ORIGINAL ARTICLE



Adsorption isotherm, kinetic and thermodynamic studies for the removal of Pb(II), Cd(II), Zn(II) and Cu(II) ions from aqueous solutions using *Albizia lebbeck* pods

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Received: 12 November 2018 / Accepted: 28 June 2019 / Published online: 10 July 2019 © The Author(s) 2019

Abstract

Powdered adsorbent prepared from *Albizia lebbeck* pods as agricultural waste has been used for the adsorption of Pb(II), Cd(II), Zn(II) and Cu(II) ions from aqueous solutions. The powdered adsorbent was characterized by X-ray diffraction, Fourier transform infrared spectroscopy and Brunauer–Emmett–Teller. Effects of various parameters like contact time, solution pH, initial concentration dosage and temperature were investigated on a batch adsorption system. Equilibrium and kinetic experiments were carried out at the optimum pH of 6, 8 and 10 at 29 °C using particle size of 250 µm for Cd(II), Pb(II), Zn(II) and Cu(II) ions. Changes in free energy, enthalpy and entropy were also evaluated. The adsorption data fitted well with the Langmuir isotherm model with correlation coefficient ($R^2 > 0.94$), whereas the adsorption kinetics followed the pseudo-second-order kinetics. The thermodynamic parameters proved that adsorption of metal ions is endothermic and non-spontaneous at low temperatures, while spontaneity occurred at higher temperatures. This study shows that powdered *Albizia lebbeck* pods prove to be a promising inexpensive adsorbent for metal ion removal from aqueous solutions.

Keywords Albizia lebbeck · Characterized · Aqueous solutions · Thermodynamic · Endothermic

Introduction

Industrial activities in developed, underdeveloped and developing countries in recent times have faced a lot of problems due to improper disposal of wastes. These have resulted in emerging contaminants in water bodies causing severe health implications even at low concentrations. Effluents

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from industries such as tanning, mining, textile, fertilizer, pharmaceutical and inputs from other anthropogenic activities have contributed to the increase in contaminated waters all over the globe. Therefore, it is very important to do check and balancing of water quality, especially when their heavy metal ion concentrations are higher than the permissible limits in order to make them fit for human consumption and other purposes.

Several analytical methods have been pointed out and used for the removal of heavy metals from aqueous solutions. These include chemical precipitation, ion exchange, ultra-filtration, reverse osmosis, electrodialysis and adsorption (Reddy et al. 2014; Zare et al. 2015; Banerjee et al. 2016). These methods have some setbacks due to the inherent operational problems they possess. For instance, microbial electrochemical technology has been employed for the wastewater treatment (Zhang and Angelidaki 2014; Escapa et al. 2014, 2016) but was also reported to be expensive as reported by (Zhang and Angelidaki 2016). However, the method that has been described by numerous researchers to be highly selective, efficient, easy to operate and costeffective is adsorption. Adsorption has been an alternative



technique for heavy metal removal at low concentrations, and it depends on the adsorbent surface area, surface morphology, pore size distribution, polarity and functional groups attached to the adsorbent surface (Ali et al. 2016). The high cost of activated carbon in the markets has motivated researches to use low-cost biomass as adsorbents for the removal of heavy metals from wastewater. Therefore, there is a need to find alternative adsorbents of comparable effectiveness with lower costs for the removal of heavy metals. Several authors have used raw adsorbents for the removal of toxic heavy metal ions from aqueous solutions and industrial wastewater (Tasar et al. 2014; Ali and Saeed 2015; Asif and Chen 2017; Asuquo et al. 2018) and these were found to be promising.

Albizia lebbeck (Linn.) Benth is widespread tree grown in Senegal, Kenya, Angola, South Africa and in some parts of West African countries. It is called a woman's tongue in English. It is planted along roadsides and in gardens. The pods of the tree do not have much importance to the environment and thus litter the environment especially during the dry season and often constitute an environmental nuisance. This calls for research efforts in using this waste as an adsorbent for wastewater treatment. In the present work, raw *Albizia lebbeck* pods which are highly abundant in Nigeria area were used. This raw material is low cost with high ease of preparation. Batch experiments, kinetics, isotherms and thermodynamic studies of the lead, cadmium, copper and zinc on this adsorbent were carried out.

Materials and methods

All the chemicals used were of analytical grade (reagents \geq 98.5%) supplied by Sigma-Aldrich (UK).

