Biosorption Study of Zn(Ii), Cu(Ii), Pb(Ii) And Cd(Ii) Ions by Palm Leaves Activated Carbon

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Abstract

The aim of the present study is to investigate the efficiency of palm leaves activated carbon on the removal of lead (Pb), zinc (Zn), copper (Cu), and cadmium (Cd) from the aqueous solution. The effect of various process parameters such as pH (2 – 10), initial metal ion concentration (50 – 1000 mg/L), particle size (125, 500, 800 µm), and temperature (303, 313, 323 K) was studied using batch adsorption technique. Thermodynamic parameters were also evaluated. The maximum metal ion removal efficiency of 94.5, 94.1, 87.4, and 90.7% for Pb, Cd, Zn, and Cu, respectively, was reached at an optimum pH of 5, biosorbent dosage of 1.0 g, and initial metal ion concentration of 50 ppm. The Freundlich adsorption isotherm model best described the removal of metal ions on palm leaves activated carbon with high correlation coefficients (0.98 – 1.00). The adsorption process was found to be favorable since the intensity of adsorption, n lies within 1 to 10. The adsorption capacity values were 40.0, 38.3, 38.0, and 40.00 mg/g for lead (Pb), zinc (Zn), copper (Cu), and cadmium (Cd), respectively. The metal ion adsorption was also found to be endothermic in nature. The efficiency was increased with an increase in temperature implying the process should be performed at a controlled temperature.

Keywords: Palm Leaves, Heavy Metals, Biosorption, Equilibrium, And Thermodynamics.

Introduction

The unequaled destruction of water quality all over the world is due to the fast-growing residents, uncontrollable civilization, accelerated mechanization, and unsuitable usage of water sources. This issue is becoming presently critical and deteriorating steadily. Latterly, the precise balance of nature has changed by the water quality destruction. Chemical pollutants, like heavy metals and organic dyes, are caused by these fast-growing manufacturing and civilization. Heavy metals, such as Lead, cadmium, arsenic, copper, mercury, nickel, zinc, are non-biodegradable in character and hazard to the ecological environment even at trace levels. Moreover, heavy metals are easily soluble in the aquatic environment and therefore can readily be absorbed by living organisms and subsequently get accumulated in the body and throughout the food chain. Additionally, the great tendency of heavy metals for complex formation with biological matter, particularly those containing nitrogen, oxygen, and sulfur, could change the molecular construction of nucleic acids, proteins, or suppression of enzymes could happen, and lastly heavy metals exhibit its toxicological and carcinogenic effects (1). On the other hand, the occurrence of various heavy metals into the aquatic environment is caused by wide types of anthropogenic resources and industries (2), and therefore their levels are raising progressively than the permissible flux levels in the effluents. Accordingly, the elimination of heavy metals from wastewaters by proper handling becomes more essential before releasing them into the environment. For heavy metals removal from wastewaters, several technologies have been utilized. These include chemical precipitation, coagulation, filtration, ion exchange, reverse osmosis, and adsorption (3-15). However, these methods have their limitations as separation processes of limited productivity, elevated operation budget, precise working circumstances, and production of polluted mud (16). Starting from 1990, the biosorption of heavy metals onto biosorbent materials has acquired notable thrust due to its high efficiency, eco-friendly, low cost, lowest possible slurry formation, and opportunity of metal retrieval. However, biosorption is considered to be a physicochemical method, in which the adsorbent is a biological solid matrix (17). Moreover, biosorbents could be chemically activated, with the aim of improving the removal features of bio sorbents material (18). The activated carbon prepared from biomaterials displays a significant improvement in the adsorption of heavy metal ions (19). In our previous study, we applied olive leaves, tea, coffee, and orange peel powders as biosorbents for removing heavy metals from their aqueous solutions [20-24]. In the current work, factors affecting the biosorption efficiency of lead (Pb), cadmium (Cd), zinc (Zn), and copper (Cu) were studied by activated carbon prepared from palm leaves. We have been also determined the stability constant using various models. Furthermore, some of the thermodynamic parameters of the system have also been measured by activated carbon prepared from palm leaves.

