Journal of Medicinal and Chemical Sciences 3 (2020) 1-10

Journal of Medicinal and Chemical Sciences

Journal homepage: www.jmchemsci.com

Original Research Article

Equilibrium and thermodynamic studies of Pb(II), Zn(II), Cu(II) and Cd(II) adsorption onto mesembryanthemum activated carbon

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ARTICLE INFORMATION

Received: 27 December 2018
Received in revised: 22 March 2019
Accepted: 18 May 2019
Available online: 20 July 2019

DOI: 10.26655/JMCHEMSCI.2020.1.1

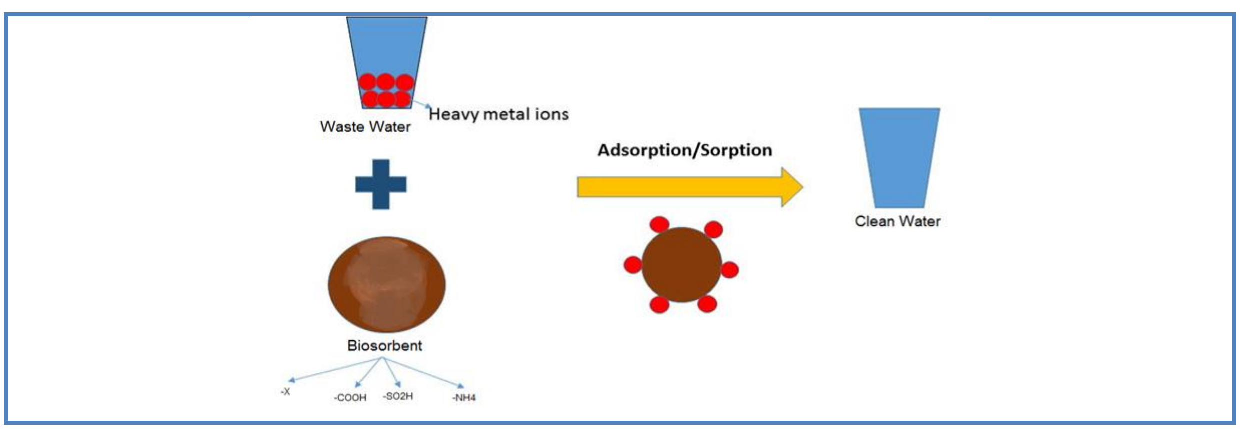
KEYWORDS

Heavy metals
Adsorption
Equilibrium
Thermodynamics

ABSTRACT

Adsorption of Pb(II), Zn(II), Cu(II), and Cd(II) ions onto Mesembryanthemum activated carbon in a batch experimentby taking the consideration of adsorbent particle size, initial concentration, temperature, and pH was studied. Langmuir and Freundlich isotherm models were tested to fit the equilibrium data. Freundlich isotherm model gave a better fit to our experimental data than the Langmuir model. The adsorption capacity values were 66.67, 52.63, 45.45, and 40.00 mg/g for Pb(II), Zn(II), Cu(II), and Cd(II), respectively. The ideal pH for all metal ions adsorption was at pH 5. The obtained thermodynamic parameters suggested that the adsorption process was physical, spontaneous ($\Delta G^o < 0$), and endothermic ($\Delta H^o > 0$).

Graphical Abstract



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Introduction

The skin Heavy metals are considered to be as metallic elements that have a higher density (at least 5 times) than water [1] and they can be divided into three different sorts, including: radionuclides (such as Ra, Th, U, Am etc.), precious metals (such as Au, Pt, Pd, Ag, Ru etc.), and toxic metals (such as Cd, Pb, Hg, Cr, Zn, Cu, Ni, Co, Sn etc.) [2].

The instantaneous evolution and mutation technologies, industrial outputs and practices of the current days have led to enormous growing in the application of heavy metals over the previous few decades and unavoidably caused an increased flux of metallic materials in the surrounding soils and aquatic environment. The prevalent nature of heavy metals, their toxicity even in trace levels, their trend for bioaccumulation in food chain, their non–biodegradability, their capability to subjectto transformations, the economic influence and the rigorous environmental arrangements related to heavy metals discharges have motivated the establishment of methods for heavy metals removal from wastewaters and soils. Furthermore, the progressively high requirement for heavy metals drives the enlargement in the research into effective recovery of heavy metals from all waste materials, especially wastewaters [3].