Preparation of adsorbent

Albizia lebbeck pods were washed with deionized water in order to remove dust and other debris. They were then ovendried for 24 h at 378 K for the reduction in moisture content. The dried biomass was ground and sieved to particles (250 μ m). The sieved powder was stored and used for batch experiments.

Adsorbent characterization

The crystalline structure of *Albizia lebbeck* pod was determined by X-ray diffraction (XRD) analysis via XRD 6000 (Shimadzu, Japan), with CuK α radiation, and their diffraction patterns were recorded between diffraction angles of 0° and 90°. The functional groups that could influence the adsorption method were determined using Fourier transform infrared (FTIR) (a PerkinElmer 2000 FTIR spectrometer).



The BET surface area, average pore volume and size distribution of the raw adsorbent were detected from the plot of the volume adsorbed (cm³/g STP) against relative pressure (P/P_{o}) .

Metal solutions

The solutions of lead, cadmium, zinc and copper ions were prepared by dissolving certain amounts of Pb, Cd, Zn and Cu salts in deionized water into volumetric flasks. Initial concentrations of the metal ions were prepared by diluting the stock solutions. The desired pH of the solutions was adjusted using 0.5 M HCl and 0.5 M NaOH solutions, respectively.

Adsorption experiments

Batch adsorption techniques were carried out by varying contact time, solution pH, initial concentration, adsorbent load and temperature on the dried *Albizia lebbeck* pod powder. Adsorption experiments were carried out by adding accurate amounts of the adsorbent to 40 cm³ of the wastewater in conical flasks placed on an orbital shaker in order to attain the equilibrium time. The solution pH (2–12), adsorbent dosage (0.4–1.2 g), initial metal ion concentrations (10–30 mg/dm³) and the solution temperature (30–80 °C) were varied to study their effects on the metal ion removal efficiency. The analysis of the metal ion concentrations was done after filtering with Whatman 42 filter paper.

The metal uptake and the percentage removal were calculated according to the following respective equations:

$$Q_{\rm e} = \frac{\left(C_{\rm o} - C_{\rm e}\right)}{m} V \tag{1}$$

$$\% \text{Removal} = \frac{C_{\text{o}} - C_{\text{e}}}{C_{\text{o}}} \times 100$$
⁽²⁾

where C_0 (mg/dm³) is the initial concentration; C_e (mg/dm³) is the equilibrium concentration; Q_e (mg/g) is the adsorption capacity; and *m* (g) is the weight of the adsorbent.

Adsorption isotherms

Adsorption isotherms were investigated for 10-30 mg/ dm³ initial metal ion concentrations using 0.2 g of the raw adsorbent added to 40 cm³ of the metal ion concentrations and shaken for equilibrium time at 150 rpm. Two isotherm models, namely Freundlich and Langmuir, were employed.

Adsorption kinetics

About 40 cm³ of each aqueous solution was added to 0.2 g of the adsorbent at room temperature and shaken vigorously

at respective contact times. The obtained residual metal ion concentrations were used to calculate the pseudo-first-order and pseudo-second-order adsorption kinetics.

Adsorption thermodynamics

Adsorption thermodynamic parameters were calculated from the temperature variations at a constant adsorbent weight and initial concentration.

Results and discussion

Characterization of the adsorbent

The FTIR spectroscopy was used to identify the active groups and bonds involved in adsorption of metals onto the adsorbent. FTIR spectrum in Fig. 1 displays peaks of different functional groups attributable to the adsorption of the metal ions. As seen in the spectrum of Albizia leb*beck* pods, a broad and intense peak at around 3300 cm^{-1} corresponds to -OH group of cellulose, pectin and lignin stretching vibration. The peak at 2929 cm⁻¹ represents the asymmetric and symmetric -CH2 stretching vibrations. The peaks between 1730 and 1407 cm⁻¹ represent -C=O stretching, asymmetric and symmetric vibration of carboxylic groups, acid or ester and asymmetric and symmetric vibration of carboxylic groups which appeared at 1632 cm^{-1} and 1418 cm⁻¹. The peaks from 1240 to 750 cm⁻¹ are assigned to stretching vibration of alcohol and the stretching vibrations of C–O–C. Thus, the presence of abundant hydroxyl groups in the adsorbent abundance may be involved in the formation of coordination bonds with the metal ions.

