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Calcined cow leather as a new low-cost biosorbent for copper (II), zinc (II) and nickel (II) ions removal from aqueous solution

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Abstract

This study's prime objective was to investigate the efficiency of calcined cow leather as new low-cost biosorbent for heavy metals elimination from aqueous solutions using batch techniques. The final concentrations of Cu(II), Zn(II) and Ni(II) were obtained by ICP-MS spectrometry. The calcined cow leather was characterized by the following techniques FT-IR, XRD, SEM, XRF and BET. Series of biosorption experiments were conducted to determine the effect of biomass, initial ions concentration, pH, temperature and contact time. Therefore, the maximum biosorption capacities (q_{max}) at the optimum biosorption conditions for Cu(II), Zn(II) and Ni(II) are 9.60 mg/g, 9.30 mg/g and 8.00 mg/g respectively. The Kinetic studies indicate that biosorption well represented by the pseudo-second-order kinetic model, and well described by the Langmuir model. The thermodynamic settings such as the free energy change ($\Delta G°$), entropy ($\Delta H°$) and enthalpy were revealed that the system is spontaneous and endothermic by nature at 298-328 K. Hence, based on experimental results, the calcined cow leather could be exploited as a potential and affordable biosorbent for heavy metals.

Keywords: Biosorption, Heavy metals, Calcined cow leather, Kinetic, Isotherm.

1.Introduction

Heavy metals constitute a group of chemical elements that have a high density and are toxic or poisonous at low concentrations. Those components exist naturally on the Earth's crust beside their industrial sources [1]. For decades, water pollution has been studied because of the fast industrialization that increased along with the generation and use of heavy metals leading to high concentrations which are frequently discharged into water bodies. Industries such as metal plating [2,3], fertilizer industries, battery manufacturing , ore refineries, tanneries, pesticide production, mining and the paper industry [4] are the principal sources of heavy metals, such as iron (Fe), zinc (Zn), cadmium (Cd), copper (Cu), lead (Pb), and nickel (Ni). These latter are considered carcinogenic, toxic, tend to bioaccumulate, and persistent in nature [5]. Several methods have been examined for effective heavy metals elimination from water, including without limitation to membrane filtration, ion exchange, chemical precipitation and electrochemical technologies [6-10]. Among these processes, adsorption has shown the flexibility in operation and design. Additionally, biosorbents can be regenerated by desorption processes [11] which are of high efficiency and low maintenance cost [12]. Therefore, the adsorption technique has become one of the main techniques for heavy metals removal from wastewater. This technology is affordable and environmentally friendly if low-cost adsorbents are exploited. In the seek for affordable adsorption materials over the past years and since the charge of an adsorbent depends heavily on its effectiveness and availability, many researchers switched their concern into the use of animal wastes, such as chicken feathers [13], animal bones [14], *Ensis siliqua* Shells [15] and snail shells [16].–There are many physical-chemical parameters influencing the effectiveness of adsorption process, such as initial metal concentration ions, adsorbent dosage, temperature and pH. For example, pH can affect functional groups on the surface of the adsorbents, the metal availability, and ionic strength [17]. In the case of metal concentration and adsorbent dosage, the effectiveness mainly depends on the availability and competition for active sites [18]. The primary objective of this study is to valorize the calcined cow leather (CCL) as new abundant material and eco-friendly biosorbent, as well as to investigate its efficiency to eliminate heavy metals from wastewaters by adsorption technique. The effect of initial metals concentration, pH, contact time, adsorbent dosage and removal efficiencies are evaluated. The biosorption behaviour was tested using the Langmuir, Freundlich, Temkin, Elovich, and Dubinin-Radushkevich isotherms. The thermodynamics parameters were studied and the experimental data of this process were also investigated using the pseudo-first and pseudo-second-order kinetic models.

1. MATERIALS AND METHODS

1.1. Heavy metal ions preparation

Unless otherwise designated, all chemical products used in this study were all of analytical grade. Heavy metals synthetic wastewater stock of 1000 mg/L were prepared in 1L of 0.5% HNO_3 distilled water by dissolving respectively an appropriate amount of $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$, and $NiSO_4.6H_2O$. On the point of controlling the ionic strength for metal ions, HNO_3 was exploited as background electrolyte. Dilutions of desired concentration were prepared by diluting the appropriate volumes from stock solutions. The resulting stock solutions were stored in an airtight bottle. For pH adjustment, HCl and NaOH were used.