The remediation of heavy metals polluted waste water is anoperation that is usuallyfurther complicated than any other industrial process, due toparticularly industrial wastewaters which can have a vastly varying combination in terms of inorganic or organic compounds, excessive alkalinity or acidity, and existence of volatile substances. Various techniques were evolved for the removal and recovery of toxic and precious heavy metals from water or industrial wastewater, i.e. chemical precipitation, coagulation, ion exchange, phytoremediation, reverse osmosis, electrodialysis,adsorption on various media [4–12].

These techniques implicate disadvantages, such as: insufficient metal extraction, increased economic operating costs (reagents, energy), creation of toxic residue or another heavy metal wastes, lack of versatility in terms of handled streaming volumes and concentrations, necessity of rigorous supervision/preservation of instruments [13].

Since the past decades, adsorption by adsorbents has been appeared to be one of the most common methods for the removal of heavy metals from aquatic environment due to its minimum complication, unpretentious application in field conditions and sludge- free process. The adsorption method which displays versatility in the design and operation and in many other cases generates treated effluents appropriate for re-use, free of odour or colour. Moreover, because the adsorption is usually reversible, the reconstruction of the adsorbent with resultant economy of operation is achievable [14]. In addition, another considerable advantage of the adsorption technique in removing or decreasing the heavy metal ions even at very low concentration promotes the usage of adsorption as one practical treatment.

Heavy metal adsorption has been studied on a variety of materials like activated carbon [15]; carbon nanotubes [16]; natural and synthetic polymers, oxide minerals, inexpensiveadsorbents and so on [17]. Among them, activated carbon is the most widespread.

In our former study, we used olive leaves, coffee, tea, and orange peels powders as biosorbents for removing the heavy metals from aqueous solutions [18–22]. In the this study, factors affecting the adsorption efficiency of Pb, Cd, Zn, and Cu onto activated carbon prepared from Mesembryanthemum have been investigated. Equilibrium using various models and thermodynamics studies has been also investigated.

Results and Discussion

Effect of pH

The pH has been specified as one of the most significant variable that affects metal adsorption. It is mostlyconnected to the ability of hydrogen ions to compete with metal ions to active sites on the adsorbent surface. Ordinarily, metal adsorption comprised complex mechanisms of adsorption by physical forces, chelation, ion exchange, and spaces of the cell constitutional network of a adsorbent. The influence of pH on the adsorption of Pb, Zn, Cu and Cd ions onto Mesembryanthemum activated carbon was investigated at pH values between: 2.0–10.0. As shown in Figure 1, the maximal adsorption was detected at pH 5.0 for all metal ions. Subsequently, the remaining adsorption experiments were conducted at this pH value. The adsorption mechanisms on the Mesembryanthemum activated carbon surface consider the nature of the physicochemical interaction of the solution. At extremely acidic pH (pH<2.0), the complete surface charge on the active sites turned into positive and metal cations and protons complete for binding sites on cell wall, which results in minimal uptake of metal. As the pH increased from 2.0 to 5.0, the adsorbent surface became more negatively charged and the functional groups of the Mesembryanthemum activated carbon were further deprotonated and thus available for the metal ions.