The powdered *Albizia lebbeck* pod adsorbent shows several diffraction peaks of oxalate at major reflections

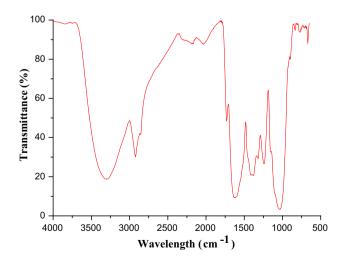


Fig. 1 FTIR analysis for Albizia lebbeck pod

at $2\theta = 15.1^{\circ}$, 24.2° , 30.5° , 38.1° and 49.7° . The information from this analysis provides supporting evidence to the effects of pH on the chemical interaction of the adsorbent with the existing hydroxyl and oxalate groups in the formation of metal oxalate complexes (Fig. 2).

Figure 3 represents the N₂ adsorption–desorption isotherms obtained at – 196 °C of the powdered *Albizia lebbeck* pod adsorbent. It displays the type IV isotherm. The calculated specific area and pore volume were 34.07 m²/g and 0.027 cc/g, respectively.

Influence of adsorption time

The effect of contact time on the adsorbent and metal ions is shown in Fig. 4. The rate of adsorption with respect to residence time on the surface of *Albizia lebbeck* pod

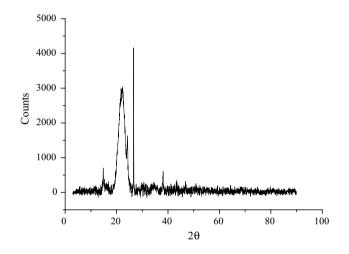


Fig. 2 XRD pattern of powdered Albizia lebbeck pods

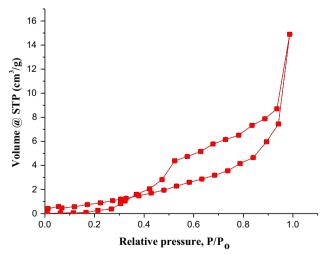
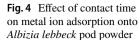
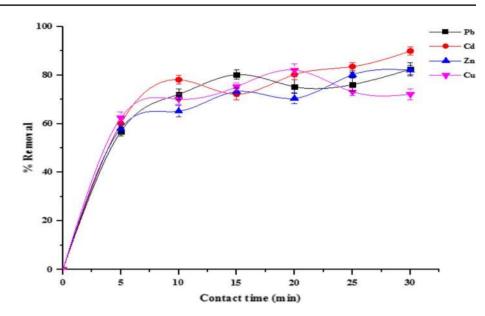


Fig. 3 Adsorption-desorption isotherm plot of powdered *Albizia leb-beck* pods







shows that the percentage removal of the metal ions firstly increased with increasing contact time; that is, the adsorption processes is fast until they reached their optimum times. This is attributed to the availability of large surface areas of the adsorbent. At these points, the equilibrium times were attained. After the plateau, the surface pores of the adsorbent became enclosed and desorption began. The slow rate of adsorption at this stage also known as the desorption process may be due to the agglomeration of metal ions on the surface of the adsorbent.

Effect of solution pH

The pH of an aqueous solution is described as a significant parameter that influences the adsorption process. During this process, the functional groups, surface charges, degree of ionization and solubility of the adsorbent are frequently responsible for the binding of metal ions onto the adsorbent. In Fig. 5, the optimum pH values ranged from 6 to 8 for the studied metal ions. It was observed that maximum removal of metal ions occurred at acidic medium and a further increase in pH above their optimum caused the formation of precipitates. At lower pH, the adsorbent is protonated and the protons compete with the metal ions, resulting in less adsorption. The interaction between these metal

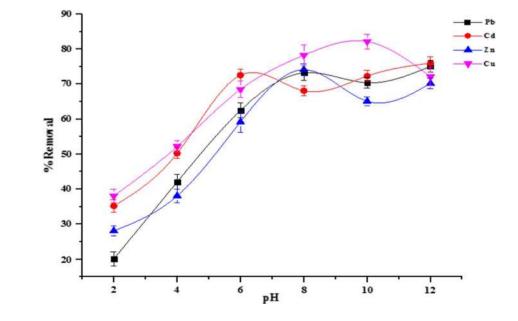


Fig. 5 Effect of pH on the percentage removal of Pb(II), Cd(II), Zn(II) and Cu(II) onto powdered *Albizia lebbeck* pods