1.2. Analysis devices

1.3. Chemical analyses of the CCL powder were performed using a fluorescence spectrometer (Wavelength dispersion spectrometer - Axios type). Fourier transform infrared spectroscopy (FTIR) analysis was conducted in the 450-4000 cm^{-1}, using an FT/IR-Vertex 70 spectrometer (Germany). The elemental composition of our material has been determined by Energy Dispersive X-rays Spectroscopy (EDXS): X'Pert Pro MPD Panalytical with Cu anode as

the source of X-rays at wavelength λ = 1.54 Å. For the specific surface area measurement, the BET method was performed using a Pore Size Micromeritics ASAP 2020 apparatus. The morphology of the adsorbent powder (CCL), was observed using an FEI Quanta 200 instrument (USA) scanning electron microscope (SEM), the images of the microstructure have been obtained with maximum voltage of 10 kV. Inductively coupled argon plasma Spectrometer ICP-OES iCAP 6000 (in) - Australian, was used for the determination of nickel, copper and zinc ions concentrations respectively at 324 nm, 213 nm, and 231 nm. The pH was measured using a Metrohm pH meter 691, Swiss, constituted with a glass electrode. The shaking of solutions was carried out with a magnetic stirrer model IKA, RT 10 power.

1.4. Biosorbent preparation

Cow leathers were provided by a slaughterhouse management waste service in Casablanca city (Morocco). Cow leathers were cleaned from blood and other dirt, and salted immediately with common marine salt, in order to avoid degradation processes, development of micro-organisms and bacteria. Then let dry in open air for many days helping to partial removal of water. After this operation, the cow leathers dried at 70°C until reaching a constant weight. The dried leathers were showed a high resistance for grinding, the reason why we opted to cut it into small pieces, then calcined for 4 hours at 525°C. The materials were ground to a fine particules and rinsed with deionized water until the filtrate reached pH = 7 and then dried for 24 hours at 105°C. The final material was kept in a plastic container and preserved in a desiccator for further use and the Calcined Cow Leathers were abbreviated (CCL).

1.5. Biosorption procedure

Series of biosorption experiments were performed in 250 mL beakers containing known volumes (100 mL) and fixed metal concentration (5 mg/L) of Cu(II), Zn(II) and Ni(II) solution by adding to each beaker known adsorbent's amounts [25-250 mg] to study the biosorbent effect. The resulting solutions were stirred with a magnetic stirrer at 600 rpm with appropriate time and temperature then filtrated using Fioroni filter paper, as final step residual filtrates were analyzed in ICP-OES. The effect of pH was examined by changing the pH from 3 to 13 with HCl and NaOH (1N).

The effect of initial metal concentration was determined by adjusting the adsorbate dose in the range of 3-15 mg/L. The effect of temperature was studied by changing temperature from 293 to 328K at optimum equilibrium studies. The removal efficiency then calculated using equation (1):

$$\% \text{ Adsorption} = (C_i - C_f) / C_i \times 100 \quad (1)$$

Where C_i is the initial metal concentration (mg/L) and C_f is the final concentration (mg/L).

The metal uptake q_e (mg/g) was calculated following equation (2) [19]:

$$q_e = [(C_i - C) / m] \text{ x } V \quad (2)$$

Where m is the quantity of biosorbent (g) and V is the volume of the suspension (L).

2. RESULTS AND DISCUSSIONS

2.1. Characterization studies

2.1.1. XRF analysis

The chemical composition is determined by X-ray fluorescence. The elemental analysis of CCL shows an abundant presence of oxygen (65.5%) and carbon (21.5%) followed up by small amounts of other elements such as calcium (2.71%), sodium (2.59%), phosphorus (2.01), chlorine (1.71), magnesium (1.32%), silicon (1.08%), sulfur (0.728%), aluminum (0.302%), iron (0.252%), potassium (0.142%), zinc (0.029%), strontium (0.019%), titanium (0.015%), iodine (0.009%), bromine (0.005%) and copper (0.004%).

2.1.2. FTIR analysis

The infrared spectra analysis as depicted in figure 1 shows the presence of carbonate ion by peaks around 2850 cm^{-1} and 2300 cm^{-1}; also the presence of silica by peak around 1030 cm^{-1}.