Material and Methods

Preparation of Activated Carbon from palm leaves

The source of Palm leaves was Misurata city in Libya. It was washed with distilled water, dried and ground. Activated with H_3PO_4, and then carbonized using the process reported by Isah et al. (25). The product was cleaned and filtered several times with distilled water and then subsequently dried in an oven at 70^{o}C for one day.

Materials

The chemicals used in this work were of analytical reagent (AR) grade. The nitrates salts of Pb, Cu, Zn, and Cd were used to prepare stock solutions of 1000 mg/L. The salts were purchased from Fluka AG, and double-distilled water was utilized to prepare the solutions. A series of standard solutions for each metal ion was prepared by suitable subsequent dilutions of the stock solution with a concentration between 50 and 750 mg/L. The examined solution pH values were adjusted using 0.1 M NaOH or 0.1 M HCl.

Analysis

Atomic Absorption Spectrometer instrument (AA7000) from Shimadzu was used to determine the metal ions concentrations in the solutions before and after the adsorption. The pH Meter from Jenway was used to measure the examined solution pH.

Biosorption Experiments

In our study, the batch biosorption procedure was performed. 50 ml metal ion concentration was mixed with the biosorbent in 250 mL conical flask, stoppered, and then placed on a temperature-controlled shaker at a speed 150 r/min. The metal uptake in (mg/g) was estimated based on the difference between the initial (C_o, mg/L) and final concentration (C_e, mg/L), using the following equation:

$$Q_e = \frac{C_o - C_e}{M} \text{ X } V \qquad (1)$$

where Q_e is the metal capacity in (mg/g), V the volume of the metal solution in (L) and M is the mass of biosorbent in (g).

The biosorption efficiency % R was estimated using the following equation:

$$\% R = \frac{C_o - C_e}{C_o} \text{ X } 100 \qquad (2)$$

Effect of heavy metal ions concentration on biosorption

The effect of initial metal ion concentration ranging from 50 to 1000 ppm was explored by mixing a biosorbent mass of 1.0 g with 50 mL of metal ion solutions at 303 K for 24 hours.

Effect of pH on the biosorption efficiency of heavy metals

Metal ion solutions (50 ml) were taken in four separate conical flasks. The pH of the metal ion solutions (50 ml) was measured at pH 2, pH 3, pH 5, pH 7, and pH 10. Palm leaves activated carbon 1.0 g was added to each flask and the solutions were stirred for 24 hours at 303 K. After the adsorption experiment, each solution was filtered and the metal ion concentration was examined by AAS.

Effect of biosorbent particle size on the biosorption efficiency of heavy metals

Activated carbon prepared from palm leaves of various particle size was studied. For that purpose, the particle size of 125, 500, 800 µm have been used. We have also tested three concentrations, 1000, 500, 250 ppm, of the elements with each particle size. The adsorbent dose and solution volumes were 1.0 g and 50 ml, respectively.

Effect of temperature on the biosorption efficiency of heavy metals

The effect of temperature on the adsorption of Pb, Zn, Cu, and Cd was experimented by mixing 1.0 g of adsorbent with 50 mL of examined metal ion solution with 100 ppm initial concentration and then tested at altered temperatures (303, 313, and 323 K).

Results and Discussion

The influence of pH on metal ion biosorption

The effect of pH is one of the most important factors which has to be considered in the metal ion adsorption experiments. The functionalization of the microbial adsorbent surface and solubility of metal ions were affected by pH altered. Fig. 1 shows extremely acidic solutions (pH < 2.0), the metal ions removal was minimal. At the higher pH values (from 2.0 to 5.0), the metal ions uptake was increased and then attained a maximum value for all metals at pH 5.0. The metal ions uptake remained mostly unchanged when the pH value was further increased. Nevertheless, the change in pH has considerably affected the speciation of the metal ions which sequentially impacts the removal capacity and that is shown by our results. The functional groups like carboxylates on the biosorbent wall will be protonated and the surface will be positively charged at quite lower pH values and therefore the H^+ ions will compete with metal ions, thereby leading to minimal biosorption of metal ions. However, the repulsion between positively charged H^+ ions and metal ions are also another reason for lower metal uptake, and as pH increases, the repulsion between the H^+ ions and metal ions also decrease which leads to more metal uptake. Moreover, the negatively charged sites increase as the pH raises resulting in a gradual increase in the biosorption of metal ions.