0

0

ions increased with pH, and at higher pH, the presence of negatively charged functional groups such as hydroxyl and oxalate ions ensure the metal oxalate complex formation, thus influencing the adsorption of metal ions onto the adsorbent. The electrostatic interaction between the positively charged metal ions and the negatively charged oxalate ions, a bidentate ligand, is responsible for the formation of the metal oxalate complexes.

$$Pb^{2+} + 2OH \implies Pb(OH)_{2}$$

$$Pb(OH)_{2} + 2OH \implies PbO_{2}^{2-} + H_{2}O$$

$$Cd^{2+} + 2OH \implies Cd(OH)_{2}$$

$$Zn^{2+} + 2OH \implies Cd(OH)_{2}$$

$$Zn(OH)_{2} + 2OH \implies Zn(OH)_{4}]^{2-}$$

$$Cu^{2+} + 2OH \implies Cu(OH)_{2}$$

$$M = Central atom (metal)$$

$$H_{2}O \qquad H_{2}O \qquad n$$

A rare interpretation of the effect of pH on the adsorption process via sorption edge, in which the concentration of the adsorbate is kept constant while the pH is varied, is displayed in Fig. 6. The adsorption coefficient, K_D , is evaluated using the equation:

$$K_{\rm D} = \frac{C_{\rm s}}{C_{\rm w}} \tag{3}$$

where C_w (mol/dm³) the concentration in the solution at equilibrium, while adsorption capacity C_s (mol/m³) is computed as follows:

$$C_{\rm s} = \frac{\text{Mole adsorbed}}{MA} \tag{4}$$

Mole adsorbed =
$$(C_{\rm o} - C_{\rm e})V$$
 (5)

where *M* the mass of adsorbent loaded in the aqueous solution (g) and *A* is the specific area of the adsorbent (m^2/g) . The plot of K_D versus pH gave similar curves to the plot of percentage removal against pH, but in contrast, the plots, in this case, gave sharper curves.

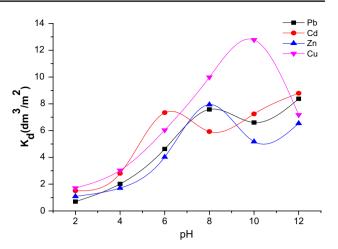


Fig. 6 Sorption edge of Pb(II), Cd(II), Zn(II) and Cu(II) onto *Albizia lebbeck* pod powder

Effect of initial concentration

Figure 7 shows the effect of the initial concentration of the metal ions $(10-30 \text{ mg/dm}^3)$ on their adsorption on the adsorbent. The results obtained show that as the initial heavy metal ion concentration increased, at 25 °C, constant pH and constant adsorbent mass for the respective optimum times, the % removal of the metal ions decreased. The higher initial metal ion concentrations provide a strong driving force between the liquid/solid phases (Ali et al. 2016). At lower concentrations, the ratios of available binding sites to the initial metal ion concentrations were larger, while at higher concentrations, the saturation of the adsorption sites occurred. This behaviour is attributed to less availability of surface-active sites.

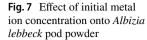
Effect of dosage

The influence of adsorbent dose of *Albizia lebbeck* pod powder was investigated in the range of 0.4–1.2 g for the initial metal ion concentrations. The plots of percentage removal of metal ions against dosage are presented in Fig. 8. It is worth noting that the % removals of the studied metal ions increased as the adsorbent dose increased. This could be due to the increased adsorbent surface area, pore size and volume, and the availability of vacant sites. The higher adsorbent dosage gave rise to higher removal of metal ions, providing an important driving force to overcome all mass transfer resistances of the metal ions between the aqueous and solid phases.

Effect of temperature and thermodynamics of adsorption

The effect of temperature parameter on the uptake of metal ions by *Albizia lebbeck* pod describes the relationship





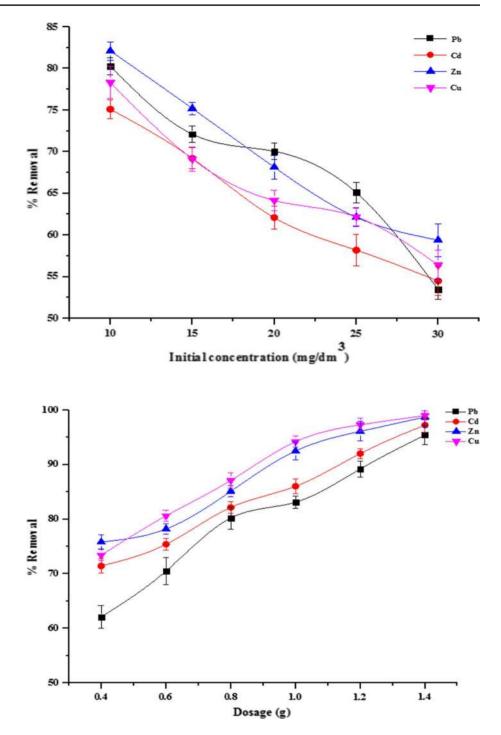
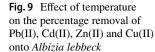