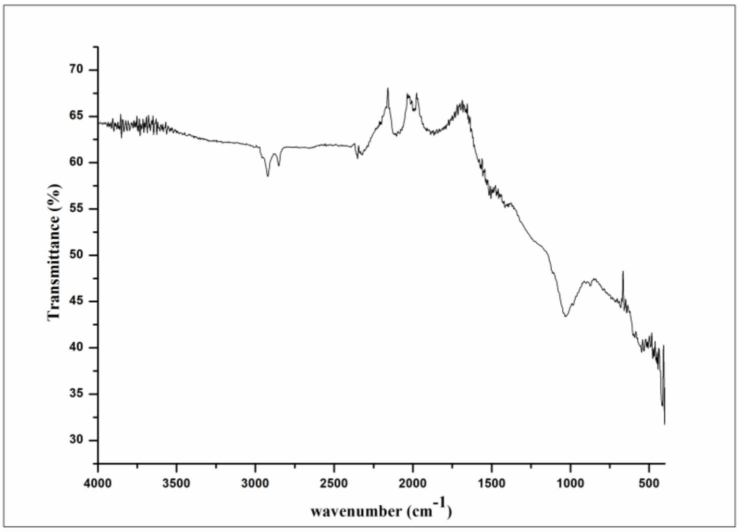

Figure 1. IR spectra of biosorbent (CCL)

2.1.3. XRD analysis

The DRX diffractogram of the CCL sample is presented in figure 2. The intensity of the diffraction peaks mainly observed in the range 2θ = 20-80° is 20.8673°, 26.6418 °, 27.4364°, 29.4410°, 31.5664°, 39.4772°, 45.3652°, 47.5004°, 48.5601°, 59.8923°, and 83.8580°, which confirm the presence of two compounds :calcite ($CaCO_3$) and silicate (SiO_2).

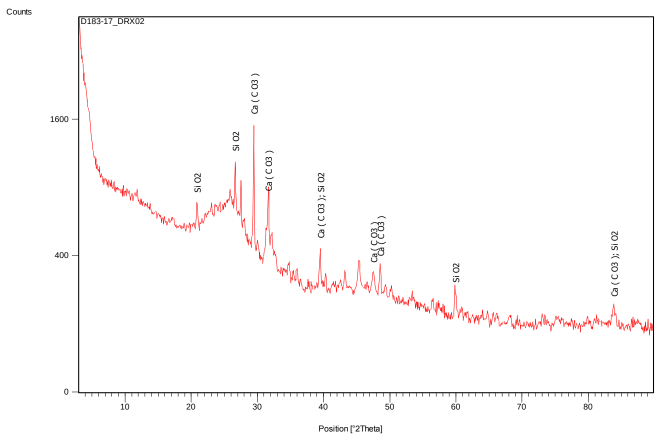

Figure 2. X-ray diffraction of the CCL material

2.1.4. SEM analysis

Scanning electron microscopy was performed to measure the morphological features of the CCL adsorbent. The micrograph of the CCL material shown in figure 3 indicates that the biosorbent has large distribution of grains of different sizes. The specific surface area of CCL was defined by Brunauer-Emmett-Teller (BET) multipoint technique [20] from adsorption-desorption isotherm of nitrogen at its liquid temperature (77K) and was found to be S_p = 15 m^2/g.

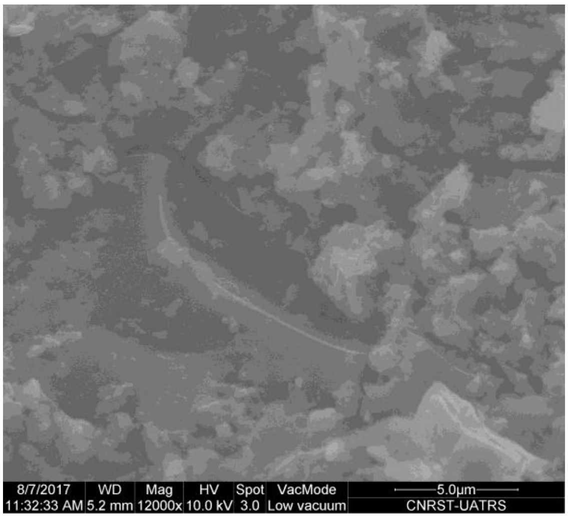

Figure 3. SEM photograph of CCL material

2.1.5. pH point of zero charge

Several methods have been studied to determine the pH point of zero charge; among these methods mentioned in literature are Immersion Technique (IT), Mass Titration (MT) and Potentiometric Mass Titration (PMT) [21-25]. In this paper, we are opted for the salt addition method [26-27] to determine the pH point of zero charge (pHpzc) of CCL, thus provides information about the possible attraction and repulsion that could happen with metal species in solution [28].

A volume of 95mL of 0.01 M sodium chloride (NaCl) solution was used as an electrolyte with an increasing pH values in the range of 3-13 by adding HCl (1N) or NaOH (1N) as needed, with a constant weight of CCL (50 mg) in each beaker using Metrohm pH meter 691, Swiss. The final pH of suspensions was recorded at the equilibrium after 48h of shaking. The difference of pH ($\Delta pH = pH_f - pH_i$) was plotted against the initial pH [29], from figure 4 the value of pH_{PZC} is determined and was found equal to 6.6.