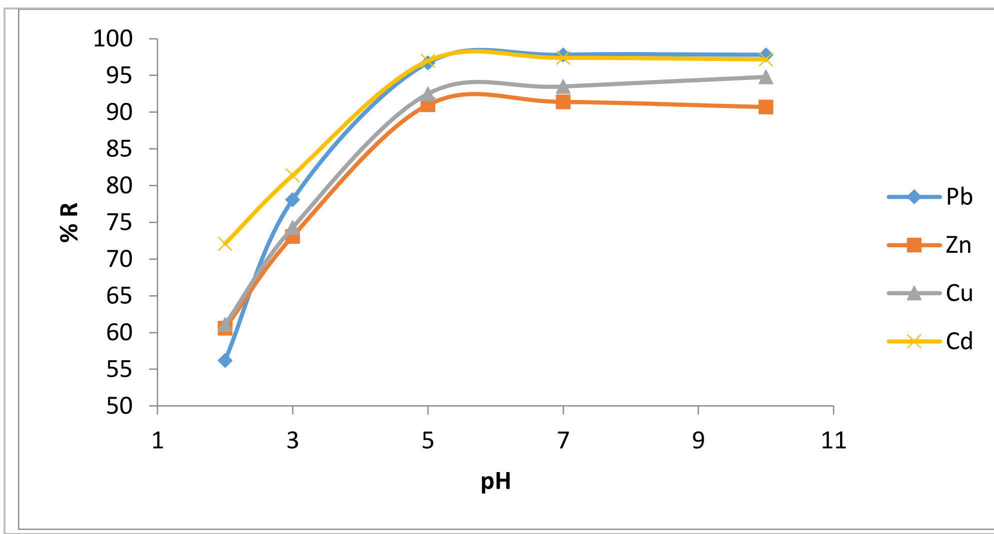

Figure 1. Effect of pH on Pb, Zn, Cu, and Cd adsorption

Effect of adsorbent particle size

The effect of particle size as presented in Figure 2 showed that as the particle size of adsorbent increases, the metal ions uptake decreased. The effect of particle size of activated carbon prepared from Mesembryanthemum was investigated for three metal ion concentrations which were 1000, 500, and 250 ppm.

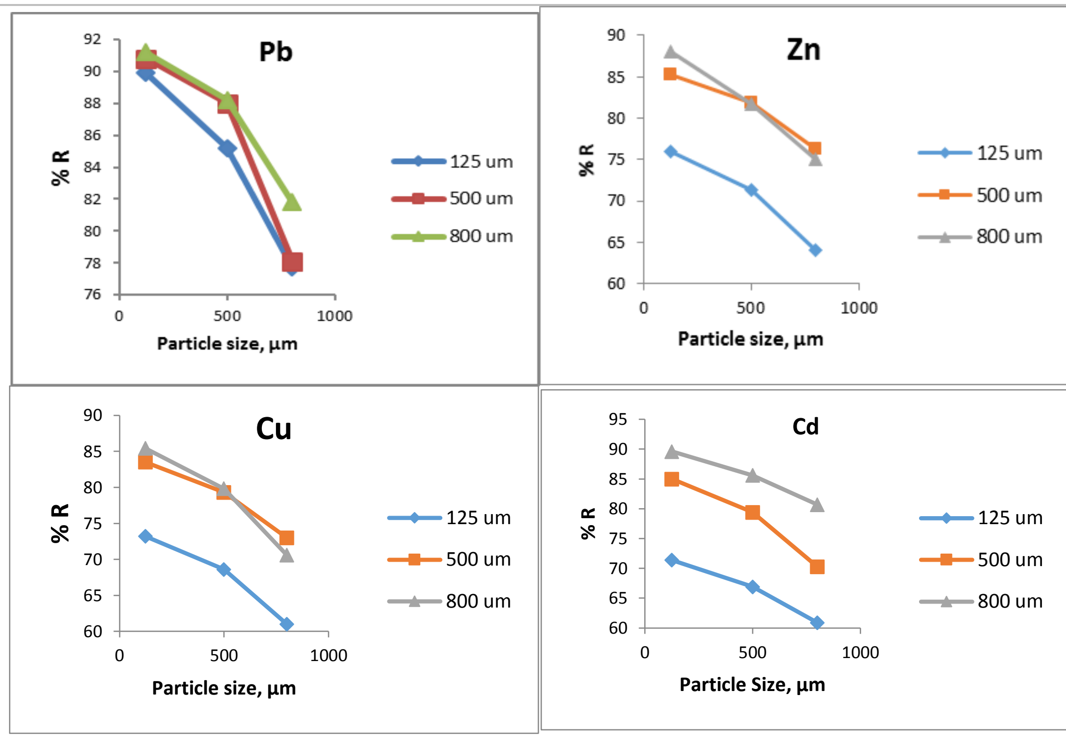

Figure 2. Effect of particle size on Pb, Zn, Cu, and Cd adsorption

Effect of metal ion concentration (Adsorption Isotherms)