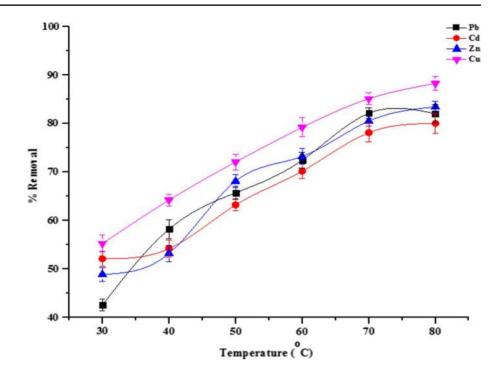
Fig. 8 Effect of adsorbent dosage on metal ion adsorption onto *Albizia lebbeck* pod powder

between temperature and the concentrations of the metal ions adsorbed onto the adsorbent at optimum contact time. As illustrated in Fig. 9, the adsorption of the metal ions on the adsorbent increased as the temperature increased from 30 to 80 °C. The increase in adsorption of metal ions could be the result of an increase in the mobility of the metal ions as a result of acquired energy in the system. This indicated that the interaction of metal ions with active sites at the surface of the adsorbent is an endothermic process, which could also be considered as a chemical adsorption process.

In order to describe the spontaneity of the adsorption process by thermodynamic parameters, temperature was varied from 303 to 353 K. Thermodynamic parameters of adsorption such as change in standard Gibbs free energy (ΔG^{θ}) , change in standard enthalpy (ΔH^{θ}) and change in standard entropy (ΔS^{θ}) were computed by from the following equations:







$$K_{\rm e} = \frac{q_{\rm e}}{C_{\rm e}} \tag{6}$$

$$\Delta G^{\theta} = -RT \ln K_{\rm e} \tag{7}$$

$$\Delta G^{\theta} = \Delta H^{\theta} - T \Delta S^{\theta} \tag{8}$$

$$\ln K_{\rm e} = \frac{\Delta S^{\theta}}{RT} - \frac{\Delta H^{\theta}}{RT}$$
(9)

where ΔG^{θ} is the change in standard free energy (kJmol⁻¹), R is the universal gas constant (8.314 Jmol⁻¹K⁻¹), K_{e} is the thermodynamic equilibrium constant and T is the absolute temperature (K). The values of ΔH^{θ} and ΔS^{θ} were determined from the slope and the intercept from the plot of ln K_{e} against $\frac{1}{T}(K^{-1})$. The recorded values of ΔH^{θ} and ΔS^{θ} are presented in Table 1. The positive values of ΔH^{θ} indicate that the adsorption was endothermic in nature, while the positive values of ΔS^{θ} show the affinity of the adsorbent for the metal ions, indicating an increase in sorbate concentration in the solid–liquid interface. The thermodynamic parameters show that the adsorption of metal ions is non-spontaneous at low temperature, while spontaneity occurs at high-temperature

values. This confirms the increasing randomness at the solid solution interface during sorption. Furthermore, the activation energy (E_a) is determined from the straight-line plot of $\ln K_e$ against $\frac{1}{\tau}$ using the Arrhenius equation:

$$\ln K_{\rm e} = \ln A - \frac{E_{\rm a}}{RT} \tag{10}$$

The calculated E_a from the slopes $\left(-\frac{E_a}{R}\right)$ from this plot was found to be between 33.161 and 25.685 kJ/mol, indicating chemisorption adsorption (Fig. 10).

