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The Thermodynamics of Heavy Metal Sorption onto Lignocellulosic Biomass

Carlos Escudero-Oñate and Isabel Villaescusa

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Abstract

The sorption equilibrium and thermodynamics of Cu(II), Ni(II), Pb(II), and Cd(II) onto grape stalks (GS), a lignocellulosic waste from wine production industries, have been investigated. Different equilibrium models have been assessed to describe the experimental sorption equilibrium profile in the range of 5–60°C. Maximum sorption capacities have been calculated by means of Langmuir equilibrium model and mean free sorption energies through the Dubinin-Radushkevich (D-R) model. Mean free energies suggest that metal sorption takes place mainly through an ion exchange mechanism, except for Pb(II), where an additional contribution connected to a stronger bond might take place. The calculation of thermodynamic parameters, ΔG^0, ΔH^0 and ΔS^0, puts into evidence that the sorption of all the metals onto GS is a spontaneous and exothermic process that occurs with an increase of randomness at the solid/liquid interface.

Keywords: sorption, divalent metals, lignocellulosic sorbent, isotherm, thermodynamic

1. Introduction

Metals can enter the environment through a large variety of processes such as weathering of soils and rocks, volcanoes, and from a variety of anthropogenic activities [1, 2]. From the anthropogenic sources, modern industry is, to a large degree, a major responsible of environmental pollution. They are frequently released into the soil and water as from various polluting sources, such as foundries, tanneries, textile, microelectronic, fertilizer and pesticide industries, mining activity and other industrial activities [3]. These inorganic species occur naturally as ions, compounds and complexes, and they can lead to health problems

and degradation of natural environments due to their toxicity and persistent character. Developing sustainable and environmentally friendly technologies to remove toxic metal from industrial effluents is a relevant topic nowadays.

Several remediation techniques to remove metal ions from aqueous solutions are available, which range from traditional physico-chemical methods to emerging bioremediation methods [3–10]. Methods that have been successfully deployed in industrial environments include the use of physico-chemical processes such as chemical precipitation, ion exchange, oxidation/reduction, reverse osmosis and electrochemical treatment [2, 11–13]. These methods however exhibit a set of drawbacks such as high acquisition and operation costs, low performance at relatively low—but still relevant—concentration of metals and being sources of secondary pollution [14–16]. To overcome the aforementioned issues, bioremediation-based methods have appeared as potential candidates in the treatment of heavy metal effluents. Bioremediation methods include bioaccumulation, biosorption and phytoremediation. Biosorption in some cases has demonstrated an outstanding potential, comparable to the performance obtained in ion exchange-based methods.

In regular sorption studies, the performance of a sorbent is evaluated by studying the kinetics of the process and assessing the amount sorbed versus the sorbate concentration in solution at equilibrium to get the isotherm curve. Obtaining the characteristics sorption isotherms themselves do not provide automatically any information about the reaction involved in the sorption phenomenon [17]. The study of the effect of temperature on the sorption process and the evaluation of the thermodynamic properties such as Gibb's free energy, enthalpy and entropy of the process provide valuable information about the strength of the interactions between sorbate and sorbent and the energy associated with the sorption process. The standard free energy of the reaction (ΔG^0, J·mol^{-1}) is the difference between the initial state (free solute compound)and the final equilibrated state (sorbed compound), and the parameter is related to the spontaneity of the sorption process. Negative values of ΔG^0 indicate that the process is spontaneous. The magnitude of the enthalpy of the process (ΔH^0, kJ·mol^{-1}) gives an idea about the type of sorption interactions (physical or chemical). Whilst in physisorption-based processes enthalpy range is comprised between 2.1 and 20.9 kJ·mol^{-1}, higher enthalpy values are characteristic from chemisorption (20–800 kJ·mol^{-1}) [18]. The value of the change of enthalpy $\Delta H^0 < 0$ or $\Delta H^0 > 0$ also suggests the character exothermic or endothermic of the process, respectively.

The change of entropy (ΔS^0) reflects essentially the variation on the disorder of a system (on macroscopic level) along a process. A positive value of this parameter indicates increased randomness at the solid/solution interface that may also include some changes in the sorbent and sorbate structure. Moreover, $\Delta S^0 > 0$ implies an increase in the degree of freedom of the adsorbed species. The negative value of change of entropy ($\Delta S^0 < 0$) suggests that the adsorption process involves an associative mechanism. Also a negative value of ΔS^0 implies a decreased disorder at the sorbent/solution interface during the sorption process causing the sorbate species to escape from the solid phase to the solution phase.

In this chapter, the sorption equilibrium of Cu(II), Ni(II), Pb(II), and Cd(II) onto a lignocellulosic material, grape stalks (GS), has been investigated. The studies were performed at different temperatures and allowed gathering relevant thermodynamic parameters to better describe the interactions established between the divalent metals and the sorbent.

2. Effect of temperature on Cu(II), Ni(II), Pb(II) and Cd(II) equilibrium

The residues of grape stalk (GS) obtained from a wine production industry were washed with distilled water, cut in small pieces, dried and ground to obtain a sorbent with a particle size range 0.25–0.50 mm. The sorption equilibrium of Cu(II), Ni(II), Pb(II) and Cd(II) in single metal solutions onto GS was explored at different temperatures within the range of 5–60°C. The characteristic sorption isotherms were obtained contacting 0.1 g of GS powder with 15 mL of different Cu(II), Ni(II), Pb(II) and Cd(II) solutions within the initial concentration range of 5–1000 mg·L^{-1}. Stoppered glass tubes were employed, and the initial pH was adjusted to 5.2. For an accurate temperature control, the samples were placed in an incubator (ICP-500, Memmert). After equilibration of the sorbent biomaterials with the metal solutions for 24 hours, the samples were filtered and acidified adding 100 μL of ultra-high-quality HNO$_3$, and metal concentration in solution was determined by flame atomic absorption spectrophotometry (Varian SpectrAA 220FS).

