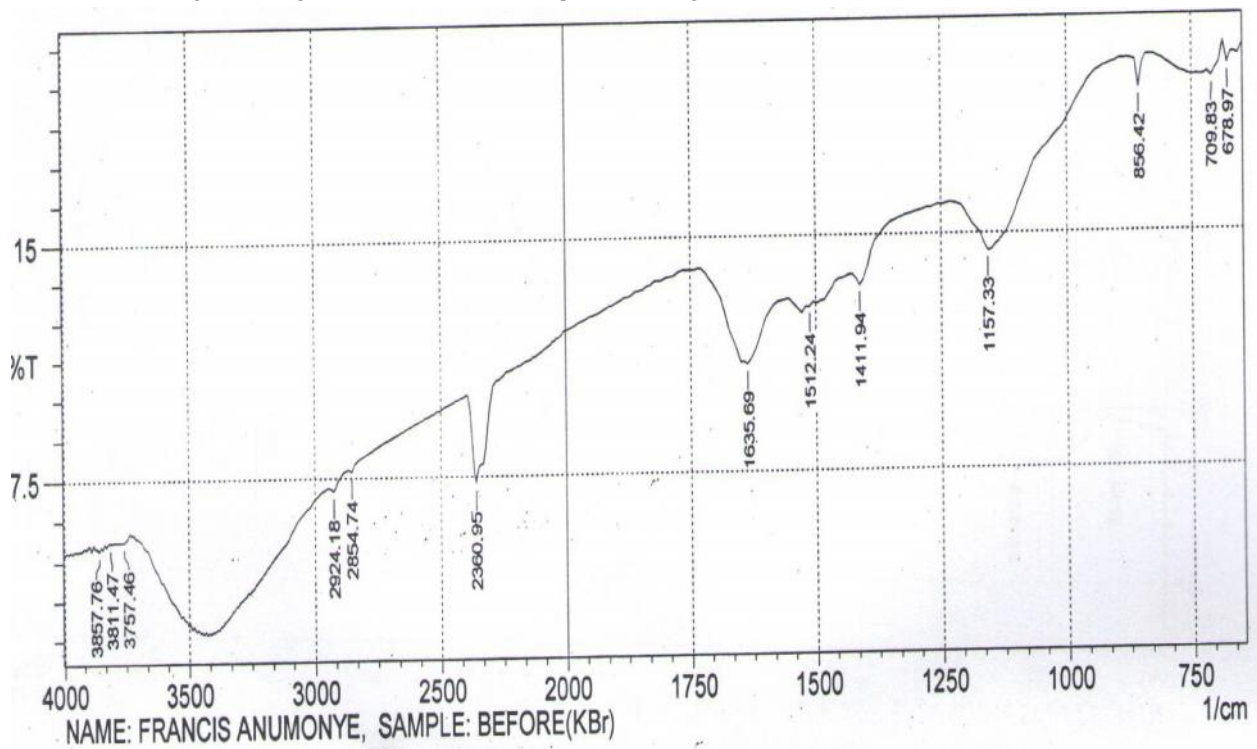


Figure 5: Fourier transform infrared (FTIR) analysis of unloaded biosorbent (ACCF)