Adsorption isotherm

Langmuir isotherm

The Langmuir adsorption isotherm assumes that monolayer adsorption exists at all surface sites that is homogeneity, with the ability of no interaction of adsorbed molecules with the neighbouring adsorption sites. The linear Langmuir equation is represented as follows:

Langmuir :
$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{1}{Q_m} C_e$$
 (11)

Table 1Thermodynamicparameters of Pb, Cd, Zn andCu ion removal from aqueoussolution by Albizia lebbeck podpowder

| Metal ion | $\Delta H (\text{kJ/mol})$ | ΔS (J/molK) | $E_{\rm a}$ (kJ/mol) | ΔG (kJ/mol) | | | | | |
|-----------|----------------------------|---------------------|----------------------|---------------------|-------|-------|-------|--------|--------|
| | | | | 303 K | 313 K | 323 K | 333 K | 343 K | 353 K |
| Pb | 33.161 | 94.489 | 33.161 | 4.530 | 3.586 | 2.641 | 1.696 | 0.751 | -0.194 |
| Cd | 25.685 | 71.105 | 25.685 | 4.140 | 3.429 | 2.718 | 2.007 | 1.296 | 0.579 |
| Zn | 31.586 | 89.944 | 31.586 | 4.333 | 3.428 | 2.534 | 1.635 | 0.735 | 0.164 |
| Cu | 32.761 | 96.248 | 32.761 | 3.598 | 2.36 | 1.673 | 0.711 | -0.252 | -1.214 |



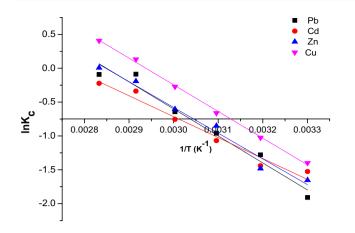


Fig. 10 van't Hoff plots for the adsorption of Pb, Cd, Zn and Cu ions

where C_e is the equilibrium concentration (mg/dm³), q_e is the amount (mg/g) adsorbed at equilibrium time, and Q_m and b are Langmuir constants related to maximum adsorption capacity (mg/g) and energy of adsorption related to the heat of adsorption (L/mg), respectively. The Langmuir parameters were computed from the slopes and intercepts of the linear plot of C_e as the abscissa and C_e/q_e as the ordinate as displayed in Fig. 12.

The Langmuir isotherm parameters were used to calculate the affinity between the adsorbent and adsorbate via dimensionless separation factor, R_L , as determined using the following equation:

$$R_{\rm L} = \frac{1}{\left(1 + bC_{\rm o}\right)}\tag{12}$$

where *b* is the Langmuir constant and C_0 is the initial concentration of metal ions. The R_L values promulgate whether the adsorption is irreversible (($R_L = 0$), favourable ($0 < R_L < 1$) or linear or unfavourable ($R_L = 1$ or $R_L > 1$). The values of R_L calculated for different initial concentrations are given in Table 3.

Freundlich isotherm

The empirical Freundlich isotherm model is applied to describe the adsorption on a non-uniform (heterogeneous) surface with the interaction between adsorbed molecules in the reversible and non-ideal adsorption process. The Freundlich adsorption isotherm linear form is given as:

$$\ln q_{\rm e} = \ln K_{\rm F} + \frac{1}{n} \ln C_{\rm e} \tag{13}$$

where $K_{\rm F}$ and *n* are Freundlich constants representing coefficient and intensity, respectively. The experimental values for *n* and $K_{\rm F}$ based on the slope and the intercept, respectively,



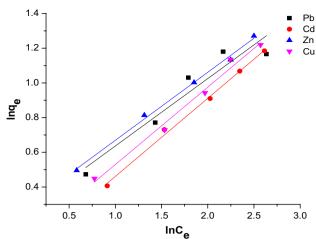


Fig. 11 Freundlich isotherm for Pb(II), Cd(II), Zn(II) and Cu(II) ion removal at various concentrations

 Table 2
 Freundlich and Langmuir isotherm constants for the removal of Pb, Cd, Zn and Cu ions from aqueous solution by *Albizia lebbeck*

| Isotherm model | Constant | Metal ion | | | | | |
|----------------|-----------------------|-----------|--------|--------|--------|--|--|
| | | Pb | Cd | Zn | Cu | | |
| Freundlich | K _F | 1.28 | 1.011 | 1.32 | 1.087 | | |
| | n | 2.57 | 2.22 | 2.55 | 2.24 | | |
| | R^2 | 0.8913 | 0.9953 | 0.9951 | 0.9838 | | |
| Langmuir | $Q_m (\mathrm{mg/g})$ | 7.17 | 7.81 | 8.26 | 8.68 | | |
| | B (L/mg) | 0.43 | 0.34 | 1.79 | 0.32 | | |
| | R^2 | 0.9410 | 0.9975 | 0.9957 | 0.9857 | | |