From the experimental sorption equilibrium results, thermodynamic parameters related to the affinity and energy of the sorbent-sorbate interaction were obtained and discussed.

2.1. Sorption isotherms

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms and reflect the relationship between the quantity adsorbed and that remaining in solution at a given temperature [19]. Sorption isotherms provide essential information for optimization of the adsorption mechanism pathways since they are expression of the surface properties and capacities of the sorbents. They become therefore relevant tools in the design of sorption systems, since they help understanding how sorbates interrelate with the sorbent materials [20].

Cu(II), Ni(II), Pb(II) and Cd(II) sorption isotherms onto GS for the different temperatures explored were obtained by plotting the amount of metal adsorbed per GS sorbent mass unit (q_e; mol·g^{-1}) as a function of the remaining metal concentration in solution (C_e; mol·L^{-1}). The amount of sorbed metal was computed according to the equation presented below:

$$q_e = \frac{(C_0 - C_f)}{m} * V \tag{1}$$

where C_o and C_f are the initial and final metal concentration in solution, respectively (mol·L^{-1}), m(g) is the sorbent mass (g) and V(L) represents the volume of the solution. The characteristic isotherms are presented in **Figure 1**. This figure clearly demonstrates that the amount of metal sorbed increases as it does the remaining metal concentration in solution until a maximum value is achieved. In the studied range, the temperature seemed not to have a clear effect on the maximum sorption capacity of GS for the divalent metals, except for Cu(II). In this case, the increase of temperature involved an increase on the maximum sorption capacity at equilibrium from 0.22 mmol·g^{-1} (at 5°C) to approximately 0.28 (at 60°C). The experimental Cu(II), Ni(II), Pb(II) and Cd(II) sorption equilibrium results onto GS were submitted to Langmuir, Freundlich and D-R models. The different models and the results obtained are presented and discussed in the next section.
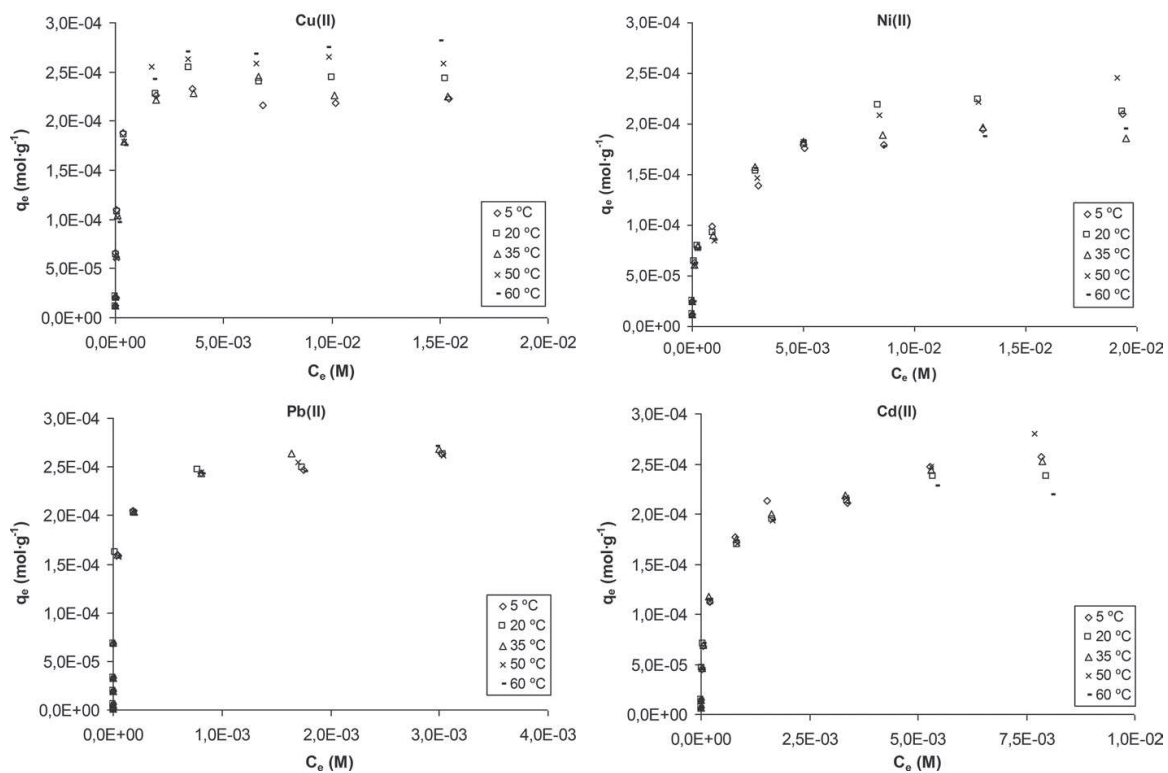
Figure 1. Sorption isotherms of Cu(II), Ni(II), Pb(II) and Cd(II) onto GS. T: 5–60°C.