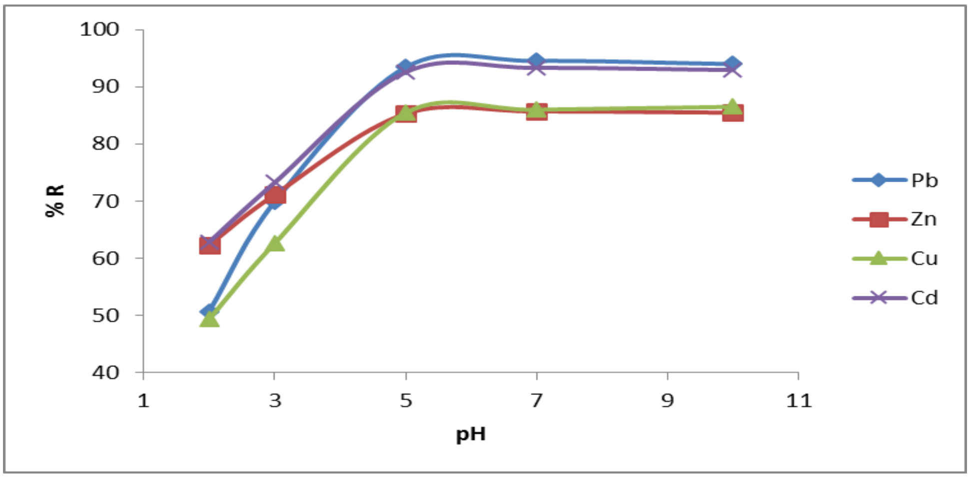

Figure 1. The pH effect on biosorption of Pb, Zn, Cu, and Cd onto palm leaves activated carbon

The influence of biosorbent particle size on metal ion biosorption

The effect of particle size as presented in Fig. 2 showed that the metal ions uptake decreased as the particle size increases. The influence of particle size of activated carbon prepared from palm leaves was studied for three metal ion concentrations (1000, 500, and 250 ppm). It was noted that the removal efficiency % was very low at a particle size of 800 μm and increased with decreasing the particle size. This was due to the smaller surface area of the biosorbent was available at higher particle size.

