Comparative study of biosorption of Cu^{+2}, Ni^{+2}, Cd^{+2}, Zn^{+2} and Co^{+2} ions on the *Pleurotus mutilus* biomass

A. Madani[1], A. Selatnia[1,4*], A. Chergui[2] , A.R.Yeddou [1,3]And B.Nadjemi[1]

1 Laboratoire d'Étude et de Développement des Techniques de Traitement et d'Épuration des Eaux et de Gestion Environnementale (LEDTEGE). Département de Chimie, École Normale Supérieure Kouba, BP 92, Vieux Kouba, Alger 16050, Algérie.
2 Laboratoire des Sciences et Techniques de l'Environnement, Département Génie de l'Environnement, École Nationale Polytechnique, 10 Avenue Hassen Badi, BP 182, El-Harrach 16200, Alger, Algérie
3 Département Génie de l'Environnement, Université M'Hamed Bougara, Boumerdès, Avenue de l'Indépendance 35000 Boumerdès, Algérie
4 Département Génie de Chimique, École Nationale Polytechnique, 10 Avenue Hassen Badi, BP 182, El-Harrach 16200, Alger, Algérie

*Corresponding author: ammarselatnia@yahoo.fr

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ABSTRACT/RESUME

Abstract : In this study the biomass *Pleurotus mutilus* was used for the biosorption of Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{+2} and Co^{+2} ions. The effect of different parameters such as contact time, adsorbate concentration, pH of the medium and temperature were investigated. The sorption capacities were in the order of Cd^{2+} > Zn^{+2} > Co^{+2} >Cu^{2+} > Ni^{2+} . This order can be explained by their different values of affinities respectively. In order to prediction of the rate controlling step(external or internal mass transfer) , Boyd model was used in all case. Results showed that the external mass transfer is the rate controlling step. Different thermodynamic parameters such as enthalpy and entropy and change in standard free energy have also been evaluated and it has been found that the reaction was spontaneous and exothermic in nature. The Freundlich, Langmuir, Temkin and Dubinin-Raduskuvich adsorption models were used for the mathematical description of the biosorption equilibrium.

I. Introduction

Several studies[1,2,3,4,5] have been cited on metal biosorption by *Pleurotus mutilus* biomass so no study could explain the order in the adsorption capacities of these heavy metals.

In order to examine the adsorption capacities of these ions on *Pleurotus mutilus* biomass, several solutions containing heavy metals were prepared .The tests were performed under the same operating conditions.

The purpose of the present work is to examine the order in metal ions biosorption capacity on the *Pleurotus mutilus* biomass. In this study, the effect of different parameters such as contact time, adsorbate concentration, pH of the medium, temperature, were investigated. Langmuir, Freundlich, Dubinin-Raduskevich and Temkin models were applied for the experimental biosorption equilibrium data.

II. Sorption equilibrium

Biosorption isotherms characterised by certain constant values express the surface properties and affinity of the biosorbents [6], and can be used as a comparison in biosorptive capacity of biomass of various heavy metals. Metal uptake by microorganisms has been shown to occur in two stages as initial rapid stage (passive uptake)

followed by a much slower process (active uptake) [7]. The biosorption isotherms of (Cu^{+2}, Ni^{+2}, Mn^{+2}, Cd^{+2}, Zn^{+2} and Co^{+2}) were investigated using five isotherm models: the Langmuir, Freundlich, Dubini-Raduskevich, Temkin isotherm models.