 Table 3
 Separation factor for the removal of Pb, Cd, Zn and Cu ions from aqueous solution

| Initial conc. | R _L values | | | | | | |
|---------------|-----------------------|-------|-------|-------|--|--|--|
| | Pb | Cd | Zn | Cu | | | |
| 10 | 0.303 | 0.227 | 0.062 | 0.238 | | | |
| 15 | 0.134 | 0.164 | 0.058 | 0.172 | | | |
| 20 | 0.132 | 0.128 | 0.044 | 0.135 | | | |
| 25 | 0.103 | 0.105 | 0.036 | 0.111 | | | |
| 30 | 0.084 | 0.089 | 0.030 | 0.094 | | | |

are determined by plotting $\ln C_{\rm e}$ against $\ln q_{\rm e}$ as shown in Fig. 11.

The Langmuir isotherm showed better fit to the experimental data with higher correlation coefficients for all the metal ions; as given in Table 2, the maximum adsorption capacities of the adsorbent were found to be between 8.68 and 7.17 mg/g. The $R_{\rm L}$ in the range of 0–1 decreased with increasing initial metal ion concentration which indicates favourable uptake of metal ions.

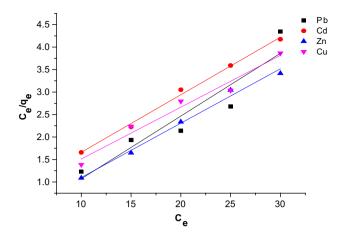


Fig. 12 Langmuir isotherm for Pb(II), Cd(II), Zn(II) and Cu(II) ion removal at various concentrations

The *n* values measure the favourability of the adsorption process. The *n* values for the metal ions correspond to the favourable adsorption process of 0 < n < 10. The correlation coefficient of Freundlich isotherm was found to be far away from unity when compared to the Langmuir isotherm model. Table 3 shows that the equilibrium data for the adsorption of metal ions onto the powdered *Albizia lebbeck* pod fitted the Langmuir more than the Freundlich isotherm model (Figs. 12, 13).

Adsorption kinetics

The adsorption kinetics and rate constants were determined from kinetic models including the pseudo-first-order and pseudo-second-order models. The pseudo-first-order and pseudo-second-order adsorption kinetics based on equilibrium adsorption are represented as follows:

$$\ln\left(q_{\rm e} - q_t\right) = \ln q_t - k_1 t \tag{14}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(15)

where q_e and q_t are the amounts of metal ions adsorbed onto the powdered *Albizia lebbeck* pods (mg/g) at equilibrium and at a time, *t*, respectively. k_1 and k_2 are the rate constants for pseudo-first-order and pseudo-second-order kinetics, respectively. The first-order constant (min⁻¹) was determined in linear form by plotting ln ($q_e - q_t$) against t. A plot of $\frac{t}{q_t}$ against *t* was used to determine pseudo-second-order constant (mg/g min).

Adsorption kinetics provides information on the reaction pathways and the mechanisms of the adsorption of sorbate by the sorbent. Table 4 describes the kinetics of the adsorptions of studied metal ions on powdered *Albizia lebbeck* pods

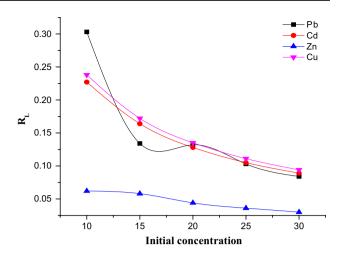


Fig. 13 Separation factors of Pb(II), Cd(II), Zn(II) and Cu(II) ion removal at various concentrations

by using pseudo-first and pseudo-second-order models. For the pseudo-first-order model, the low k_1 suggests that a slow adsorption process takes place, while for the pseudo-secondorder model, k_2 values were high indicating an increase in adsorption rates. The R^2 values for the adsorption kinetics of the metal ions were higher for the pseudo-second-order model compared to those of the pseudo-first-order model. Thus, it appears that pseudo-second-order model is a better model fitting the kinetics of the adsorption of the metal ions employed in this study (Figs. 14, 15).