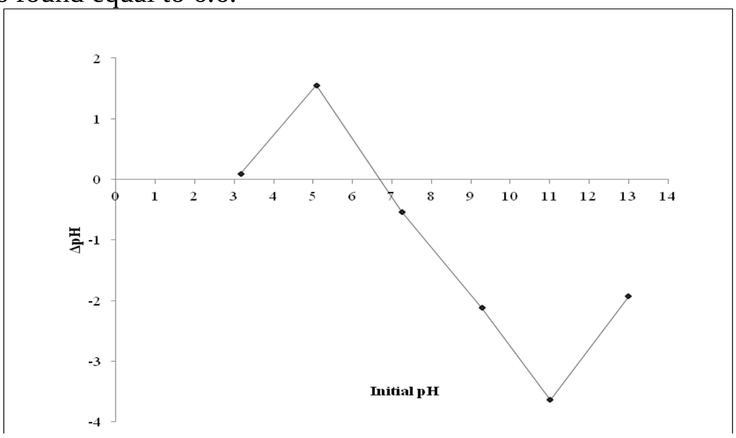

Figure 4. pHpzc of the CCL material

2.2. Adsorption studies

2.2.1. The Effect of pH

It is commonly known, that the pH effect provides information about the ionization of functional groups, different interaction and the surface charge of the adsorbent, as well as the electrostatic force between sorbate and sorbent during biosorption process [30,31]. Therefore, the surface charge of biosorbent can play a fateful role in protonation-deprotonation behavior's characterization of biosorbent and might be helpful to find out the biosorption mechanism of CCL. As shown in figure 5, in the lowest pH range, the uptake of the three metals was approximately small, whereas,

biosorption increased with the increase of pH from 3.0 to 6.0 and maintained in the pH range 6.0 and 13.0. Based on the pH_{pzc} study, the lowest uptake observed at weak pH may be owing to the strong repulsion between copper, zinc, and nickel cations and CCL biosorbent positively charged. At higher pH, the H^+ concentration decreases and the surface of CCL is negatively charged which favors the electrostatic attraction between copper, zinc, and nickel cations and CCL biosorbent. Same results were mentioned by many authors using different adsorbents such as sawdust, activated carbon, fly ash and Bentonite [32-36]. It should be noted that pH maintained at the optimal value of 4.5 for all the subsequent steps of this investigation. Therefore, it is clearly observed that heavy metals ions were not precipitated.

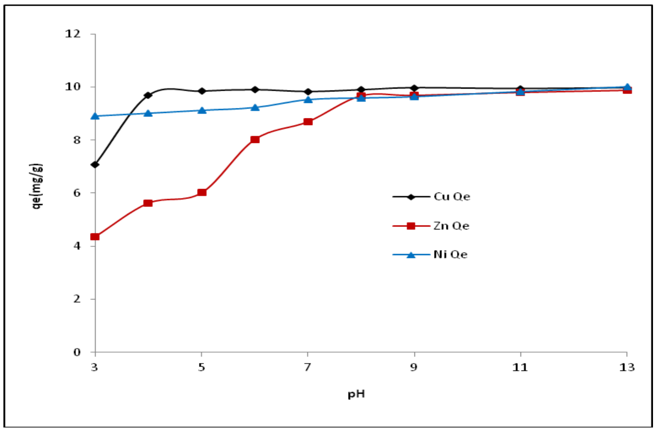

Figure 5. pH effect's of Cu(II), Zn(II) and Ni(II) by adsorption onto CCL

2.2.2. The Effect of contact time

The effect of contact time was investigated at the range of 0-240 min in order to explain its influence on the biosorption efficiency of CCL biosorbent. As depicted in figure 6 for the three metals, the results showed that the uptake of Cu(II), Zn(II) and Ni(II) increases with time until it reached the equilibrium. This may be due to the fill of the biosorbent vacant sites with metal ions when the solution reached the equilibrium at 90min.