II.1. Langmuir isotherm:

Theoretically, the Langmuir isotherm is used to examine the adsorption of gases on a solid surface. The isotherm has been successfully applied to many pollutant biosorption processes and has been the most widely used isotherm for the biosorption of solute from a liquid solution. However, it should be realised that the Langmuir isotherm offers no insights into the mechanistic aspects of biosorption [8]. This model can be written in nonlinear form as in equation (1): Nonlinear Langmuir isotherm [8,9]:

$$q_e = (q_{max}.K_d.C)_e /(1+ K_d.C_e) \qquad \textbf{(1)}$$

Were q_e is the biosorption capacity at equilibrium (mg/g), q_{max} is the maximum uptake (mg/g) and K_d (L/mg) represents the equilibrium constant of the biosorption reaction. The model was linearized as equation (2) and equation (3) in order to obtain q_{max} and K_d values.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \left(\frac{1}{K_d.q_{max}}\right) \textbf{(2)}$$

$$\frac{1}{q_e} = \frac{1}{q_{max}.K_d.C_e} + \frac{1}{q_{max}} \quad \textbf{(3)}$$

II.2. Freundlich isotherm:

The Freundlich isotherm is applied under the assumption of a heterogeneous adsorption surface and active sites with different energies involved the model is represented as follows:

$$q_e = k_f.C_e^{1/n} \quad \textbf{(4)}$$

Where kf (g/mg) is a Freundlich constant relating the binding capacity and (1/n) is an empirical parameter relating the biosorption intensity which varies with the heterogeneity of the biosorbents. The parameter can be determined through the linearization of equation (5) as follows:

$$\ln q_e = \frac{1}{n}\ln C_e + \ln k_f \qquad \textbf{(5)}$$

II.3. Temkin isotherm:

The Temkin isotherm is based on the assumption that the heat of biosorption decreases linearly with an increase in biosorbent coverage [8]. The model is represented by equation (6):

$$q_e = \left(\frac{RT}{B}\right)\ln\left(K_T.C_e\right) \qquad \textbf{(6)}$$

$$q_e = \left(\frac{RT}{B}\right)\ln\left(K_T\right) + \left(\frac{RT}{B}\right)\ln\left(C_e\right) \qquad \textbf{(7)}$$

Where: (Kr) is the Temkin isotherm constant (L/mg)

(B) is the constant related to the heat of biosorption (J/mol)

(T) is Temperature (K)

$R = 8.314$ J/(mol.K)

II.4. Dubinin –Radushkevich (D-R) isotherm:

The D-R model does not assume a homogeneous surface or a constant adsorption potential as the Langmuir model.

The D-R isotherm was developed to account for the effect of the porous structure of a biosorbent [8,10]. The model can also be used to determinate whether the metal biosorption process is physical or chemical in nature. The linearized D-R isotherm is expressed as follows:

$$Ln(q_e) = Ln(q_{max}) - \beta\varepsilon^2 \qquad \textbf{(8)}$$

Where β ($mol^2.J^{-2}$) is the activity coefficient related to mean biosorption energy (E) , and ε ($J.mol^{-1}$) is the polanyi which can be determined from equation (9):

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad \textbf{(9)}$$

The plot of the (q_e) versus ε^2 results in a straight line, and its slope is equal to ($-\beta$).Thus, the mean biosorption energy (E) (J/mol) can be calculated using equation(10):

$$E = \frac{1}{\left(\sqrt{-2(-\beta)}\right)} \quad \textbf{(10)}$$

The obtained E values provide useful information with regard to weather biosorption is subject to a physical or chemical process [8,11].

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If 0< E < 8 kJ/mol: the sorption type is physisorption
If 8< E < 16 kJ/mol: the sorption type is ion exchange
If 16< E < 40 kJ/mol: the sorption type is chemisorption

III. Rate controlling step

Prediction of the rate controlling step is an important factor to be considered in biosorption process [12]. For solid-liquid biosorption process, either external mass transfer or intraparticle diffusion or both usually characterize the metal ion transfer process.

In our case, the sizes of particle are of the order of a few microns. For this, the size of pore was very small and in this case, we can neglect the intraparticle mass transfer.

In order to predict which the intraparticle or external mass transfer or both will be controlled the overall rate of biosorption, the kinetic data are further analyzed using Boyd kinetic expression which is given by [13]:

$$F = 1 - \frac{6}{\pi^2} exp(-\beta_t) \quad (11)$$

Which: $F = \dfrac{q_t}{q_e}$

F : represents the fraction of solute adsorbed at any time t.