The effect of concentration in the removal of Pb, Zn, Cu, and Cd ions from aqueous solutions using activated carbon prepared from Mesembryanthemum isdisplayed in Figure 3. It demonstrated that the metal uptake was increased with concentration. This is adenotation that the adsorbent can remove heavy metal ionsfrom solutions containing elevated concentrations. The result also demonstrated that the rate of adsorption started to decrease when the active sites on the adsorbent were saturated, i.e. indicating a concentration gradient build-up.

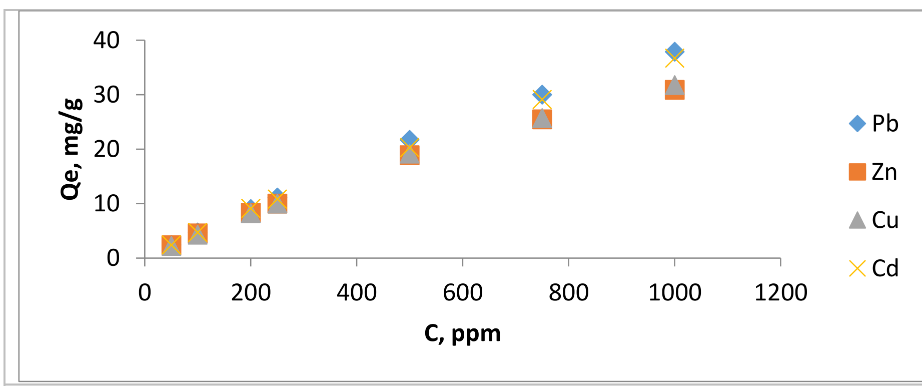

Figure 3. Effect of initial concentration on metal ion adsorption

However, to study the adsorption mechanism of metal ions, the acquired equilibrium data were analysed using Langmuir and Freundlich adsorption isotherm model equations [20] and the plots are

presented in Figures 4 and 5. The equations are expressed as follows:
For Langmuir model;

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

And for Freundlich model;

$$LogQ_e = LogK_F + \frac{1}{n} LogC_e \qquad (2)$$

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_L and K_F are the constants related to its intensity and n is a measure of probability of the adsorbents.

The outcomes acquired from the modelling demonstrated that the removal of Pb, Zn, Cu, and Cd ions using the activated carbon prepared from Mesembryanthemum were followed by Freundlich adsorption equation with correlation coefficients (R^2) of 0.99 for all metal ions. The implication of Langmuir correlation disclosed that the Pb (II) ion has a maximum adsorption capacity while the Cd (II) ion has the lowest. Generally, the resultsdemonstrated that the interaction between the metal ions and the surface of the Mesembryanthemum activated carbon was representative of a physical type of adsorption. The parameters for these model are given in Table 1.

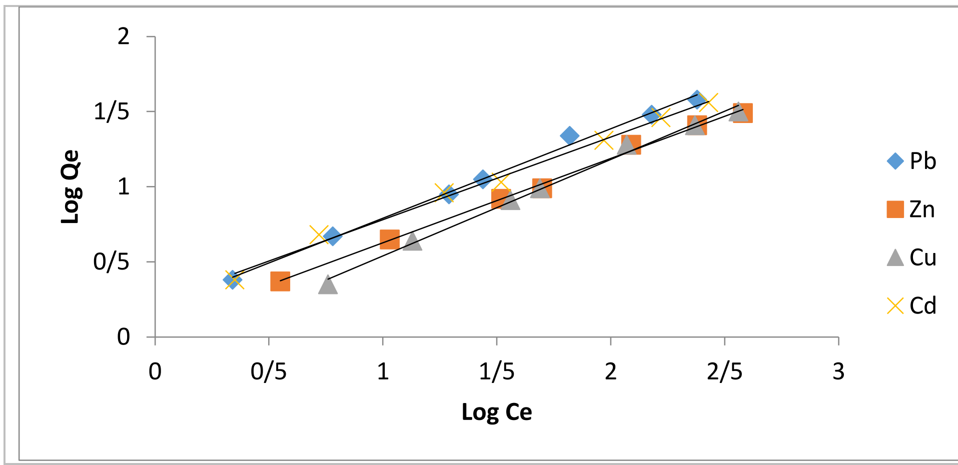

Figure 4. Equilibrium studies of metal ions adsorption onto Mesembryanthemum activated carbon, Freundlich isotherm