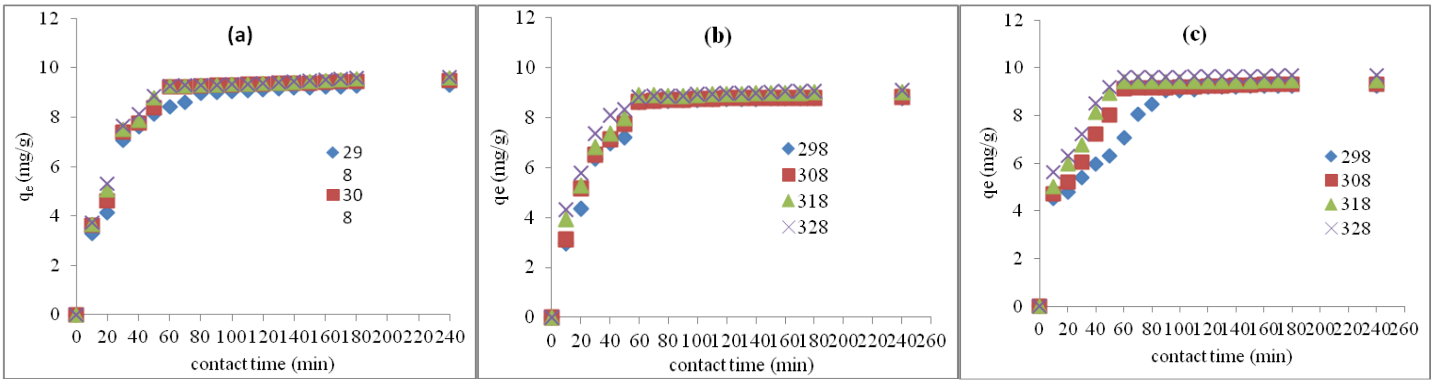

Figure 6. Contact time effect's of heavy metals (a) Cu(II), (b) Zn(II) and (c) Ni(II) by adsorption onto CCL

2.2.3. The Effect of biosorbent dose (CCL)

The result of biosorbent dose's effect on metal ions biosorption presented in figure 7**,** shows the uptake efficiency increment of the three metals Cu(II), Zn(II) and Ni(II) with biosorbent's amount increment from 92.40% to 99.40% for copper (II), from 89.00% to 98.30% for zinc (II) and from 81.00% to 92.40% for nickel (II). Therefore, it is understood that the increment of removal capacity depends on the surface activity of CCL such as the availability of

more vacant sites and the large surface area, which can lead with time to the enhancement of metal ion uptake. So, the optimal value of the biosorbent dose is found to be 50 mg.

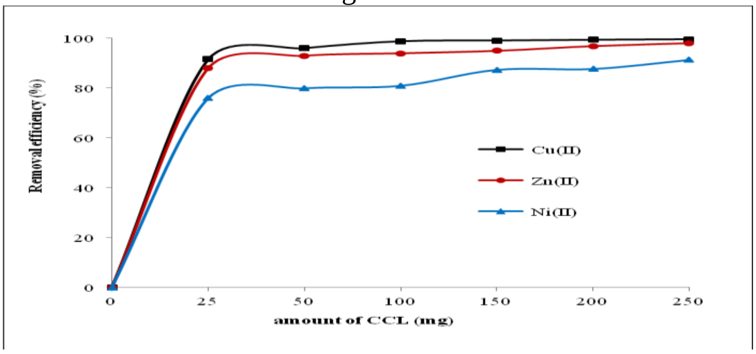

Figure 7. Effect of the adsorbent amount on the uptake of Cu(II), Zn(II) and Ni(II) by adsorption onto CCL

3.2.4. The effect of initial metals concentration

As to evaluate the behavior of the CCL biosorbent, the initial metal ions concentration's effect was examined at the range of 3-15 mg/L and the results are shown in figure 8. Therefore, it is observed that the uptake percentage of Cu(II) decreased from 94.3% to 87.1%, it also decreased for Zn(II) from 90.3% to 69.1% and for Ni(II) from 85.3% to 66.8% with increasing initial metals concentration from 3 to 15 mg/L, due to the saturation of vacant sites that are filled. As it was mentioned similarly elsewhere by adsorption using tea wastes, watermelon seed hulls, and cashew nut shell as biosorbents [37-39]. Therefore, the optimal initial metal concentration is found to be 5 mg/L.

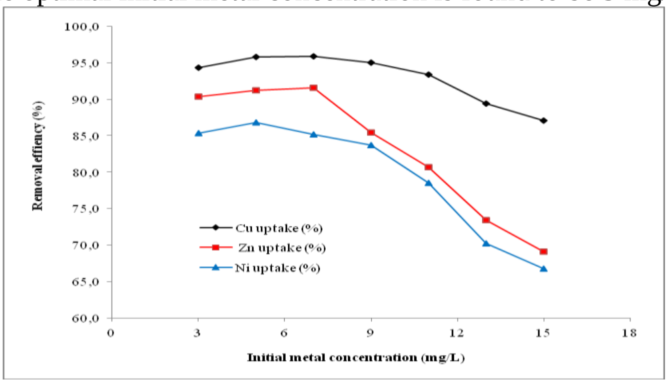

Figure 8. Initial metal concentration effect of Cu(II), Zn(II) and Ni(II) by adsorption onto CCL