β_t : is a mathematical function of (F).

Rearranging Eq (11):

$$\beta_t = -0.4977 - ln(1 - F) \quad (12)$$

Equation is used to calculate (β_t) values at different time (t).

The linearity of the plot of (β_t) vs time is used to distinguish whether external and intraparticle transfer controls the overall biosorption rate.

If the relation between (β_t) and (t) is linear but does not pass through origin confirm that the external mass transfer is the rate controlling step [14] and the intraparticle mass transfer is negligible. The intraparticle diffusion coefficient (D'_i) can be determinated from the linear plot of (β_t) vs (t):

$$\beta_t = \pi^2 \frac{D'_i}{r^2} t \quad (13)$$

Where (r) represents the radius of the particle by assuming it as spherical particles.

IV. Thermodynamic parameters

The Gibbs free energy, $\Delta G°$ is used in order to determine, which process will occur spontaneously. Reactions occur spontaneously at a given temperature if $\Delta G°$ is negative.

The thermodynamic parameters such as changes in standard free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$), were determined by using the following equation:

$$K_d = \frac{C_a}{C_e} \quad (14)$$

$$\Delta G^0 = \Delta H° - T.\Delta S° \quad (15)$$

$$ln\, K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (16)$$

Where k_d is the distribution coefficient for the biosorption.

C_a : is the amount of metal ion (mg) adsorbed on the adsorbent per liter of solution.

C_e : is the equilibrium concentration (mg/l) of metal ion in the solution.

T : is the temperature (°K)

R : is the gaz constant.

$\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept of ($ln\, k_d$) vs ($\dfrac{1}{T}$).

V. Materials and methods

V.1. Biosorbent material

Pleurotus mutilus biomass produced during pleuromutiline antibiotic productions was collected after fermentation. This biomass was washed with distilled water and dried at $50°C$ during 24h. It was then crushed and sieved in order to obtain a particle size in the range of 100-200μm.

V.2. Metal solution

The metal stock solution was prepared by dissolving accurately weighted amounts of Cd^{+2}, Co^{+2}, Cu^{+2}, Ni^{+2}, Zn^{+2} prepared with $(Cd(NO_3)_2,4H_2O)$; $(Co(NO_3)_2, 6H_2O)$;$(Cu(NO_3)_2,3 H_2O)$;$(Ni(NO_3)_2, 6 H_2O)$;$(Zn(NO_3)_2, 6 H_2O)$ in

100ml distilled water and the experimental solutions were obtained by diluting the stock solution to the required concentrations .

The solution pH was adjusted with 0.1M of HNO_3 and 0.1M of NaOH using a pH meter (Hanna, pH 211).

V.3. Batch biosorption experiments

All experiments were carried out by added of a known amount of biosorbent to 100ml of metal solution.

The effect of experimental parameters such as pH, biosorbent dosage, metal concentration, and temperature and contact time on the biosorption capacity was studied.

After each sorption, metal residual concentrations in solution were determined a Unicam 939 Atomic absorption spectrophotometer at wavelengths of 228.8 nm (cd^{+2}); 240.7nm (Co^{+2}); 324.8nm (Cu^{+2}); 232nm (Ni^{+2}); 213.9nm (Zn^{+2}). The amount of sorption q($mg.g^{-1}$) was calculated by:

$$q = \left(\frac{C_0 - C_e}{M} \cdot V \right) \quad (17)$$

Where C_0 and C_e are the initial and equilibrium concentrations of metal ($mg.L^{-1}$) respectively.

V is the volume of solution(L) and M is the amount of biosorbent used(g).
The metal removal percentage can be calculated as:

$$\text{Removal percentage} = \frac{C_0 - C_t}{C_0} \cdot 100 \quad (18)$$

Where C_t ($mg.L^{-1}$) is the metal concentration at time t (min).