2.2. Modeling and calculation of sorption equilibrium parameters

The equilibrium adsorption isotherms are one of the most important data that help understanding the sorption mechanism/s and provide fundamental insight for optimization and scale-up of sorption-based processes. Among the different isotherm models available, three of the most representative and largely employed have been chosen for this study: Langmuir, Freundlich and D-R isotherms.

The Langmuir model involves homogenous distribution of sorption sites and is based on the next set of assumptions: (i) the maximum sorption capacity corresponds to a saturated monolayer of solute in the surfaces, (ii) all the active sites are equivalent and the sorption energy remains constant, and (iii) there is no migration of adsorbed species in the plane of the surfaces. From this model, the maximum uptake, q_{max} (mol·g^{-1}), and the Langmuir constant, K_L (L·mol^{-1}), can be obtained. While q_{max} reflects the maximum uptake of the sorbent, the parameter K_L is a constant related to the energy of adsorption that quantitatively reflects the affinity between the sorbent and the sorbate. Fitting the experimental dataset to the Langmuir model, the effect of the temperature and of the nature of the metal on the different sorption equilibriums can be ascertained. By means of the Langmuir constant, it can also be discussed whether an adsorption system is favorable or unfavorable. The essential feature of the Langmuir isotherm can be expressed by means of the parameter R_L, a dimensionless constant referred to as separation factor or equilibrium parameter. R_L is calculated using the following equation [15, 21–27]:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \tag{2}$$

being K_L the Langmuir constant (L·mol^{-1}) and C_0 the initial metal concentration (mol·L^{-1}). The R_L parameter is considered as a reliable indicator of the adsorption being the next four the possible situations [15, 25] (**Table 1**).

The Freundlich model is based in an empirical equation largely employed in the description of sorption processes in heterogeneous systems. On its linear form, the Freundlich equation takes the form:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

where K_F and 1/n are empirical constants indicate of the relative sorption capacity and sorption intensity, respectively.

The experimental dataset was also submitted to the D-R isotherm model. The selection of this model was supported by the fact that it is considered as more general than Langmuir and it does not rely necessarily in the formation of a homogenous monolayer surface or a constant adsorption potential. D-R model has been used by several authors to distinguish between physical and chemical adsorption onto different biomaterials [28, 29]. This model can be linearized and described by the next equation:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{4}$$

being β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2·J^{-2}), q_m is the theoretical saturation capacity of the monolayer and ε is the Polanyi potential. The expression of this last parameter is RTln(1 + (1/C$_e$)), being R (8.314 J·mol^{-1}·K^{-1}) the gas constant and T (K) the absolute temperature. Hence, by plotting ln(q$_e$) against ε^2, it is possible to generate the value of q$_m$ (mol·g^{-1}) from the intercept and the value of β from the slope.

The constant β provides information about the mean free energy, E (J·mol^{-1}). The parameter E is defined as the free energy change required to transfer 1 mol of sorbate from the solution to the solid surface and can be calculated using the relationship [30, 31]:

$$E = \frac{1}{\sqrt{2\beta}} \tag{5}$$

The fitting of the experimental sorption datasets to the linearized expressions of Langmuir, Freundlich and D-R adsorption isotherms for the different temperatures explored is presented

R_L value	Type of isotherm
>1	Unfavorable
1	Linear
0 < R_L < 1	Favorable
0	Irreversible

Table 1. The isotherm characteristics according to the R_L value.

in **Figures 2–4**, respectively. The separation factor (R_L) calculated for the different initial metal concentrations has been also plotted and is presented in **Figure 5**.

From the linear plots of the different isotherm models, the characteristic sorption parameters of the divalent metals onto GS were calculated and are presented in **Table 2**. The separation factor (R_L) has been also plotted for the different initial metal concentrations and temperatures (**Figure 5**). As it may be observed, all the R_L values are found in the range $0 < R_L < 1$, indicating that the sorption of all the metals onto GS is a favorable process regardless on the initial concentration.

According to the R^2 values presented in **Table 2**, the best fitting to the experimental dataset is provided by the Langmuir model. In general, the calculated values of maximum capacity and affinity M(II)-GS obtained through this model indicate that there is not a dramatic effect of the temperature on the sorption process. Cu(II), however, seems exhibiting a slight increase on maximum sorption capacity when the temperature is increased.

When Q_{max} is compared at a standard temperature of 20°C, it can be observed that a very similar capacity (about $2.5 \cdot 10^{-4}$ mol·g^{-1}) is achieved regardless of the metal. The Q_{max} values obtained at 20°C through the Langmuir model for the four metals is in agreement with previously reported data [32, 33]. The effect of temperature on the strength of the interaction sorbent-sorbate will be explored later by calculating specifically the thermodynamic parameters of the adsorption process.