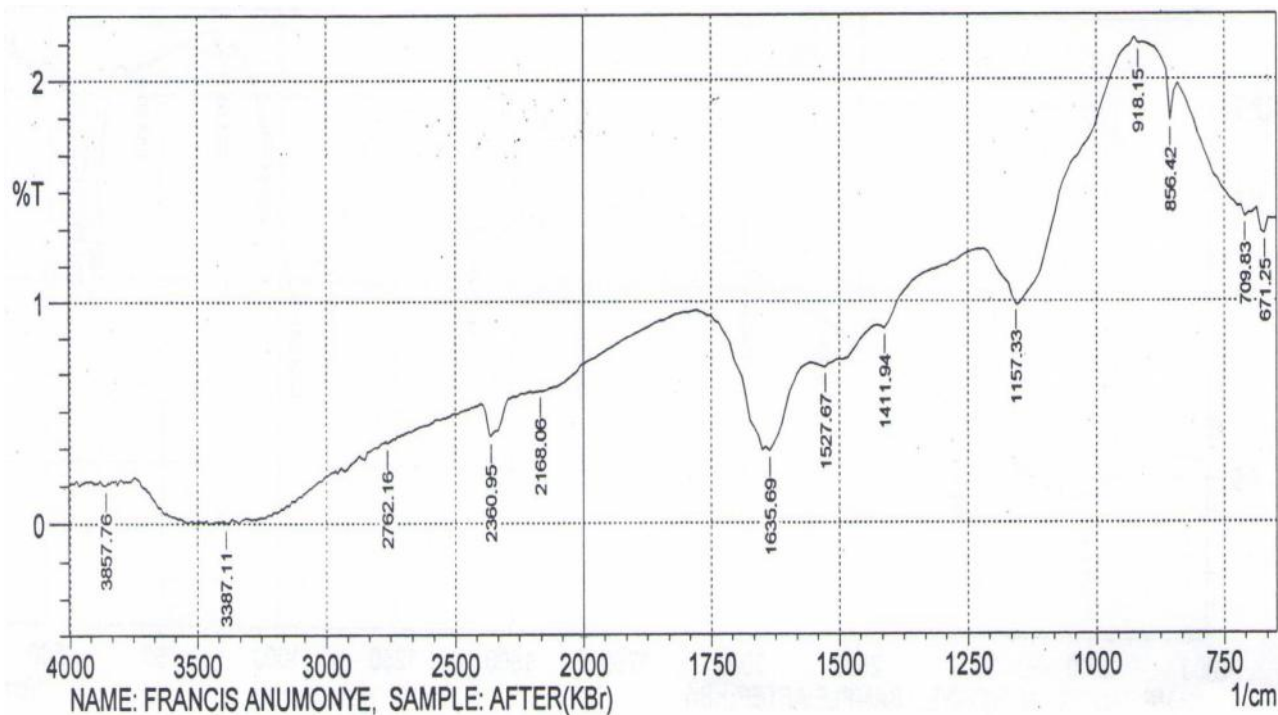


Figure 6: Fourier transform infrared (FTIR) analysis of loaded biosorbent (ACCF)

The FTIR technique was an important tool to identify functional groups, which are capable of adsorbing heavy metal ions. FTIR spectroscopy was therefore, done for preliminary quantitative analysis of major functional groups present in ACCF. The measurement was done in the range of 400-4000 cm^{-1} .

The FTIR spectrums of ACCF before and after sorption showed that the most prominent peaks in the spectrum originate from H-C-H asymmetric and symmetric stretching vibrations from alkanes (2924.18 to 2854.74 cm^{-1} pre-sorption), which disappeared after the adsorption process. At (1635.69 cm^{-1}) is a stretching mode of carbonyls mainly ketones of C=O. Intense peaks in region (1512.24 to 1411.94 cm^{-1} before adsorption) and (1527.67 to 1411.94 cm^{-1} after adsorption) originate from the secondary Amines N-H, while stretching at (1157.33 cm^{-1}) for C-O come from ethers. O-H and N-H stretching at (3387.11 cm^{-1}) attributable to the existence of amino and hydroxyl groups was observed only after the sorption process had occurred. Peaks observed at (2360.95 cm^{-1}) before adsorption and (2360.95 to 2168.06 cm^{-1}) after adsorption originated from C C or C N.

Adsorption Isotherm

Basically adsorption isotherm showed the interactions between the adsorbate and biosorbent (ACCF). Adsorption isotherm is considered as an important factor in designing of adsorption process. Fitted isotherms can be used to figure biosorbent capacity in adsorbing the adsorbate. In this study, most optimum performance of biosorbent was then applied for linear equations of Langmuir, Freundlich and Tempkin to fit the data. The results are shown in **Figure 7-24**.