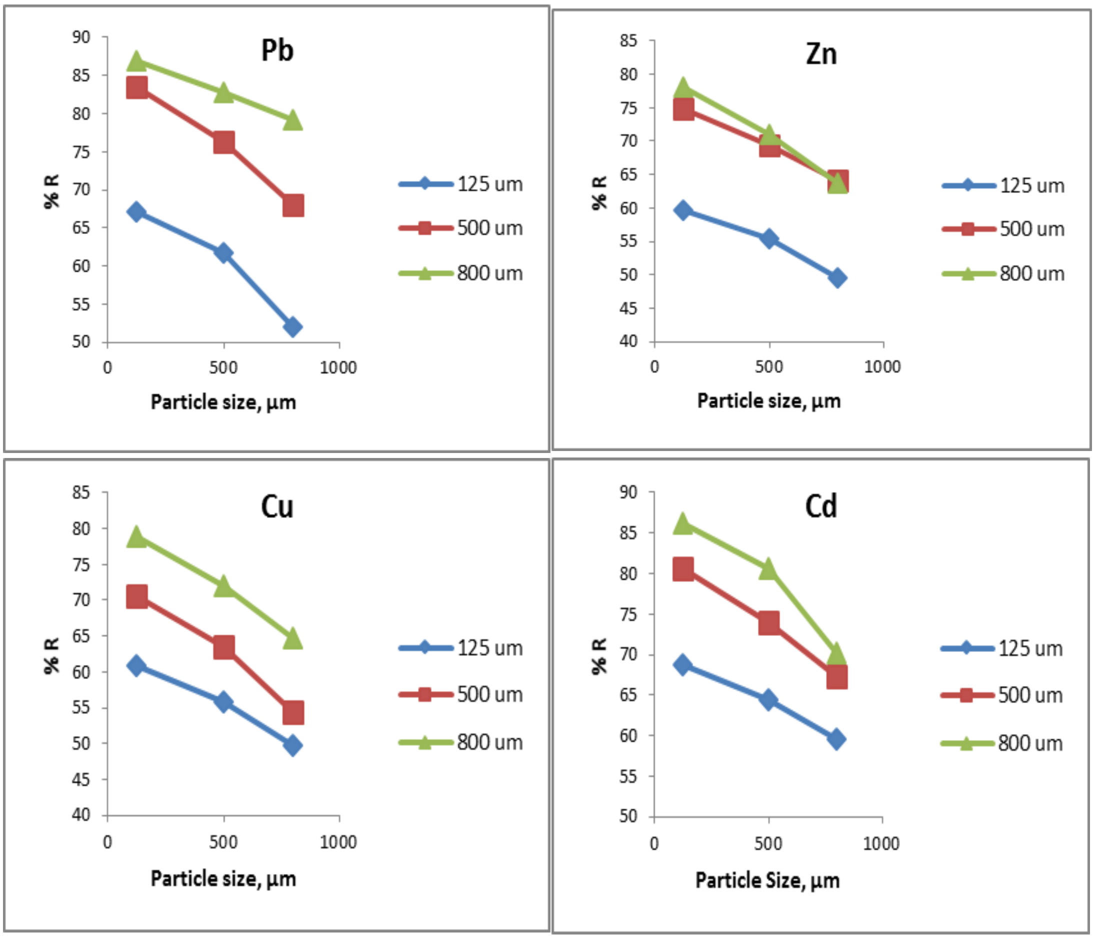

Figure 2. Effect of particle size on biosorption of Pb, Zn, Cu, and Cd onto palm leaves activated carbon

The influence of initial concentration on metal ion biosorption (Biosorption Isotherms)

The effect of initial metal ion concentration on biosorption is ordinarily explored to discover the dependent of the biosorbent capacity on the aqueous phase concentration. As shown in Fig. 3, the metal ions uptake is dependent on initial concentration, and it increases with an increase in initial concentration. At different metal ion concentrations, the motivating gradient force is changed and accordingly the biosorption capacity enhanced. At higher concentrations, there was a greater driving force to transport metals. However, at extremely high metal ions concentrations, the binding sites at biosorbent walls will be saturated leading to maximum capacity. To conduct the experiment at the highest possible mental concentration, it is substantial to find out the maximum biosorption capacity of biosorbent. Therefore, the initial metal ions concentration supplies a driving force and also reduces the mass transfer resistance for allowing metal biosorption

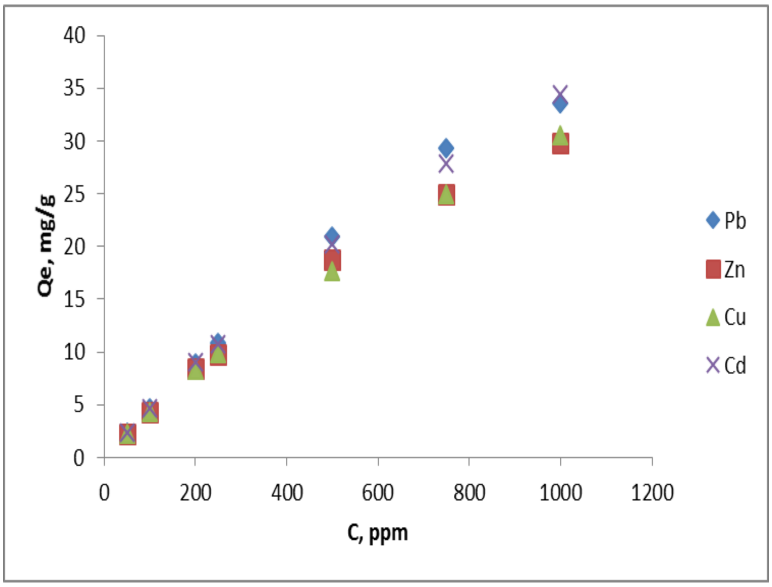

Figure 3. Effect of initial concentration on metal ion biosorption onto palm leaves activated carbon