The modeling of the experimental dataset according to the D-R equation was also able to provide a good fitting of the experimental trends observed. This model allowed computing the mean
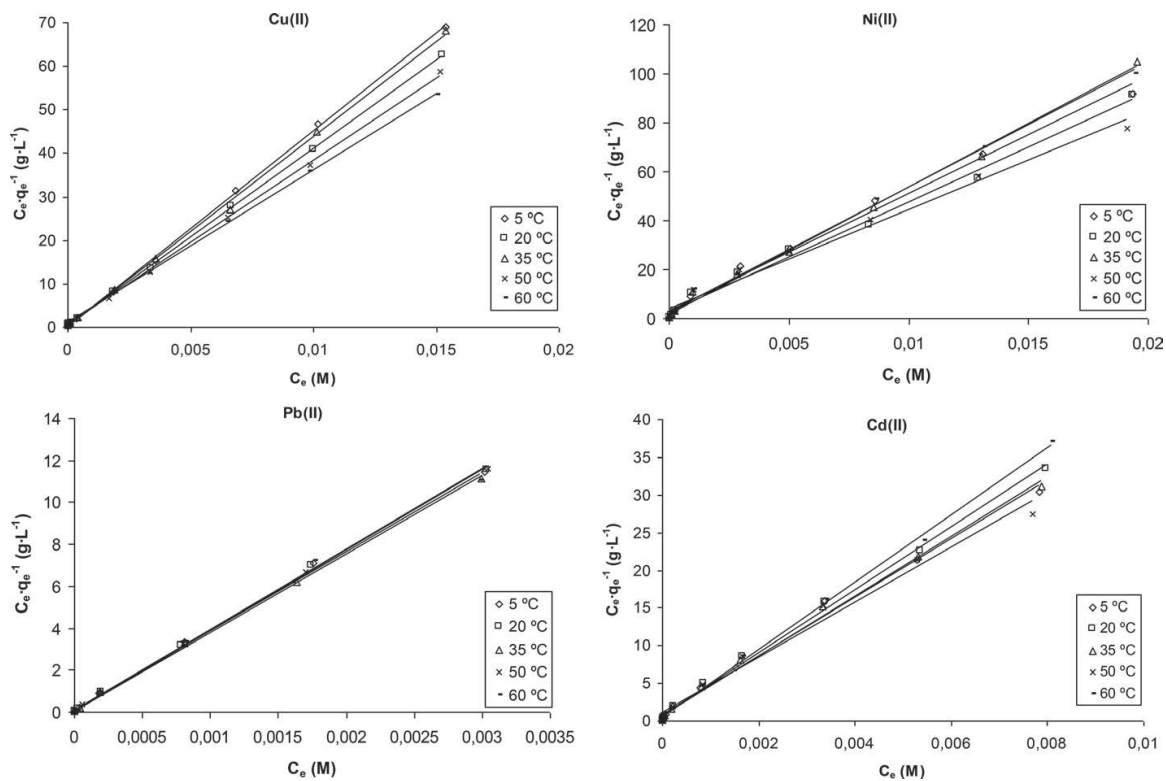

Figure 2. Langmuir model fitting of Cu(II), Ni(II), Pb(II) and Cd(II) sorption results in the temperature range of 5–60°C.
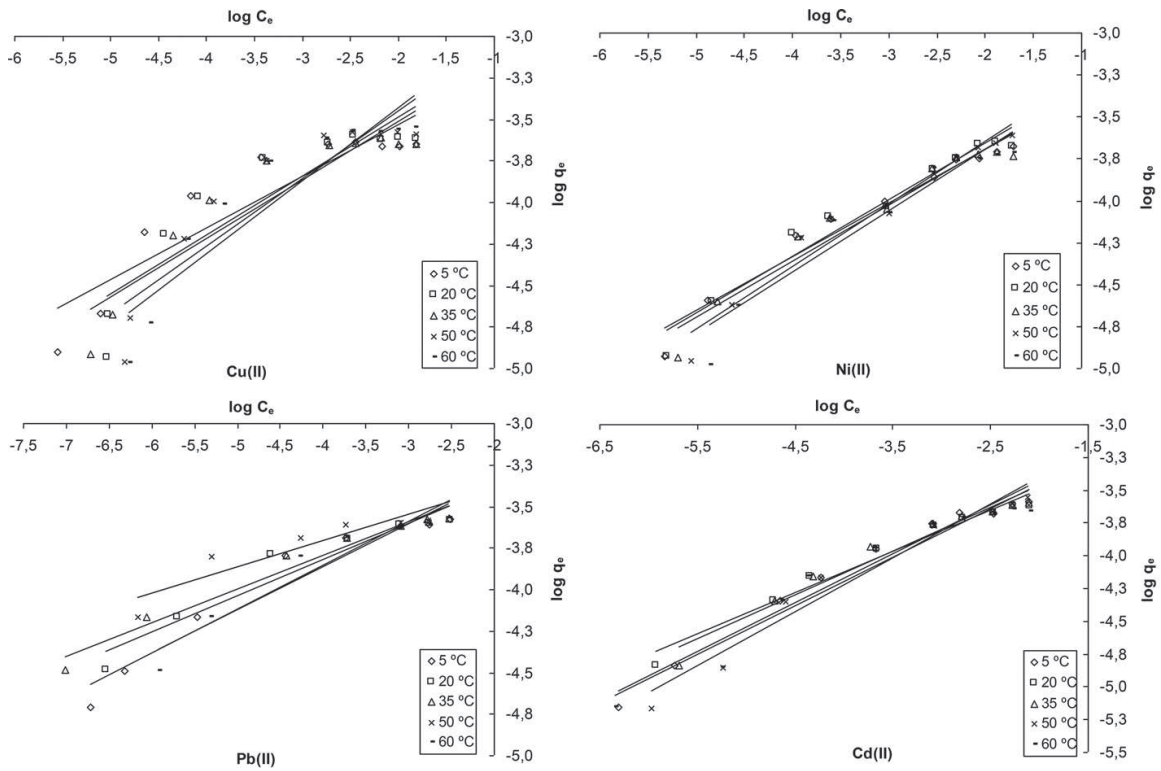
Figure 3. Freundlich model fitting of Cu(II), Ni(II), Pb(II) and Cd(II) sorption results in the temperature range of 5–60°C.
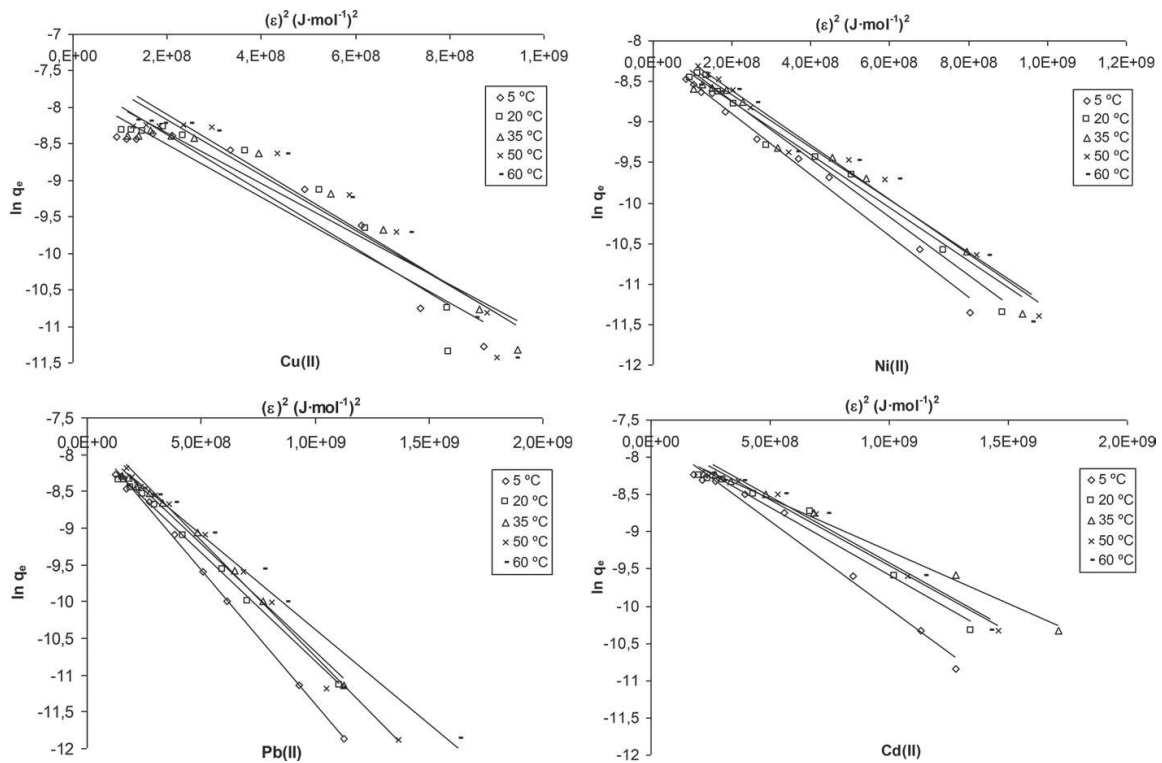