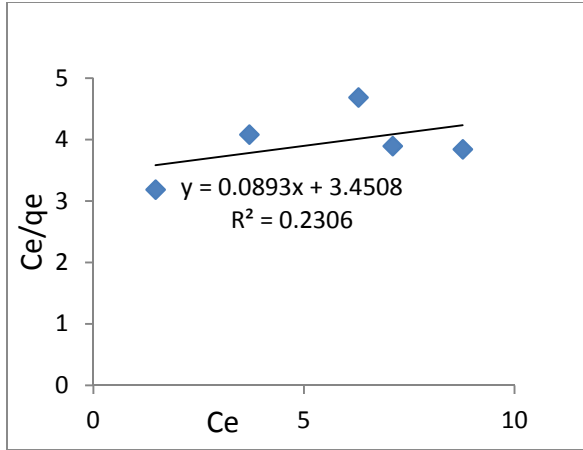


Fig 7: Langmuir Adsorption Isotherm for Cd

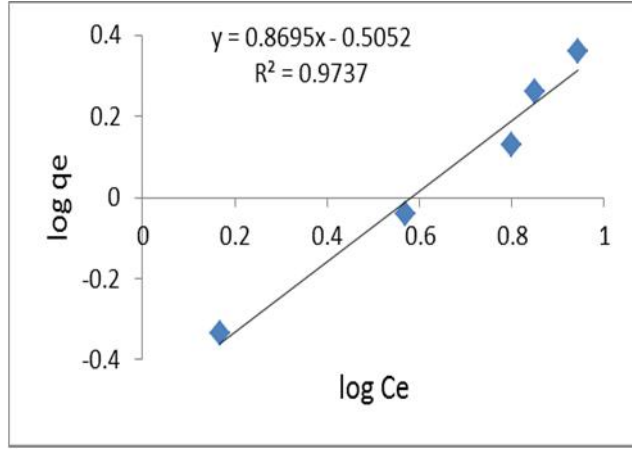


Fig 8: Freundlich Adsorption Isotherm for Cd

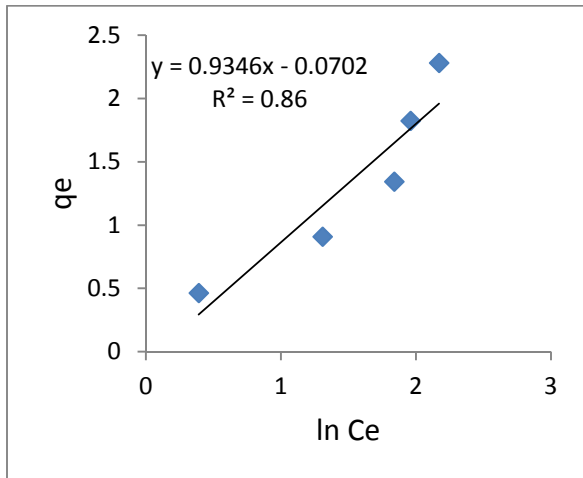


Fig 9: Temppkin Adsorption Isotherm for Cd

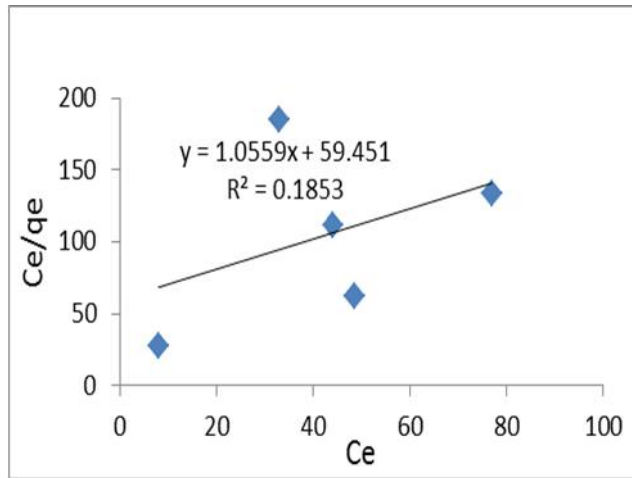