Furthermore, in order to select a better model that fits the experimental data, Chi-square (χ^2) , the mean square error (MSE), correlation coefficient (R^2) and the validation by the normalized standard deviation (q) listed in Table 4 were used to justify the favoured adsorption kinetic model. The smaller the χ^2 value, the closer the agreement in the fit between the experimental data and linearized forms of the kinetic equations using the following relationships.

$$\chi^{2} = \sum_{i=1}^{n} \frac{\left(q_{\rm e,exp} - q_{\rm e,cal}\right)^{2}}{q_{\rm e,cal}}$$
(16)

MSE =
$$\frac{1}{n} \sum_{i=1}^{n} (q_{e,exp} - q_{e,cal})^2$$
 (17)

$$\Delta q\,(\%) = 100 \sqrt{\left[\frac{\sum_{1}^{n} (q_{\rm e,exp} - q_{\rm e,cal})/q_{\rm e,exp}}{N - 1}\right]}$$
(18)

where N is the number of data points, $q_{e,exp}$ is the experimental adsorption capacity and $q_{e,cal}$ is the calculated adsorption capacity.



 Table 4
 Kinetic parameters of pseudo-first-order and pseudosecond-order expressions

| Kinetic model | Constant | Metal ion | | | | | |
|---------------------|----------------------|-----------|---------|---------|----------|--|--|
| | | Pb | Cd | Zn | Cu | | |
| Pseudo-first-order | $q_{\rm e}$ (mg/g) | 5.6050 | 3.435 | 4.8350 | 3.1203 | | |
| | k_1 | 0.04439 | 0.03299 | 0.03886 | 0.02572 | | |
| | R^2 | 0.4902 | 0.6794 | 0.6856 | 0.4106 | | |
| | χ^2 | 3.3522 | 2.1684 | 3.5878 | 1.9148 | | |
| | MSE | 2.2053 | 1.0729 | 2.4782 | 0.8535 | | |
| | q | 14.2201 | 13.1851 | 14.3571 | 13.0559 | | |
| Pseudo-second-order | $q_{\rm e}$ (mg/g) | 0.8237 | 0.9004 | 0.8332 | 0.7477 | | |
| | k_2 (g/mgmin) | 1.4739 | 1.2335 | 1.4405 | 1.7887 | | |
| | R^2 | 0.9899 | 0.9814 | 0.9827 | 0.9900 | | |
| | χ^2 | 0.03277 | 0.03495 | 0.03939 | 0.006876 | | |
| | $MSE \times 10^{-3}$ | 3.1165 | 4.4958 | 3.8043 | 0.7344 | | |
| | q | 3.6415 | 3.2837 | 3.2645 | 1.7678 | | |

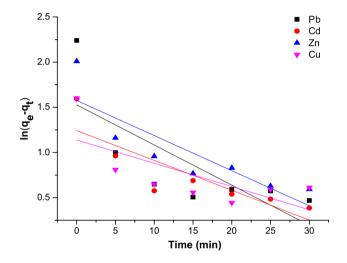


Fig. 14 Pseudo-first-order plots for Pb(II), Cd(II), Zn(II) and Cu(II) ion removal at different times

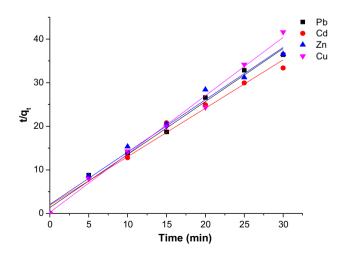


Fig. 15 Pseudo-second-order plots for Pb(II), Cd(II), Zn(II) and Cu(II) ion removal at different times



Conclusion

The present study has demonstrated that Albizia lebbeck pods powdered can be used as a natural, promising, economic and environmentally friendly adsorbent for Pb(II), Cd(II), Zn(II) and Cu(II) from aqueous solutions. BET, XRD and FTIR were used to analyse for the surface area, phase identification and functional groups that are responsible for the metal ion removal from aqueous solutions. The batch adsorption method is dependent on the contact time, dosage, solution pH, initial metal ion concentrations and temperature. The experimental data in the adsorption process indicated good correlations with the pseudo-second-order kinetic model and Langmuir isotherm. The thermodynamic study showed that the process is highly endothermic in nature, with positive values of enthalpy changes (ΔH^{θ}) and changes in the entropy (ΔS^{θ}) . Based on this study, the readily available Albizia lebbeck pods which are nuisance to the environment could be used as a natural adsorbent, due to its high removal efficiencies of the metal ions involved in this study.

Acknowledgements The authors acknowledge Shuaib, Damola Taye, a Ph.D. student in the Department of Chemistry, Illinois Institute of Technology, Chicago, USA, and Department of the Chemistry Federal University of Technology, Minna, for supporting this research work.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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