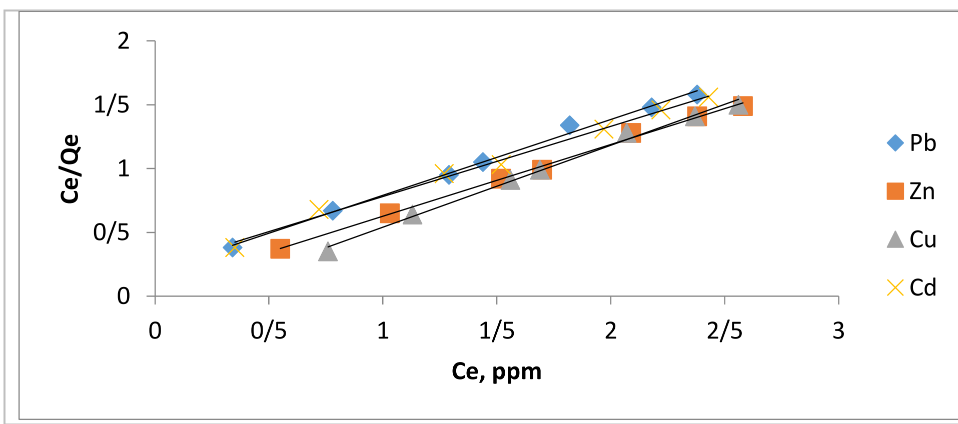

Figure 5. Equilibrium studies of metal ions adsorption onto Mesembryanthemum activated carbon, Langmuir isotherm

Table 1. Langmuir and Freundlich parameters

	Pb	Zn	Cu	Cd
Freundlich Model				
R^2	0.99	0.99	0.99	0.99
K_F	2.10	1.85	1.37	2.34
n	1.39	1.48	1.67	2.09
Langmuir Model				
R^2	0.80	0.99	0.97	0.98
K_L (L/mg)	0.015	0.015	0.012	0.023
Q_m (mg/g)	66.67	52.63	45.45	40.00

Effect of temperature(Thermodynamic Parameters)

The temperature influences on metal ion adsorption by the Mesembryanthemum activated carbon are shown on Figure 6. It displays that adsorption efficiency were highest at 323 K and lowest at 303 K. This finding proposes the endothermic nature of metal ion adsorption from aqueous solution by Mesembryanthemum activated carbon.

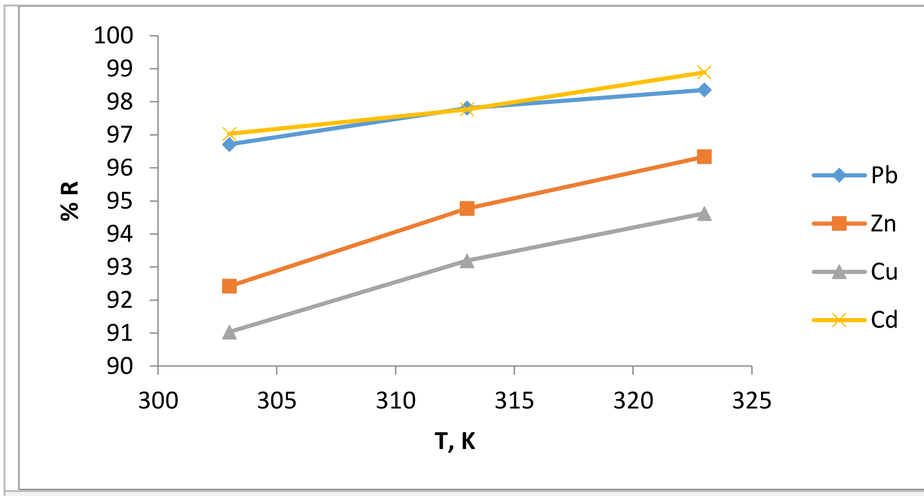

Figure 6. Effect of temperature on adsorption efficiency of metal ions

In order to characterize thermodynamic behaviour of metal ions adsorption onto Mesembryanthemum activated carbon, thermodynamic parameters,encompassing the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), were calculated from following equations [24]:

$$\Delta G^O = -RT \ln K_D \qquad (3)$$

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

From thermodynamics, the Gibb's free energy change is also linked to the enthalpy change (ΔH°) and entropy change (ΔS°) at constant temperature by the Van't Hoff equation [23]:

$$\Delta G^O = \Delta H^O - T\Delta S^O \qquad (4)$$

Equations (3) and (4) can be combined as:

$$\ln K_D = -\frac{\Delta H^O}{RT} + \frac{\Delta S^O}{R} \qquad (5)$$

According to the equation 5, 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 (Figure 7). The calculated values of thermodynamic paramours ΔG°, ΔH°, and ΔS° for the adsorption of metal ions onto Mesembryanthemum activated carbon are displayed in Table 2.

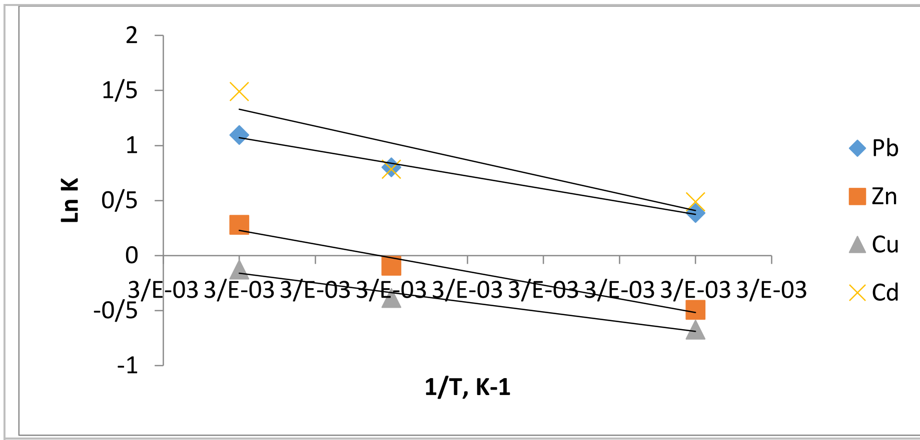

Figure 7. Plots of In Ka against 1/T for metal ions adsorption

Table 2. Thermodynamic parameters for adsorption of metal ions onto Mesembryanthemum activated carbon

Metal ion	T, K	ΔGº, kJ/mol	ΔHº, kJ/mol	ΔSº, J/mol.K	R^2
	303	-0.94			
Pb	313	-1.61	19.34	66.93	0.99
	323	-2.28			
	303	1.31			
Zn	313	0.67	20.71	64.04	0.97
	323	0.03			
	303	1.74			
Cu	313	1.31	14.67	42.67	0.98
	323	0.89			
	303	-1.03			
Cd	313	-1.9	25.56	87.74	0.84
	323	-2.78			

The spontaneous nature of the adsorption process is indicated by the negative value of the free energy (ΔG°). For the physical adsorption, the free energy change (ΔG°) extends from −20 to 0 kJ/ mol and for chemical adsorption it ranges between −80 and −400 kJ/ mol. The ΔG° [24], for metal ions adsorption onto Mesembryanthemum activated carbon was found in the range of (−2.78 to 1.74) kJ/mol and so the adsorption was predominantly physical adsorption. A positive values of ΔSº which were between 42.67 and 87.74 J/mol.Kindicated increased randomness at solid solution interface during the adsorption of metal ions.