Fig 10: Langmuir Adsorption Isotherm for Cr

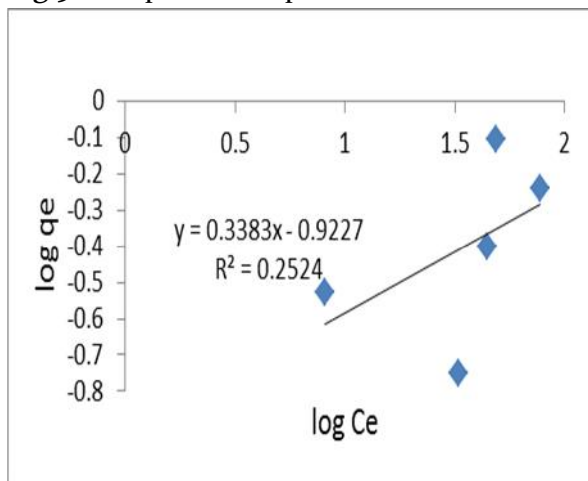


Fig 11: Freundlich Adsorption Isotherm for Cr

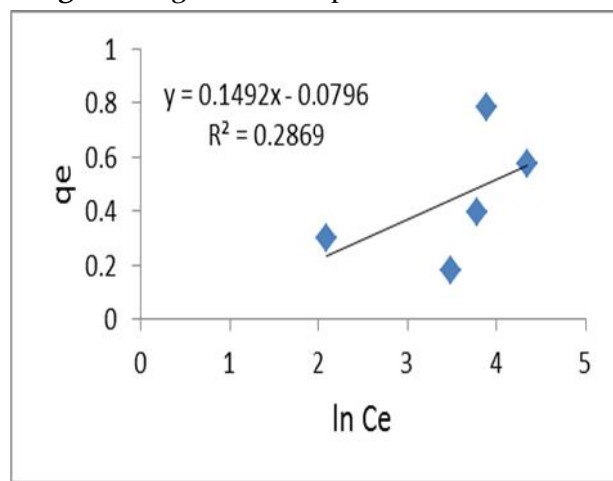


Fig 12: Temppkin Adsorption Isotherm for Cr

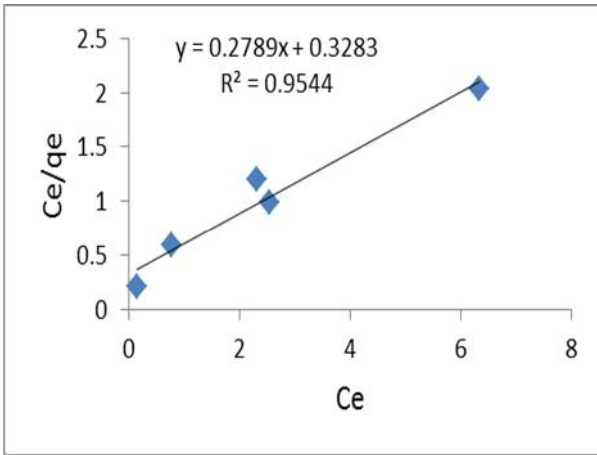


Fig 13: Langmuir Adsorption Isotherm for Cu