VI. Results and discussion

VI.1. Effect of solution pH

The pH of the aqueous solution is an important controlling parameter in the sorption process of metal ion. The effect of solution pH on metal ion sorption was studied at the pH ranges of 2.5-11 and the results are shown in Fig.1. The sorption of metal ion was found to be maximum at the initial pH= 6.

The removal of metal ion increase for pH greater than 6 and can be explained by sorption and microprecipitation mechanisms.
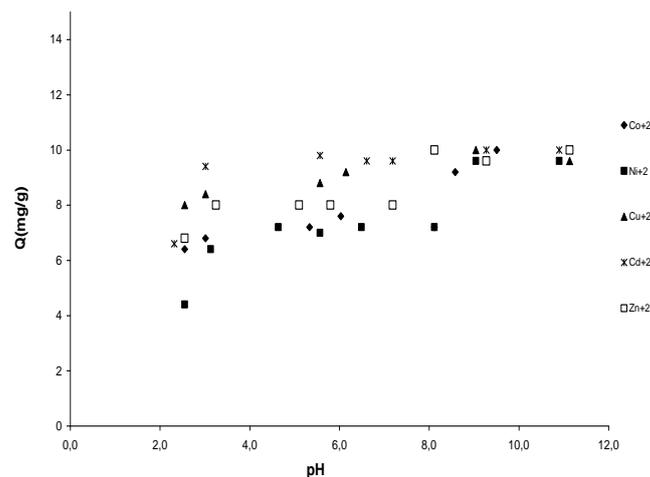
Figure 1.*Effect of pH on the $Co^{+2}, Ni^{+2}, Cu^{+2}, Cd^{+2}, Zn^{+2}$ adsorption capacity by the Pleurotus mutilus biomass(w=300rpm,$C_0(Co^{+2}, Ni^{+2}, Cu^{+2}, Cd^{+2}, Zn^{+2})$ =100mg/l;$C_{biomass}$=10g/l; PS: 100-200μm.*

VI.2. Effect of biosorbent dose

The effect of biosorbent dose ranging from $5g.L^{-1}$ to $40g.L^{-1}$ on metal ion sorption is presented in Fig.2. From this figure it is observed that the maximum removed amount of different metals were obtained at biosorbent concentration $Co^{+2}(20g.L^{-1})$; $Cu^{+2}(10g.L^{-1})$; Cd^{+2} ($10g.L^{-1}$);Zn^{+2};($15g.L^{-1}$) ; $Ni^{+2}(20g.L^{-1})$.

All next cited experiments were carried out at bisorbent concentration of $10g.L^{-1}$.
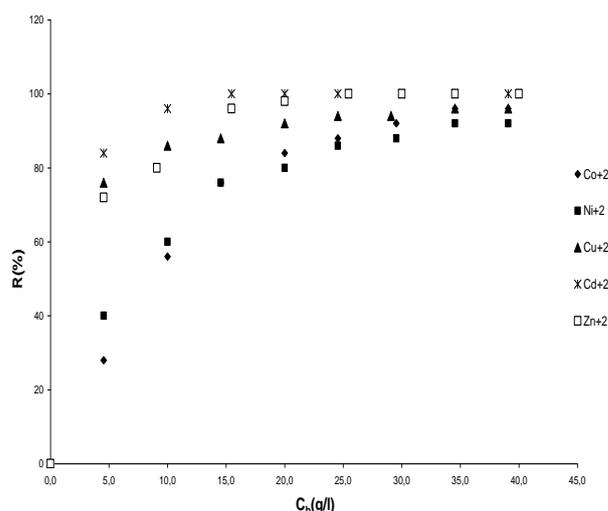
Figure 2*. Effect of the biosorbent dose on the biosorption capacity of the Pleurotus mutilus biomass (w=300rpm, $C_0(Co^{+2}, Ni^{+2}, Cu^{+2}, Cd^{+2}, Zn^{+2})$=100mg/l;$C_{biomass}$=10 g/l;pH=6, PS: 100-200μm.*

VI.3. Metal ion biosorption kinetics

The biosorption of metal ion onto *Pleurotus mutilus* biomass as a function of contact time is shown in Fig.3.