However, the equilibrium data gained was analyzed using Langmuir and Freundlich adsorption isotherm model equations [23, 24] and the plots are presented in Figs. 4 and 5 as shown in equations 3 and 4

For Langmuir;

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \qquad (3)$$

For Freundlich;

$$Log Q_e = Log K_F + \frac{1}{n} Log C_e \qquad (4)$$

Where Q_e represents metal uptake capacity in mg/g, Q_m represents maximum metal uptake capacity in mg/g, C_e represents equilibrium concentration in mg/L; K_F is a constant indicating the adsorption capacity (mg/g), while n is a measure of the intensity of adsorption.

The obtained results from the modeling showed that the removal of lead, zinc, copper, and cadmium ions using activated carbon prepared from palm leaves followed the Freundlich adsorption equation with higher correlation coefficients (R^2) of about 0.99 for all metal ions. The implication of Langmuir correlation revealed that the Cu(II) ion has a maximum adsorption capacity while the Zn(II) ion has the lowest. Generally, the result displayed that the interaction between the surfaces of the palm leaves activated carbon and the metal ions was indicative of a physical type of adsorption. The parameters for these models are shown in Table 1.

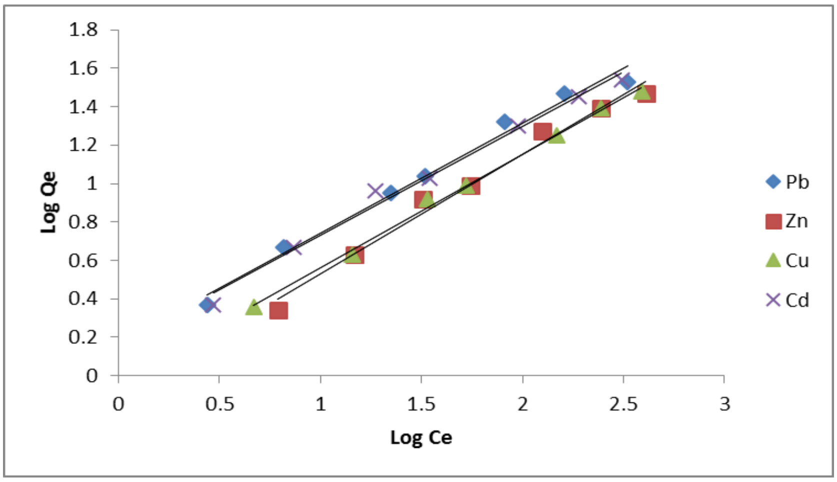

Figure 4. Equilibrium studies of metal ions biosorption onto palm leaves activated carbon, Freundlich isotherm.

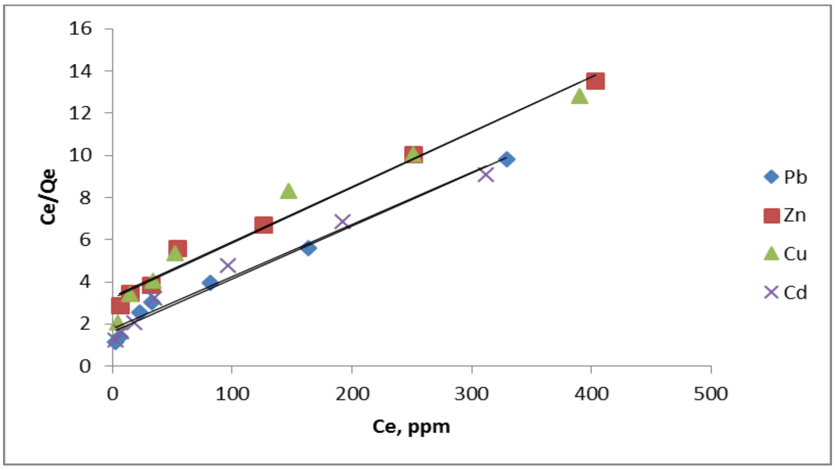

Figure 5. Equilibrium studies of metal ions biosorption onto palm leaves activated carbon, Langmuir isotherm.