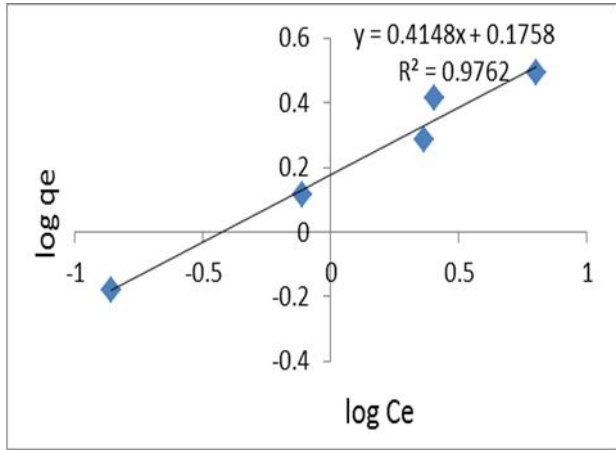


Fig 14: Freundlich Adsorption Isotherm for Cu

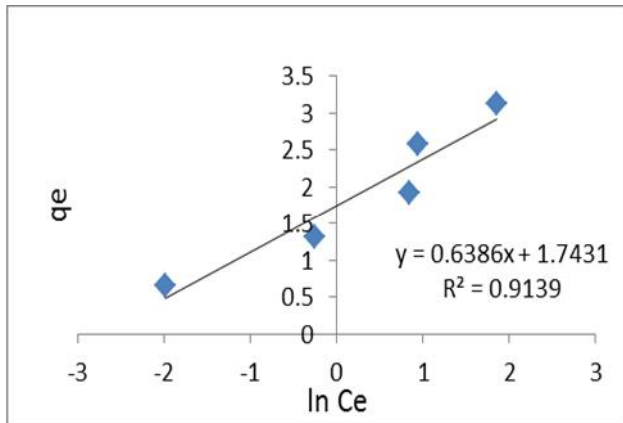


Fig 15: Tempkin Adsorption Isotherm for Cu

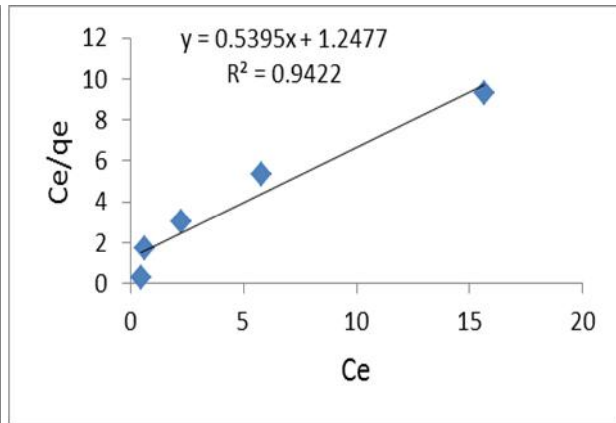


Fig 16: Langmuir Adsorption Isotherm for Ni