Biosorption studies were carried out for 300min.It was observed that the amount of metal ion increased with time and the equilibrium were established in Co^{+2}(15min); Ni^{+2}(23min); Cu^{+2}(15min); Cd^{+2}(23min); Zn^{+2}(30min). At equilibrium, the adsorbed quantity obtained tends to values of Ni^{+2}(6.9 $mg.g^{-1}$); Cu^{+2}(7.3 $mg.g^{-1}$); Co^{+2}(8mg.g^{-1});Zn^{+2}(8.8 $mg.g^{-1}$); Cd^{+2}(10mg.g^{-1});
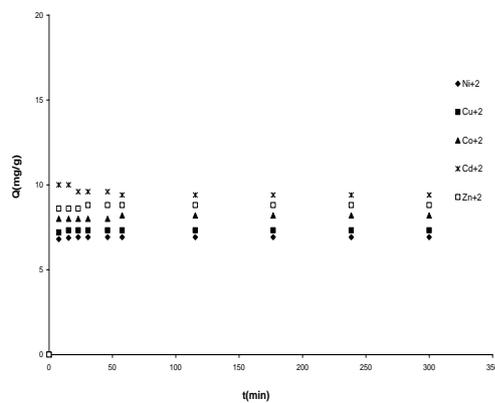
Figure 3. *Effect of time on the uptake of metal ions of Co^{+2}, Ni^{+2},Cu^{+2},Cd^{+2},Zn^{+2} by the biomass Pleurotus mutilus (w=300rpm , C_0(Co^{+2},Ni^{+2},Cu^{+2},Cd^{+2},Zn^{+2})=100mg/l ,biomass dose 10g/l , pH=6, PS:100-200μm.*

The order observed of the adsorption capacity of ions Co^{+2}, Ni^{+2}, Cu^{+2},Cd^{+2},Zn^{+2} on the biomass *Pleurotus mutilus* can be explained by their different individual affinity [A(cd)=-26kJ/mol), A(Zn)=9kJ/mol, A(Co)=63.8kJ/mol, A(Cu)=118.5kJ/mol, A(Ni)=156kJ/mol], therefore with a lower affinity we have a higher adsorption capacity.

In order to determinate the rate controlling step, the experimental kinetics values were analyzed by the Boyd model. By plotting (B_t) versus time (Fig.5), we can deduce that the relation between(B_t) and time is linear but does not pass through origin and confirm that the external mass transfer is the rate controlling step and the intraparticle mass transfer is negligible.

In general, when the particle size was around some micrometer, we can negliged the intraparticle mass transfer, because the particle pore was very smaller and the intraparticle mass transfer become difficult**.**
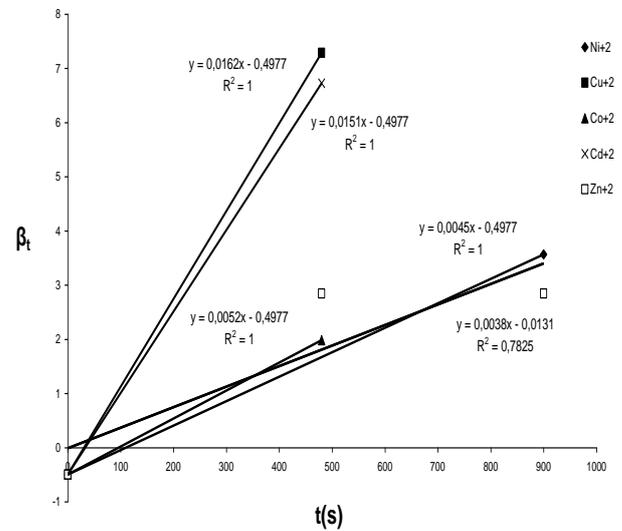
Figure 4. *(B_t) versus (t) according to the boyd model for the biosorption of (Co^{+2}, Ni^{+2},Cu^{+2},Cd^{+2},Zn^{+2}) on the Pleurotus mutilus biomass.*

We can deduce, the values of $D_i^{'}$ from Boyd model .