Figure 4. Dubinin-Radushkevich model fitting of Cu(II), Ni(II), Pb(II) and Cd(II) sorption results in the temperature range of 5–60°C.
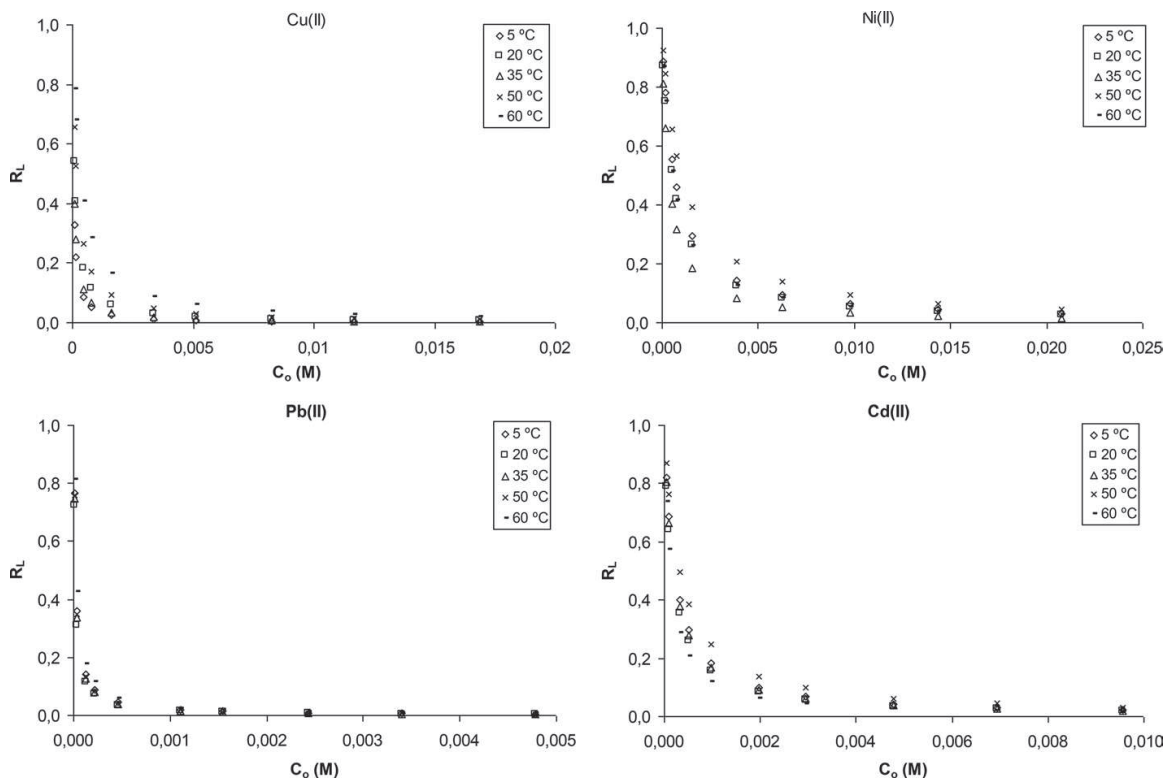
Figure 5. Variation of adsorption intensity (R_L) for Cu(II), Ni(II), Pb(II) and Cd(II) with the initial metal concentration in the temperature range of 5–60°C.

