THERMODYNAMIC STUDIES ON Cd (II) RETENTION FROM AQUEOUS MEDIUM ON SARKANDA GRASS LIGNIN NANOPARTICLES

STUDII TERMODINAMICE PRIVIND RETENȚIA Cd (II) DIN MEDII APOASE PE NANOPARTICULE DE LIGNINĂ DIN IARBĂ SARKANDA

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Abstract. *Due to its high toxicity and its capacity to accumulate and contaminate, cadmium is a potentially harmful substance for all ecosystems and humans or animals in the contaminated area. The present study proposes as a substrate for the adsorption of Cd (II) from aqueous medium, in static conditions, a fraction of biomass represented by chemically unmodified Sarkanda Grass lignin nanoparticles, demonstrating through thermodynamic considerations the efficiency of this bioresource.*
Key words: Sarkanda Grass lignin, cadmium ions, adsorption, thermodynamic parameters

Rezumat. *Prin toxicitatea ridicată și capacitatea de acumulare și contaminare, cadmiul este o substanță cu potențial dăunător pentru toate ecosistemele, respectiv pentru oamenii și animalele din arealul contaminat. Prezentul studiu propune ca substrat de adsorbție a Cd (II) din medii apoase, în condiții statice, o fracțiune a biomasei reprezentată de nanoparticule de lignină Sarkanda Grass nemodificată chimic, demonstrând prin considerente termodinamice eficiența acestei bioresurse.*
Cuvinte cheie: lignină Sarkanda Grass, ioni de cadmiu, adsorbție, parametri termodinamici

INTRODUCTION

In general, heavy metals such as Co, Cu, Fe, Mn, Mo, Ni, V and Zn are needed in trace amounts in the body, but excessive amounts of these elements can become harmful. Some heavy metals, such as mercury, cadmium and lead, have no physiological role and moreover, have harmful effects on human health. (Ungureanu *et al,* 2023). The biosorption, which is the property of certain types of biomass to bind and concentrate heavy metals even from very dilute aqueous solutions, is one of the most promising technologies involved in the removal of toxic metals from industrial waste streams and natural waters. (Garg *et al*, 2008).

Lignin is a polyaromatic and cross-linked biopolymer, with three-dimensional branched amorphous structure, made up of thousands of monomeric phenylpropane

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units, polymerized $C_3 - C_6$, with ion exchange capacity, facilitated by the functional groups it possesses, that can be involved in the process of retaining polluting species. Moreover, there is literature evidence of the quantitative retention of metal ions on lignin, but currently, the complexation mechanisms involved in the adsorption of metal ions on lignin are still under debate. (Ungureanu *et al,* 2023; Kumar *et al,* 2006).

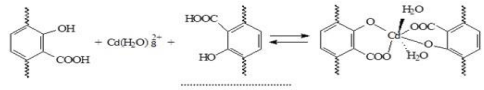

Fig. 1 - Initial interaction between the lignin structural units and Cd (II)

Also, the thermodynamic parameters (free energy, enthalpy and entropy) provide information about the chemical or physical nature of the adsorption and about the type of interactions that are established between the metal ion and the lignin fraction.

The present experiment analyzes from the point of view thermodynamically, the adsorption capacity under static conditions of Cd (II) from aqueous solutions on an unmodified Sarkanda Grass lignin substrate, after other studies demonstrated the efficiency of the adsorbent by kinetic. (Ungureanu *et al,* 2023).

MATERIAL AND METHOD

The following materials have been used:

- Biosorbent - Unmodified Sarkanda Grass lignin, supplied by Granit Recherche Development S.A. Lausanne, Switzerland, with the following characteristics: insoluble in acids - 87 %, insoluble in acids - 2 %, nitrogen - 1.2 %, COOH - 3.3 mmol/g, aromatic OH - 1.7 mmol/g, ash - 2.2 %, t - 160 ºC and $CdSO_4 \bullet 8H_2O$. (Ungureanu *et al*, 2023).
- The preparation of the stock solutions (0.001 mg/L) consisted of the dissolution of $CdSO_4 \bullet 8H_2O$, in distilled water. The working solutions were prepared by diluting with distilled water an exactly measured volume of the stock solution, and the concentrations of cadmium in aqueous solutions are shown in table 1.