2.3. Adsorption Kinetic models

The kinetic study of heavy metals is essential to understand the mechanism of adsorption and the potential constants rate monitoring stages such as chemical reaction and mass transport processes, by testing the pseudo-first-order and the pseudo-second-order models on the CCL particles, represented respectively by the following forms according to Lagergren equation [40,41]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (3)$$

The kinetics data were applied too for the pseudo-second-order model, which is represented by the following expression:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + t\frac{1}{q_e} \qquad (4)$$

Where q_e and q_t are the biosorption's quantities at equilibrium (mg/g) at time t (min), k_1 and k_2 are respectively the rate constant of the pseudo-first-order model (1/min) and pseudo-second-order model (g/mg.min). Table 1 presents the

$K_{ads,1}$, $K_{ads,2}$ and q_e values determined from the two models. As depicted at the table and by comparing q_{exp} with q_{cal} and on the basis of the correlation coefficients R^2, it is clear that the biosorption of Cu(II), Zn(II) and Ni(II) onto CCL biomass fitted most to pseudo-second-order kinetics since the values of q_{cal} and q_{exp} are comparable and R^2 are close to unity for all system Metal-CCL at different temperatures.

Table 1. Lagergren pseudo-first and second order kinetics biosorption for Cu(II), Zn(II) and Ni(II) onto CCL

Adsorbate	T(K)	$q_{e,exp}$ (mg/g)	First-pseudo-order $q_{e,cal}$ (mg/g)	First-pseudo-order $K_{ads,1}$ (min^{-1})	First-pseudo-order R^2	second-pseudo-order $q_{e,cal}$ (mg/g)	second-pseudo-order $K_{ads,2}$ ($g.mg^{-1}.min^{-1}$)	second-pseudo-order R^2
Cu(II)	298	9.254	4.884	0.027	0.742	10.309	0.006	0.993
	308	9.450	3.522	0.026	0.665	10.417	0.007	0.994
	318	9.541	3.418	0.023	0.674	10.526	0.008	0.995
	328	9.583	3.367	0.022	0.676	10.638	0.008	0.996
Zn(II)	298	8.769	4.968	0.039	0.680	9.804	0.006	0.992
	308	8.795	3.971	0.036	0.674	9.615	0.008	0.995
	318	8.995	3.343	0.031	0.650	9.709	0.009	0.996
	328	9.063	2.829	0.024	0.661	9.615	0.012	0.998
Ni(II)	298	9.224	11.989	0.043	0.713	10.753	0.004	0.988
	308	9.310	4.129	0.031	0.676	10.204	0.008	0.995
	318	9.448	2.349	0.039	0.586	10.101	0.011	0.997
	328	9.694	2.277	0.027	0.586	10.204	0.013	0.997

2.3.1. Biosorption isotherms

With a view to investigate the biosorption isotherms when the equilibrium is reached, several models have been developed to predict the adsorption mechanism, which connect the amount of biosorbate on the biosorbent with its pressure (gas) or its concentration (liquid). Among those models, the system was studied using Langmuir, Freundlich, Temkin, Elovich and Dubinin-Radushkevich models, which are widely used by researchers in this field. The Langmuir isotherm model assumes that the quantity of the particles adsorbed is proportional to the surface area (active sites). The surface of the adsorbent containing a monolayer of adsorbing sites (all sites are equivalent), is thus by far supposing that the surface is homogeneous and that there are no interactions (competition) on adjacent sites between adsorbate molecules. The Langmuir isotherm model is given by equation (5) [42, 43]:

$$c_e/q_e = c_e/q_m + 1/q_m k_L \qquad (5)$$

Where q_m is the maximum uptake of copper (II), zinc (II) and nickel (II) ions (mg/g), and K_L (L/mg) is equilibrium constant of adsorption. Moreover, the values of q_m and K_L can be determined from the linear plot of C_e/q_e against C_e. Thus, another indispensable parameter of the Langmuir equation can be expressed to describe the affinity of the adsorption, which is a dimensionless separation factor R_L [44]. It can be defined by the following expression:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (6)$$

The Freundlich model is a specific case of the Langmuir model, which is an empirical equation supposing that adsorption is multilayer and the absorbent surface is heterogeneous. It can be expressed by the following expression [45]:

$q_e = k_f\, c_e^{\ 1/n}$ (7)

Where K_f is the constant of energy and adsorption capacity, and 1/n is an empirical parameter of the adsorption intensity. As stated by Langmuir model, when 1/n > 1 means that the intensity of adsorption is higher. The Temkin model supposes that the heat of adsorption of all molecules in the adsorbent surface would decrease linearly instead of logarithmic manner with the coverage because the b_T factor is taking into consideration the adsorbent-adsorbate interactions [46]. The model is given by the following equation (8):

$q_e = B_T \ln(K_T\, c_e)$ (8)

and

$B_T = RT/b_T$ (9)

The Dubinin–Radushkevich isotherm is usually used to describe the mechanism of adsorption with energy distribution onto a heterogeneous layer. It differentiates between the physical and chemical adsorptions and estimates the characteristic solids porosity and apparent free energy of adsorption. This model is given by the following equation [47]: The resulting values of systems constants are given in table 2.