free energy of adsorption E (kJ·mol^{-1}) according to Eq. (5). This parameter provides useful information that allows classifying the adsorption mechanism as chemical ion exchange or physical adsorption. If the magnitude of E is between 8 and 16 kJ·mol^{-1}, the adsorption process follows a chemical ion exchange [15, 30]. On the other hand, values of E < 8 kJ·mol^{-1} indicate that the adsorption process is of a physical nature [34]. Values higher than 16 kJ·mol^{-1} would be indicative of more energetic interactions than the corresponding to an ion exchange process. As it can be seen in **Table 2**, the values of adsorption mean free energies are in the range 8 < E (kJ·mol^{-1}) < 16 for Cu(II), Ni(II) and Cd(II) sorption at all the temperatures and for Pb(II) at the lowest one, 5°C. These results point out that Cu(II), Ni(II) and Cd(II) sorption onto GS at all the studied temperatures and Pb(II) sorption at 5°C proceeds mainly via ion exchange. For Pb(II) at the temperature of 20°C and higher, the values in the range 16.64 < E < 18.81 indicate that there is an extra contribution to sorption by ion exchange and stronger Pb(II)-GS bonds are being formed.

With the dataset generated in the equilibrium experiments performed at different temperatures, the characteristic thermodynamic parameters of Cu(II), Ni(II), Pb(II) and Cd(II) sorption onto GS were calculated.

2.3. Thermodynamic parameters of adsorption

The temperature dependence of the sorption process is associated with several thermodynamic parameters that allow concluding whether the process is spontaneous or not. The Gibbs free energy change, ΔG^0, is an indicative of the spontaneity of a chemical reaction, and

		Langmuir			Freundlich			Dubinin-Radushkevich			
Metal	T (°C)	$Q_{max} \cdot 10^4$ (mol·g^{-1})	$K_L \cdot 10^{-4}$ (L·mol^{-1})	R^2	1/n	K_F	R^2	$Q_{max} \cdot 10^4$ (mol·g^{-1})	$\beta \cdot 10^9$ (mol²·kJ^{-2})	E (kJ·mol^{-1})	R^2
Cu(II)	5	2.22	2.34	0.999	0.31	2.04	0.836	4.20	3.61	11.76	0.913
	20	2.46	0.97	0.999	0.36	2.26	0.824	5.04	3.89	11.34	0.895
	35	2.29	1.72	0.998	0.31	2.02	0.858	4.67	3.44	12.06	0.931
	50	2.69	0.60	0.999	0.41	2.55	0.840	6.07	3.78	11.50	0.919
	60	2.85	0.32	0.999	0.44	2.75	0.859	6.64	3.88	11.35	0.926
Ni(II)	5	2.09	0.15	0.992	0.32	2.09	0.976	2.93	3.79	11.49	0.913
	20	2.22	0.18	0.993	0.34	2.17	0.958	3.24	3.58	11.82	0.895
	35	1.93	0.28	0.997	0.33	2.16	0.941	3.06	3.28	12.35	0.931
	50	2.45	0.10	0.986	0.37	2.36	0.958	3.55	3.37	12.18	0.919
	60	1.97	0.18	0.997	0.37	2.32	0.914	3.31	3.23	12.44	0.926
Pb(II)	5	2.61	4.71	0.999	0.37	2.35	0.972	4.67	2.36	14.55	0.913
	20	2.60	5.86	0.999	0.31	2.06	0.972	4.22	1.81	16.64	0.895
	35	2.68	5.23	0.999	0.33	2.15	0.957	3.92	1.41	18.81	0.931
	50	2.61	4.95	0.994	0.41	2.55	0.957	4.59	1.76	16.84	0.919
	60	2.65	3.55	0.997	0.37	2.34	0.940	4.81	1.77	16.80	0.926
Cd(II)	5	2.57	0.46	0.993	0.26	1.83	0.938	4.37	3.66	11.69	0.913
	20	2.40	0.56	0.997	0.22	1.65	0.926	3.84	2.95	13.03	0.895
	35	2.52	0.51	0.995	0.20	1.59	0.966	4.33	2.93	13.06	0.931
	50	2.73	0.31	0.985	0.16	1.44	0.850	5.02	3.15	12.60	0.919
	60	2.24	0.76	0.998	0.26	1.81	0.921	4.12	2.58	13.92	0.926

Table 2. Adsorption isotherm constants for the adsorption of cu(II), Ni(II), Pb(II) and cd(II) onto GS as a function of temperature.

therefore, it is an important criterion when it comes to spontaneity assessment of a sorption process. Both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if ΔG^0 has a negative value, and this parameter can be determined from the following equation:

$$\Delta G^0 = -RT \ln K_L \tag{6}$$

being R the ideal gas constant (8.314 J·mol^{-1}·K^{-1}) and T the absolute temperature (K). Besides, the standard Gibbs free energy can be defined in terms of enthalpy (ΔH^0) and entropy (ΔS^0) using the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{7}$$

Including the Langmuir equilibrium constant (K_L) in the Van't Hoff equation, the enthalpy and the entropy of the process can be calculated:

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{8}$$

From the equation presented above, the values of ΔH^0 and ΔS^0 can be determined using the slope and the intercept of the plot of ln K_L versus 1/T. ΔG^0, ΔH^0 and ΔS^0 were calculated for the different temperatures, and the results are presented in **Table 3**.