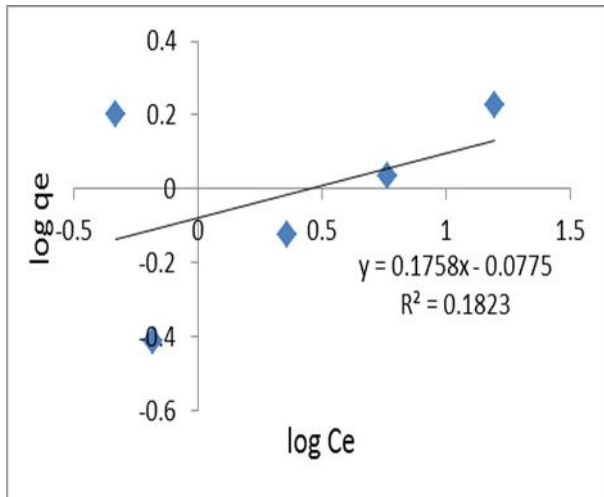


Fig 17: Freundlich Adsorption Isotherm for Ni

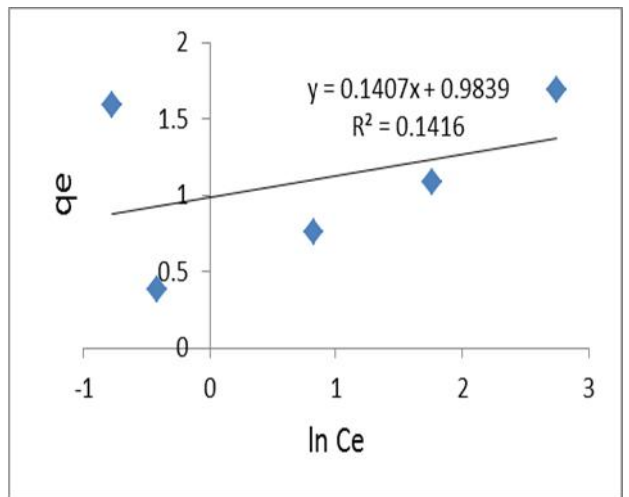


Fig 18: Tempkin Adsorption Isotherm for Ni

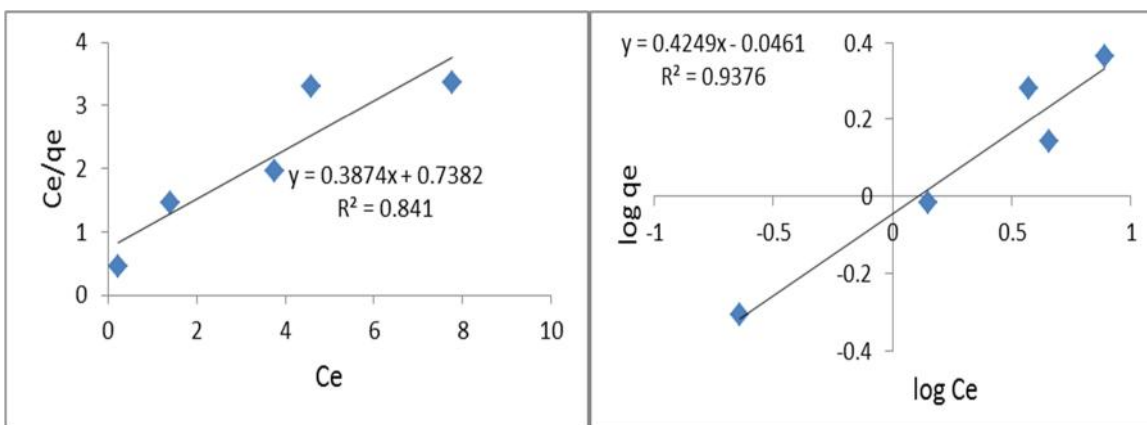


Fig 19: Langmuir Adsorption Isotherm for Pb **Fig 20:** Freundlich Adsorption Isotherm for Pb