Table 1. *Values of $D_i^{'}$ obtained from Boyd model for the biosorption of (Co^{+2}, Ni^{+2},Cu^{+2},Cd^{+2},Zn^{+2}) on the Pleurotus mutilus biomass*

Metal ion	$D_i^{'}(m^2.s^{-1})$
Co^{+2}	$3.88*10^{-12}$
Ni^{+2}	$2.57*10^{-12}$
Cu^{+2}	$9.24*10^{-12}$
Cd^{+2}	$8.61*10^{-12}$
Zn^{+2}	$2.17*10^{-12}$

VI.4 Isotherm biosorption analysis

The equilibrium experimental data were analyzed by Langmuir, Freundlich; Dubini-Radushkevich and Temkin adsorption isotherms.
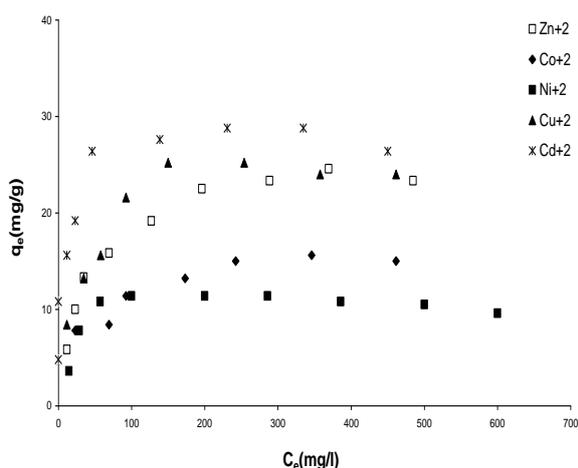
Figure 5: Biosorption equilibrium data of (Co^{+2}, Ni^{+2},Cu^{+2},Cd^{+2},Zn^{+2}) on the *Pleurotus mutilus* biomass(w=300rpm,C_b=10g/l,P.S:100-200μm).

Five correlation isotherms were used to modelise the experimental data for (Co^{+2}, Ni^{+2},Cu^{+2},Cd^{+2},Zn^{+2}) biosorption on the *Pleurotus mutilus* biomass.

From Langmuir, Freundlich; Dubini-Radushkevich and Temkin equations gives the values of the isotherm constants are calculated in table 2.

However regarding the correlation coefficient R^2 for (Co^{+2}, Ni^{+2},Cu^{+2},Cd^{+2},Zn^{+2}) biosorption, all models (R^2>0.9) were found to represent the equilibrium biosorption experimental data .

From table.2, we can be seen that the mean adsorption energy (E) and (B) were less than 8kJ/mol and may provide useful information that biosorption is subject to a physical process.

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Table2. *Equilibrium parameters of metals biosorption onto Pleurotus mutilus biomass*

Models	Equations	Values				
		Co^{+2}	Ni^{+2}	Cu^{+2}	Cd^{+2}	Zn^{+2}
Langmuir	$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \left(\frac{1}{k_d . q_{max}}\right)$$					
K_d		0.035	0.082	0.043	0.264	0.023
$q_{max}(mg.g^{-1})$		16.13	10.30	24.33	27.62	24.57
R^2		0.996	0.992	0.996	0.992	0.991
Freundlich	$$\ln q_e = \frac{1}{n} \ln C_e + \ln k_f$$					
$K_f(L.g^{-1})$		2.32	1.417	1.996	8.477	1.878
n		2.87	2.00	1.99	3.62	2.2
R^2		0.933	0.919	0.969	0.955	0.946
Dubinin-Radushkevich	$$Ln(q_e) = Ln(q_{max}) - \beta\varepsilon^2$$					
$q_{max}(mg .g^{-1})$		9.627	8.338	13.307	21.596	8.29
$\beta(mol^2.J^{-2})$		6×10^{-6}	16×10^{6}	7×10^{-6}	3×10^{-6}	5×10^{-6}
R^2		0.999	0.998	0.99	0.608	0.977
$E(kJ.mol^{-1})$		0.289	0.176	0.267	0.408	0.316
Temkin	$$q_e = \frac{RT}{B} \ln K_T + \frac{RT}{B} \ln C_e$$					
$B(J.mol^{-1})$		1.12×10^{-3}	1.13×10^{-3}	2.24×10^{-3}	2.18×10^{-3}	$2x10^{-3}$
$K_T(L .g^{-1})$		0.71	0.394	0.346	2.107	0.31
R^2		0.972	0.954	0.984	0.943	0.933