The negative values of ΔG^0 observed for all the M(II)-GS systems indicate that the sorption process is feasible and spontaneous. The negative ΔH^0 values obtained for the sorption of all the metals indicate that the sorption process is also exothermic. It is worth noting that, from the four metals, the sorption of Cu(II) is the process that involves a higher exchange of energy, releasing about 17.5 kJ per mol of sorbed metal. The sorption of other three metals involved a much lower energy release, varying from about 6 kJ·mol^{-1} in the case of Cd(II) to just 1.30 kJ·mol^{-1} in the case of Ni(II).

On the other hand, the positive values of ΔS^0 indicated that the randomness at the solid/liquid interface increases during the adsorption of these divalent metal ions onto GS [22]. A probable explanation for the observed increase of the disorder can be based on the fact that the adsorbed water molecules (which are displaced by the adsorbate species when metals are transferred from the liquid to the solid phase) gain more translational energy than the energy lost by the adsorbate ions [35].

To display the effect of the temperature on the spontaneity of the sorption process, the values of ΔG^0 obtained for the different metals have been plotted as a function of temperature in **Figure 6**.

As it may be observed in **Figure 6**, ΔG exhibits a general decreasing trend when the temperature of the system increased. The thermal effect in the spontaneity of the sorption process can be also assessed through the numerical values of the slopes of the plot for the different metals: Cu(II), −19.26; Ni(II), −56.01; Pb(II), −76.60; and Cd(II), −76.57. The negative values

Metal	T (°C)	ΔG^0 (kJ·mol^{-1})	ΔH^0 (kJ·mol^{-1})	ΔS^0 (J·mol^{-1}·K^{-1})
Cu(II)	**5**	−23.27		
	20	−22.38		
	35	−24.98	−17.48	19.99
	50	−23.36		
	60	−22.31		
Ni(II)	**5**	−16.95		
	20	−18.26		
	35	−20.34	−1.30	57.45
	50	−18.54		
	60	−20.79		
Pb(II)	**5**	−24.88		
	20	−26.76		
	35	−27.83	−3.45	78.32
	50	−29.04		
	60	−29.02		
Cd(II)	**5**	−19.52		
	20	−21.05		
	35	−21.87	−5.99	57.34
	50	−21.63		
	60	−24.76		

Table 3. Thermodynamic parameters of Cu(II), Ni(II), Pb(II) and Cd(II) sorption onto GS at different temperatures.

obtained indicate that the sorption process is spontaneous, being Pb(II) and Cd(II) the most temperature-sensitive metals.

The values of variation of enthalpy, entropy and Gibbs free energy presented in **Table 3** allow establishing a different set of comparisons between the different metals. So, in basis to the energy released when the metal is adsorbed, the next ranking can be drafted out:

ΔH^0:   Cu > Cd > Pb > Ni

In basis to the increase of randomness that metal sorption provokes in the system:

ΔS^0:   Pb > Ni ≈ Cd > Cu

And lastly, in basis to a more general criterion of spontaneity of the sorption process for temperatures within 5 to 50°C:
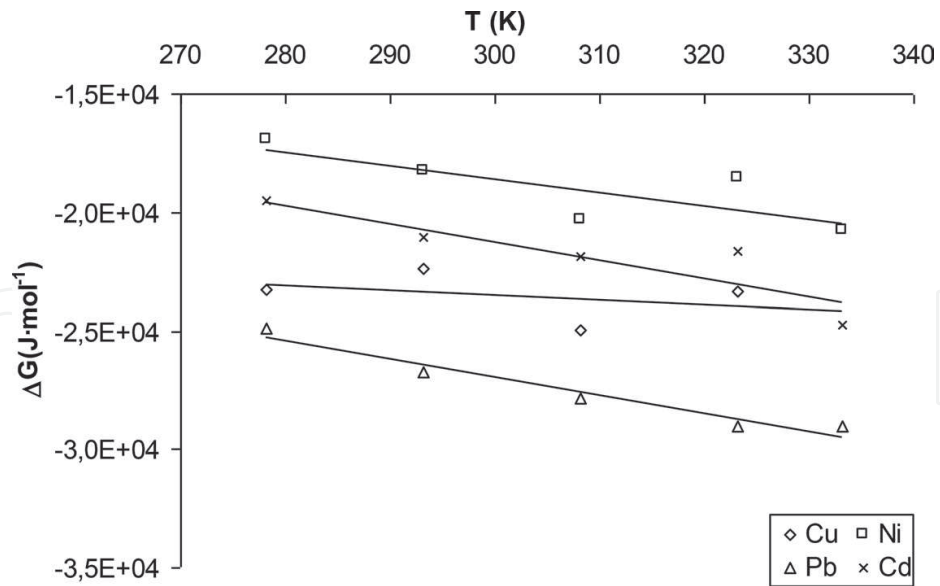
ΔG^0 (5–50°C): Pb > Cu > Cd > Ni.