$q_e = q_m \exp(-\beta\, \varepsilon^2)$ (10)

Table 2. The isotherm models constants for Cu(II), Zn(II) and Ni(II) adsorption onto CCL biosorbent

Metal	Model	Parameters			
Cu(II)	Langmuir	K_L = 2.071 L/mg	q_m = 16.341 mg/g	R_L =0.139	R^2 = 0.960
	Freundlich	K_F = 10.323 $mg^{(1-n)}\, L^n\, g^{-1}$	n = 0.426		R^2 = 0.901
	Temkin	K_T = 16.355 L/mg	B_T = 3.891		R^2 = 0.942
	Elovich	K_E = 4.891 L/mg	q_m = 6.978 mg/g		R^2 = 0.744
	Dubinin–Radushkevich	q_m = 13.993 mg/g	$\beta = 5.09\ 10^{-6}$	E= 313.431 kj/mol	R^2 = 0.904
Zn(II)	Langmuir	K_L = 1.494 L/mg	q_m = 11.701 mg/g	R_L =0.182	R^2 = 0.965
	Freundlich	K_F = 6.410 $mg^{(1-n)}\, L^n\, g^{-1}$	n = 0.342		R^2 = 0.904
	Temkin	K_T = 14.007 L/mg	B_T = 2.547		R^2 = 0.943
	Elovich	K_E = 11.800 L/mg	q_m = 4.042mg/g		R^2 = 0.650
	Dubinin–Radushkevich	q_m = 11.341 mg/g	$\beta = 3.44.10^{-6}$	E= 381.451 kj/mol	R^2 = 0.917
Ni(II)	Langmuir	K_L = 0.831 L/mg	q_m = 12.537 mg/g	R_L =0.286	R^2 = 0.969
	Freundlich	K_F = 5.495 $mg^{(1-n)}\, L^n\, g^{-1}$	n = 0.405		R^2 = 0.899
	Temkin	K_T = 6.614 L/mg	B_T = 2.969		R^2 = 0.908
	Elovich	K_E = 5.886 L/mg	q_m = 5.077 mg/g		R^2 = 0.690
	Dubinin–Radushkevich	q_m = 10.987 mg/g	$\beta = 3.24.10^{-6}$	E= 392.989 kj/mol	R^2 = 0.919

According to the values of Langmuir, Elovich, Freundlich, Temkin and Dubinin-Rdushkevich parameters cited in table 2 and considering the correlation coefficients R^2, the system was most fitted to Langmuir isotherm model, which assumes that biosorption process was a monolayer on homogeneous surfaces. Another factor is needed to give more specification to the Langmuir model is the one of R_L, which indicates that biosorption process is effective when it takes values between 0 and 1 ($0 < R_L < 1$). As noted in table 3**,** R_L takes values lower than one, which indicates that biosorption of Cu(II), Zn(II) and Ni(II), is favorable on the CCL.

2.4. Biosorption Thermodynamics

2.4.1. The temperature's effect

In order to examine the effect of temperature on the biosorption phenomenon, tests were evaluated by varying the temperature from 298 to 328K. These experiments were performed by stirring 50 mg of CCL in 100 mL of each metal contaminated solution separately at desired temperatures and are presented in figure 9. The results obtained in figure 9 showed that the biosorption capacity increases by increasing the temperature from 298 to 328K for Cu(II), Zn(II) and Ni(II) removal, which means that the biosorption is endothermic by nature. Comparable results were achieved by Slimani *et al.* [48] when the study of Cu(II) and Zn(II) adsorption on animal bone meal.