Table 1. Langmuir and Freundlich parameters

Ion metal	Pb	Zn	Cu	Cd
Freundlich				
R^2	0.99	0.98	1.00	0.98
K_F	1.49	2.72	0.33	1.45
n	1.76	1.41	1.69	1.78
Langmuir				
R^2	0.979	0.98	0.95	0.945
K_L (L/mg)	0.015	0.008	0.008	0.015
Q_m (mg/g)	40.00	38.31	38.02	40.00

The influence of temperature on metal ion biosorption (Thermodynamic Parameters)

The biosorption of metal ions is greatly affected by the temperature of the system. The biosorption of metal ions onto palm leaves activated carbon is proportionally increased with temperature from 303 to 323 K, as shown in Fig. 6. The strengthening of the interaction between the metal ion and active sites is responsible for better adsorption at higher temperature values. Moreover, higher temperatures will also reduce the liquid viscosity and motivate the mobility of the particles. Conventionally, the adsorption process takes place in two accompanying processes, which will be a fast diffusion and slow complexation. The high temperature will speed up the diffusion rate of metal ions from solution to the surface of biosorbent, and also accelerates the complexation of metal ions with the functional groups of the biosorbent.

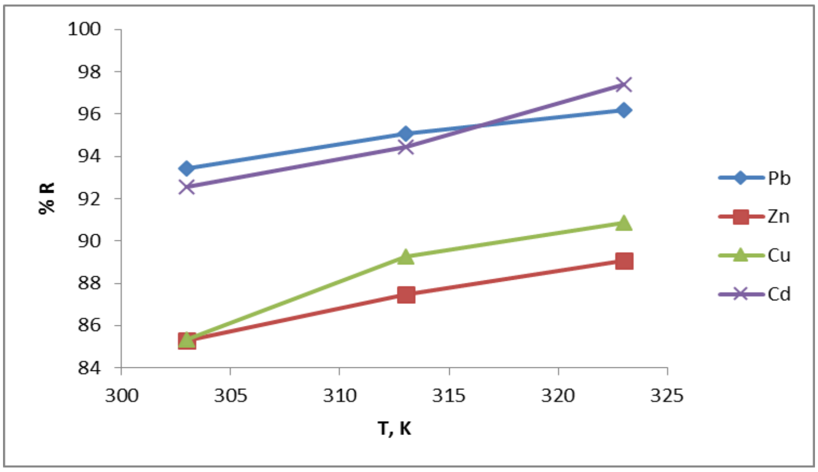

Figure 6. Effect of temperature on biosorption efficiency of metal ions onto palm leaves activated carbon

Calculating thermodynamic parameters, change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) in order to describe thermodynamic behavior of the biosorption of metal ions onto palm leaves activated carbon, using following equations (26):

$$\Delta G^{O} = -RT \ln K_{D} \qquad (5)$$

where R is the universal gas constant (8.314J/mol K), T is the temperature in (K) and K_D is the distribution coefficient between the aqueous phase and the biosorbent.

Relationship between Gibb's free energy change, enthalpy change (ΔH°) and entropy change (ΔS°) at constant temperature expressed in the equation (6) according to thermodynamics by the Van't Hoff equation (26):

$$\Delta G^{O} = \Delta H^{O} - T\Delta S^{O} \qquad (6)$$

Equations (5) and (6) can be written as:

$$\ln K_{D} = -\frac{\Delta H^{O}}{RT} + \frac{\Delta S^{O}}{R} \qquad (7)$$

The values of enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the slope and intercept of the plot of ln K_D vs. 1/T according to the equation 7, (Fig. 7). The values of thermodynamic paramours ΔG°, ΔH°, and ΔS° just calculated for the biosorption of metal ions onto palm leaves activated carbon are reported in Table 2.