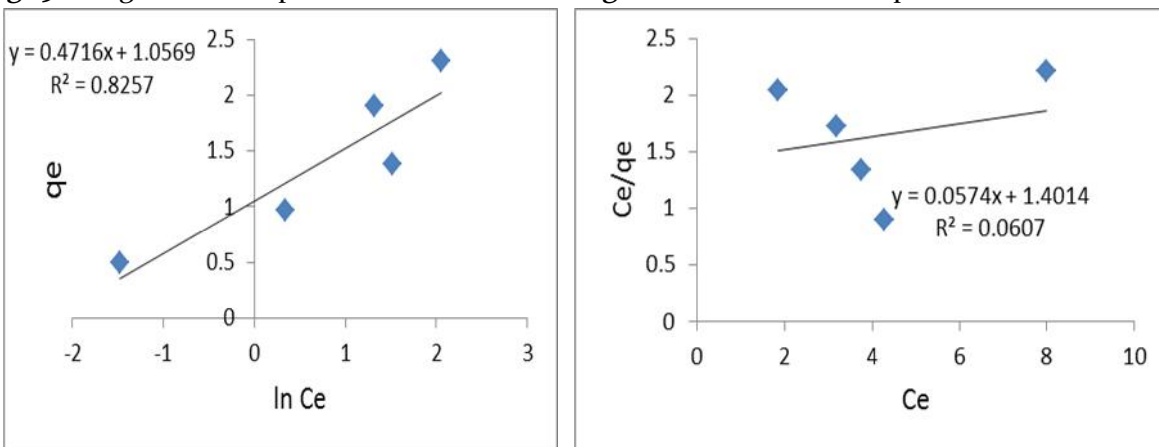


Fig 21: Tempkin Adsorption Isotherm for Pb **Fig 22:** Langmuir Adsorption Isotherm for Zn

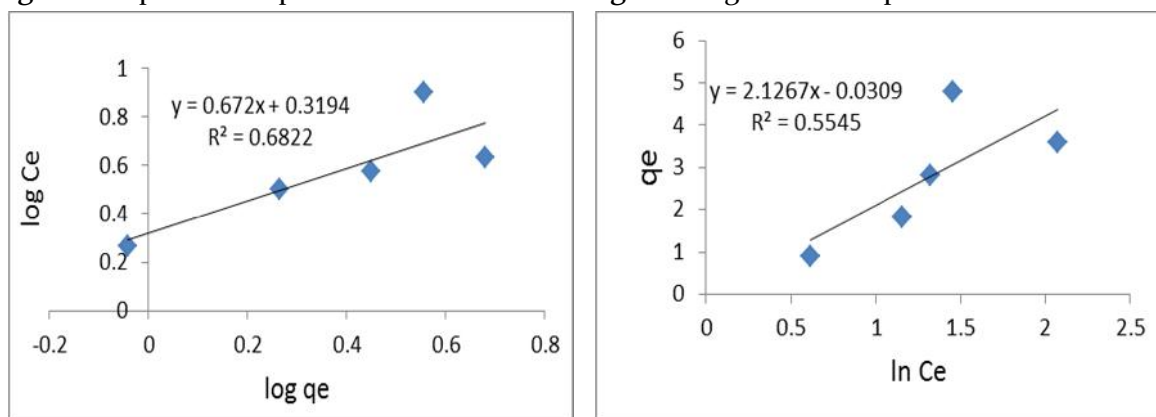


Fig 23: Freundlich Adsorption Isotherm for Zn **Fig 24:** Tempkin Adsorption Isotherm for Zn

Langmuir, Freundlich and Tempkin isotherm models have been used to describe the equilibrium established between adsorbed metal ions on the biomass (q_e) and metal ions remaining in solution (C_e) at a constant temperature using ACCF. The adsorption models were used for the description of the adsorption of Cd (II), Cr (III), Cu (II), Ni (II), Pb (II) and Zn (II) ions and this was done using the R^2 value (correlation coefficient). The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface. Freundlich model is commonly used to describe the

adsorption characteristics for the heterogeneous surface while Tempkin model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage.

The experimental results obtained for the adsorption of Cd (II), Cr (III), Cu (II), Ni (II), Pb (II) and Zn (II) under pre-defined conditions of pH, adsorbent dose and contact time, with initial concentration being varied (20, 40, 60, 80 and 100mg/L) fitted well into the langmuir isotherm model for Cu (II), Ni (II) and Zn (II). Also the data obtained fitted well into Freundlich and Tempkin isotherm models for Cd (II), Cu (II) and Pb (II). The data for Zn (II) fitted fairly well into the freundlich isotherm model and fairly into the tempkin isotherm model.

CONCLUSION

The batch studies conducted in the present study provides significant information regarding adsorption of Cd (II), Cr (III), Cu (II), Ni (II), Pb (II) and Zn (II) using ACCF in terms of adsorbent dose and initial concentration for maximum removal of adsorbate from aqueous solutions. The use of ACCF as an adsorbent clearly seems to be an economical and promising alternative over conventional methods.

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