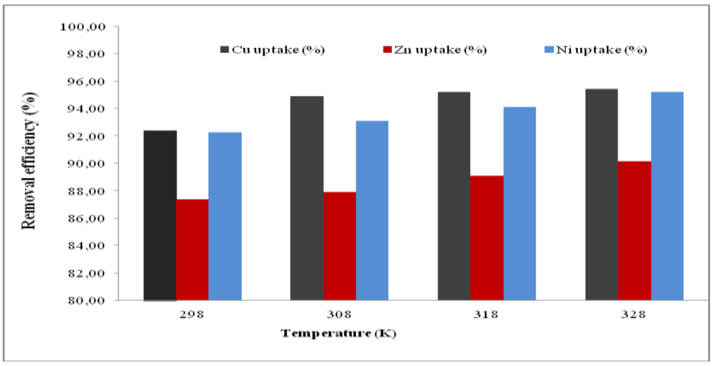

Figure 9. Temperature effect's of Cu(II), Zn(II) and Ni(II) by biosorption onto CCL

2.4.2. Thermodynamics parameters

Series of biosorption experiments occurred to the point of estimating, from equilibrium constants at different temperatures the thermodynamic settings such as enthalpy variation (ΔH°), free energy (ΔG°) and entropy variation (ΔS°). The subsequent study reflects the achievability and the spontaneous nature of the biosorption process. The free energy variation (ΔG°) of the adsorption reaction is expressed by the following equation [49-52]:

$$\Delta G° = -RT.\ln K_c \qquad (11)$$

Where $\Delta G°$ is the variation of free energy ($J.mol^{-1}$), R is the universal constant of gases ($8.314\ J.mol^{-1}.K^{-1}$), T is the absolute temperature (K), and K_c is the equilibrium constant. The values of $\Delta H°$ and ΔS° can be obtained from the equation of Van'tHoff as expressed below The plot of $\ln K_c$ versus 1/T (figure 10) is a line of slope ($\Delta H°/R$) and intercepts ($\Delta S°/R$):

$$\ln K_c = -\Delta H°/RT + \Delta S°/R \qquad (12)$$

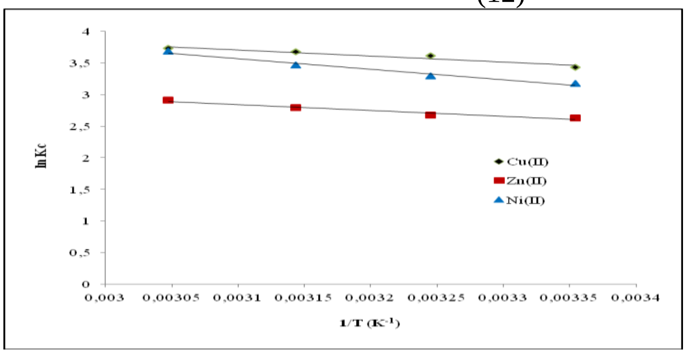

Figure 10. The plot of $\ln K_c$ vs. 1/T for the biosorption of Cu(II), Zn(II) and Ni(II) onto CCL

The thermodynamic parameters were obtained from the experimental data at the different temperatures and listed as follows in table 3.The endothermic nature of the process is confirmed by the positive value of free enthalpy. The

negative values of Δ*G*° indicate that the biosorption of the heavy metals on calcined cow leather is spontaneous [53]. On the other hand, the positive values of the free entropy Δ*S*° indicate the compatibility of the biosorbent and the random positioning of the biosorbate on the solid sorbent layer during the operation of biosorption.

Table 3. Thermodynamic parameters for the biosorption of Cu(II), Zn(II) and Ni(II) onto CCL

Biosorbate	T(K)	Δ*G*° (J/mol)	Δ*H*° (J/mol)	Δ*S*° (J/mol.K)
Cu(II)	298.15	-8495.13	17276.492	85.551
	308.15	-9265.92		
	318.15	-9735.32		
	328.15	-10175.61		
Zn(II)	298.15	-6519.16	7711.24	47.531
	308.15	-6856.17		
	318.15	-7390.79		
	328.15	-7934.48		
Ni(II)	298.15	-7861.22	13776.30	72.348
	308.15	-8442.42		
	318.15	-9158.80		
	328.15	-10047.29		

3. CONCLUSION

This study has demonstrated the effectiveness of the calcined cow leather for the decontamination of wastewaters from heavy metals. The effect of parameters such as the amount of the adsorbent, contact time, the pH, the initial concentration of heavy metals and the temperature have been examined to determine the optimum operational conditions. The kinetic study has shown that the biosorption mechanism can be better described by the pseudo-second-order model. The plot of the biosorption isotherms has shown that the Langmuir model represents perfectly the biosorption of heavy metals on the calcined cow leather with a maximum biosorption capacity. The thermodynamic data acquired have indicated that the biosorption of heavy metals on CCL is a spontaneous and endothermic process. The Calcined cow leather powder has been found to be a carrier, which has generally a high biosorption affinity to eliminate heavy metals. The abundance of this biomaterial can provide a low-cost adsorption material that can potentially contribute to the treatment of industries liquid effluents.

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