Conclusions

The presentstudyefforts to inspect the Mesembryanthemum activated carbon as adsorbent for the removal of lead, zinc, copper, and cadmium ions from the aqueous solutions. The adsorption capacity of all metals increases with increasing the initial concentration. Also, adsorption of metal ions on Mesembryanthemum activated carbon decreases with increasing the adsorbent particle size. However, the maximum removal was found at pH value of 5.0 for metal ions. Langmuir and Freundlich isotherms models were used to illustrate the experimental data. A high correlation was found for Freundlich isotherm model. Thermodynamic examination suggests that the removal of Pb, Zn, Cu and Cd from aqueous solutions onto Mesembryanthemum activated carbon is physical in nature, a spontaneous, and endothermic.

Experimental or Martials and Methods

Preparation of activated carbon from mesembryanthemum

Mesembryanthemum was collected from Misurata city in Libya. It was cleaned, dried, ground, activated with H_3PO_4, and then carbonized using the procedure reported by Isah et al. [25]. The product was washed and filtered several times with distilled water and then lastly dried in an oven at 70 ^oC for 24 h.

Materials

All chemicals used were of analytical reagent (AR) grade. Stock solutions of 1000 mg/L of lead (II), copper (II), zinc (II), and cadmium (II) were prepared from nitrates salts of the metals which was purchased from Fluka AG using deionized distilled water. Required test solutions of metal ions were prepared using suitable subsequent dilutions of the stock solution. The range of concentrations of metal ions prepared from standard solutions varies between 50 and 750 mg/L. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with 0.1 M NaOH or 0.1 M HCl.

Analysis

The concentrations of Pb (II), Cd (II), Zn (II), and Cu (II) ions in the solutions before and after equilibrium were determined by atomic absorption spectrometer from Shimadzu (AA7000). The pH of the solution was measured with pH Meter 3505 from JENWAY.

Biosorption Experiments

Batch biosorption experiments were carried out by mixing the adsorbent with metal ion solutions with desired concentration in 250 mL conical flask. The conical flasks were stoppered during the equilibration period and placed on a temperature controlled shaker at a speed of 150 r/min. The adsorption capacity was determined based on the difference between the initial (C_o, mg/L) and final concentration (C_e, mg/L) in every flask, as follows:

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

where Q_e is the metal uptake capacity (mg/g), C_o is the initial concentration, C_e is the final concentration, V the volume of the metal solution in the flask (L) and M is the dry mass of adsorbent (g).

The adsorption efficiency % E was calculated as follows:

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

Effect of initial concentration on Adsorption

The impact of initial metal ion concentration ranging from 50 to 1000 ppm was studied by contacting a fixed adsorbent mass (1.0 g) with 50 mL of aqueous solutions at 303 K for 24 hours.

Effect of pH on the adsorption efficiency of heavy metals

Metal ion solutions (50 mL) were taken in five separate conical flasks. The pH of solutions was adjusted at pH 2, pH 3, pH 5, pH 7, and pH 10. Mesembryanthemum 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 determined by AAS.

Effect of adsorbent particle size on the adsorption efficiency of heavy metals

Adsorption experiments with activated carbon prepared from Mesembryanthemum of different particle size were investigated. For that purpose, different particle size of 125, 500, 800 μm have been tested. Also, three concentrations, 1000, 500, 250 ppm, of the elements were tested with each particle size. The adsorbent dose and solution volume were 1.0 g and 50 mL, respectively.

Effect of temperature on the adsorption efficiency of heavy metals

The influence of temperature on the adsorption of Pb, Zn, Cu, and Cd was studied by mixing 1.0 g of adsorbent with 50 mL of metal solution of 100 ppm initial concentration at different temperatures (303, 313, and 323 K).

Disclosure statement

No potential conflict of interest was reported by the authors

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How to cite this manuscript: Abdulfattah Mohammed Alkherraz, Aisha Khalifa Ali, Khaled Muftah Elsherif*.Equilibrium and thermodynamic studies of Pb(II), Zn(II), Cu(II) and Cd(II) adsorption onto mesembryanthemum activated carbon. *Journal of Medicinal and Chemical Sciences*, 2020, 3(1), 1-10. DOI: 10.26655/JMCHEMSCI.2020.1.1