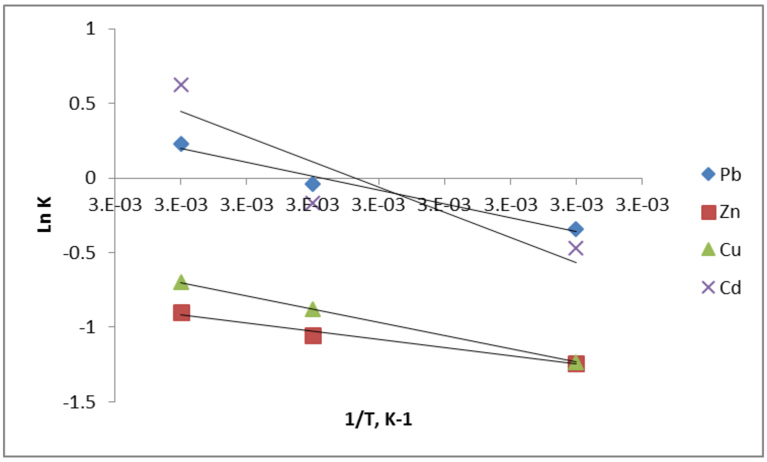

Figure 7. Plots of InK against 1/T for metal ions biosorption onto palm leaves activated carbon

Table 2. Thermodynamic parameters for biosorption of metal ions onto palm leaves activated carbon

Metal ion	T, K	ΔG°, kJ/mol	ΔH°, kJ/mol	ΔS°, J/mol. K	R^2
Pb	303	0.86	23.11	73.48	0.978
	313	0.09			
	323	-0.61			
Zn	303	3.12	13.80	35.28	0.980
	313	2.74			
	323	2.41			
Cu	303	3.10	21.73	61.68	1.000
	313	2.28			
	323	1.89			
Cd	303	1.20	2.06	19.53	0.818
	313	0.43			
	323	-1.68			

The non-spontaneous nature of the biosorption process of our system is indicated by the positive values of free energy (ΔG°). The physical adsorption the free energy change (ΔG°) ranges from (−20 to 0) kJ/ mol and for chemical adsorption it ranges between (−80 and −400) kJ/ mol. The ΔG° (27), for metal ions adsorption onto palm leaves activated carbon, was in the range of (-1.68 to 3.12) kJ/mol. At this juncture, one can say the adsorption was more likely physical adsorption. A positive value of ΔS° as 19.84-49.36 J/mol. K indicate that the randomness at solid-solution interface during the adsorption of metal ions increased.

Conclusion

The aims of current were to investigate the removal of some heavy metal ions by palm leaves activated carbon as a biosorbent. The outcomes suggest that palm leaves are greatly useful and economical for adsorption of heavy metal ions from aqueous solutions. The maximum adsorption capacity was 33.54, 34.39, 29.82, and 30.49 mg g^{-1} for Pb, Cd, Zn, and Cu, respectively. The maximum adsorption capacity was at the adsorbent dose of 1.00

g, an initial concentration of 1000 mg L^{-1}, and pH 5. The Freundlich and Langmuir adsorption models were used to describe the adsorption phenomenon of the sorbates. The equilibrium data were well illustrated by the Freundlich model. The adsorption intensity values (n = 1.76, 1.78, 1.41, and 1.69 for Pb, Cd, Zn, and Cu, respectively) of the Freundlich model indicated promising adsorption of these metals onto palm leaves activated carbon. Furthermore, thermodynamic investigations as well indicated that the positive values of free energy changes (ΔG^o) and enthalpy changes (ΔH^o) for the adsorption which revealed that the metal ions adsorption onto palm leaves activated carbon were a non-spontaneous and endothermic process.

Conflicts of Interest

Submitting authors are responsible for co-authors declaring their interests.

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