Figure 6. Variation of Gibbs free energy with temperature for in all the M(II)-GS systems.

Sorbent	Metal	ΔG^0 (kJ·mol⁻¹)	ΔH^0 (kJ·mol⁻¹)	ΔS^0 (J·mol⁻¹)	Reference
Grape stalks	Cu(II)	−22.38	−17.48	19.99	This work
	Ni(II)	−18.26	−1.30	57.45	
	Pb(II)	−27.83	−3.45	78.32	
	Cd(II)	−21.05	−5.99	57.34	
Cellulosic waste orange peel	Cu(II)	−12.48	−19.55	−24.12	[24]
Corn silk (*Zea mays* L)	Cu(II)	−17.10	10.75	95.08	[36]
	Zn(II)	−16.68	7.83	83.68	
Pseudomonas putida	Pb(II)	−21.20	−18.69	8.4	[37]
	Cu(II)	−16.50	23.12	128	
Hazelnut shells	Ni(II)	−15.05	32.49	158.54	[35]
	Pb(II)	−20.94	21.41	142.11	
	Cd(II)	−20.80	12.21	110.73	
Almond shells	Ni(II)	−12.36	47.29	199.00	
	Pb(II)	−21.57	50.55	233.32	
	Cd(II)	−17.45	17.76	118.28	
Capsicum annuum	Cu(II)	−15.93	−7.63	28.35	[22]
Modified spent Chrysanthemum	Cu(II)	−25.19	−11.42	47.0	[25]
Rapeseed biomass	Pb(II)	−35.33	10.05	155.0	[38]

Sorbent	Metal	ΔG^0 (kJ·mol^{-1})	ΔH^0 (kJ·mol^{-1})	ΔS^0 (J·mol^{-1})	Reference
Bacillus pumilus sp. *AS*1	Pb(II)	−0.56	7.53	0.027	[39]
Loquat (*Eriobotrya japonica*) leaves	Cd(II)	−8.21	29.73	125.44	[40]
Sargassum filipendula	Cd(II)	−3.82	0.26	0.87	[41]
Penicillium simplicissimum	Cd(II)	−18.27	20.03	130.9	[42]
	Zn(II)	−17.08	25.42	145.5	
	Pb(II)	−20.04	39.13	202.5	
Sporopollenin	Cu(II)	−7.54	17.55	85.58	[43]
	Pb(II)	−13.78	31.97	150.98	
	Cd(II)	−8.85	13.99	76.64	

Table 4. Comparison of the sorption thermodynamic parameters obtained for GS with these observed for other biomass.

It has to be remarked however that for the highest temperature, 60°C, an inversion on the spontaneity of the sorption process takes place between Cd(II) and Cu(II), getting therefore the ranking the next form:

ΔG^0 (60°C): Pb > Cd > Cu > Ni.

The thermodynamic results gathered in our study have been compared to those reported by other authors. A summary of the most relevant results found in a bibliographic survey are presented in **Table 4**.

As it can be observed, all the authors reported negative values of ΔG^0 and most of them also positive values of ΔS^0. These results clearly indicate that sorption is a spontaneous process that mostly takes place with an increase of the randomness of the system. On the other hand, the ΔH^0 values reported were either positive or negative. Sorption processes showing negative enthalpy values would be the sorption of Cu(II), Ni(II), Pb(II) and Cd(II) onto GS (this work), Pb(II) sorption onto *Pseudomonas putida* and Cu(II) sorption onto both, *Capsicum annuum* and modified spent chrysanthemum. On the other hand, positive enthalpy values were reported for Cu(II) sorption onto *Pseudomonas putida*, Ni(II), Pb(II) and Cd(II) sorption onto both, hazelnut and almond shells, or Cu(II), Pb(II) and Cd(II) sorption onto sporopollenin. Thus, these results indicate that metal sorption might take place through release or absorption of energy to or from the system.

3. Conclusions

The sorption of Cu(II), Ni(II), Pb(II) and Cd(II) onto grape stalk follows a Langmuirian sorption trend in the whole range of temperature explored. Freundlich and Dubinin-Radushkevich models were also capable of providing a reasonably satisfactory description of the sorption equilibrium. The mean free energy E calculated by means of the Dubinin-Radushkevich model

demonstrated that sorption of Cu(II), Ni(II) and Cd(II) onto grape stalk proceeds mainly via ion exchange. In the case of Pb(II), an extra contribution to the ion exchange at temperatures higher than 5°C was observed. This extra contribution would be based on the establishment of stronger Pb(II)-GS interactions. The enthalpy and entropy variation in the sorption process demonstrates that Cu(II), Ni(II), Pb(II) and Cd(II) sorption onto grape stalks is a spontaneous exothermic process that involves an increase of the randomness of the system.

The thermodynamic parameters of metal sorption onto GS allowed establishing different rankings: based on the energy released in the sorption process, ΔH^0, Cu > Cd > Pb > Ni; on the increase of randomness provoked by the sorption process, ΔS^0, Pb > Ni ≈ Cd > Cu; and, finally, generalizing in base to the spontaneity of the overall process, ΔG^0 (5–50°C), Pb > Cu > Cd > Ni.

Conflict of interest

The authors certify that they have no conflict of interest.

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