Table 3 shows the equilibrium biosorption capacity obtained of different metal ion on the *Pleurotus mutilus* biomass.

Table3.Equilibrium biosorption capacity for different metal ion on the Pleurotus mutilus biomass

Metal ion	Equilibrium sorption capacity(mg/g)
Co^{+2}	15
Ni^{+2}	11.4
Cu^{+2}	25.2
Cd^{+2}	28.8
Zn^{+2}	23

VII. Thermodynamic analysis

The values calculated of $\Delta G°$, $\Delta H°$, $\Delta S°$ from Eq (15) and Eq (16) for all metal ions were summarized in table 4.

Table 4.Thermodynamic parameters for the biosorption of   (Co^{+2}, Ni^{+2},Cu^{+2},Cd^{+2},Zn^{+2})   on Pleurotus mutilus biomass

Ion metal	Initial concentration of metal(mg/l)	ΔH° (kJ.mol^{-1})	ΔS° (kJ.mol^{-1}. K^{-1})	ΔG°(kJ.mol^{-1})			
				292°K	297 °K	323 °K	**333 °K**
Co^{+2}	100	-7.526	-0.0097	-4.702	-4.654	-4.402	**-4.306**
Ni^{+2}	100	-7.284	0.0033	-8.25	-8.266	-8.352	**-8.385**
Cu^{+2}	100	-5.947	-0.0117	-2.537	-2.479	-2.175	**-2.059**
Cd^{+2}	100	-21.474	-0.0644	-2.659	-2.337	-0.662	**-0.018**
Zn^{+2}	**100**	**-7.069**	**-0.0015**	**-6.639**	**-6.632**	**-6.594**	**-6.579**

The change in free energy for physisorption is between -20 and 0 kJ.mol^{-1}, and chemisorption has a range of -400 to -80 kJ.mol^{-1} (Yu et al.2001).It appears from table 6 that the free energy for biosorption of metal ion onto *Pleurotus mutilus* with a initial concentration of 100mg/l were between (-20 kJ/mol and 0 kJ/mol). Hence, this process can be considered as physisorption .The negative values of $\Delta G°$ indicate that the biosorption of metal ion onto *Pleurotus mutilus* biomass is spontaneous. The negative values of change in enthalpy ($\Delta H°$) shows that the biosorption is exothermic in nature.

VIII. Conclusion

The maximum uptake of metal ion were about Co^{+2}(15mg/g), Ni^{+2}(11.4mg/g), Cu^{+2}(25.2mg/g), Cd^{+2}(28.8mg/g), Zn^{+2}(23mg/g) at initial pH= 6. It appears, that the biosorption capacity evolves in the opposite direction of the affinity if ions. The use of Boyd model confirm that the biosorption overall rate was controlled by the external mass transfer.

The equilibrium data fitted very well with the Lagmuir, Freundlich; Dubini-Radushkevich and Temkin Isotherm model.

The monolayer biosorption of metal ion onto the *Pleurotus mutilus* biomass can be considered as physisorption. Thermodynamic parameters $\Delta H°$ and $\Delta G°$ showed that the process can be exothermic and spontaneous

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