Work procedure*:* The concentration of Cd (II) was determined by using Xylenol orange, that can be investigated spectrophotometrically, with maximum absorption at 575 nm. (Ungureanu *et al*, 2023). Quantitative determination of the metal ion obtained after filtration from the aqueous solutions was carried out by analysis of an exactly measured volume (2 mL) according to the experimental procedure, and he concentration value for each sample was calculated from the regression equation of the calibration curve. (fig. 3). A VIS Spectrophotometer V1000 SN was used to investigate the spectrophotometric analysis.

The experiment was performed at (20 ± 0.5 °C), use 5 g lignin as adsorption substrate/L of aqueous solution metal ion. 20 mL of $CdSO_4 \bullet 8H_2O$ were added over the lignin substrate in different concentrations (Table 1). Afterwards, the samples were allowed to stand for 30, 60 and 120 minutes to reach the equilibrium state and to capture the optimal solution retention time, thus obtaining information about the adsorption mechanism and to be able to interpret the thermodynamic data. After each resting period, phase separations were performed by filtration to determine the concentration of the pollutant species.

RESULTS AND DISCUSSIONS

Figure 2 shows the particle size of Sarkanda Grass lignin used for Cd (II) retention from aqueous solution and figure 3 shows the calibration curve and regression equation from which the concentration value was calculated for each sample.

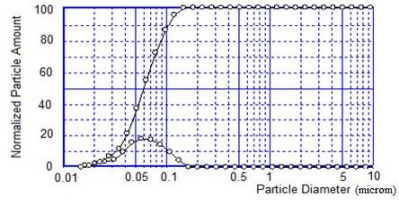

Fig. 2 - Particle size of lignin Sarkanda grass unmodified

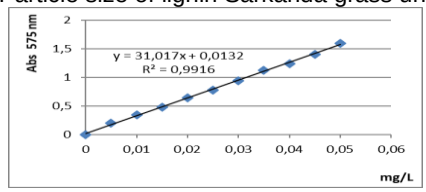

Fig. 3 - Curbe calibration

The amount of Cd (II) retained per unit mass of lignin (q, mg/g) was calculated, in order to estimate the adsorption efficiency. The increase in Cd (II) concentration, in the studied concentration domain, causes an increase in the adsorption capacity of lignin from 1.33 to 13.32 mg/g (tab. 1). The optimal contact time can be considered the 60 minutes, as in this contact time, the amount of adsorbed pollutant species retained per the unit mass of the adsorbent recorded the maximum value.

Table 1

Quantity of Cd^{2+} retained per unit mass of lignin (q, mg/g)

$C_{Cd^{2+}}$ (mg/L)	$q_{Cd^{2+}}$ (mg/g)		
	Time (minutes)		
	30	60	120
11.241	1.3326	1.3328	1.3328
22.482	2.6658	2.6659	2.6659
33.723	3.9985	3.9986	3.9986
44.964	5.3317	5.3318	5.3318
56.205	6.6645	6,6646	6.6646
67.446	7.9974	7.9976	7.9976
78.687	9.3301	9.3302	9.3302
89.928	10.6629	10.6630	10.6630
101.169	11.9958	11.9960	11.9961
112.41	13.3284	13.3285	13.3286

To characterize the thermodynamic behavior of the adsorption process the following thermodynamic parameters were used: variation free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), (tab. 2).

Table 2

The values of the thermodynamic parameters, calculated for the adsorption of ions of Cd (II) from aqueous solutions on Sarkanda grass lignin nanoparticles

pH	Time (minutes)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
1.02	30	- 25.29	12.04	99.21
	60	- 27.02	11.21	86.24
	120	- 27.98	11.43	87.31
6.03	30	- 30.67	15.18	112.32
	60	- 36.28	14.36	137.92
	120	- 37.05	14,81	126.83

The negative values of the Gibbs free energy variation (ΔG), at both pH values, show that the retention of Cd (II) from aqueous solutions on lignin occurs spontaneous. A value of the Gibbs free energy change greater than -30 kJ/mol implies a charge transfer between the metal ion and the surface of the adsorbent. In the case of ion adsorption of Cd (II) on lignin at both pH values of the initial solution, the experimentally obtained ΔG values are between -25 kJ/mol and -37 kJ/mol, which suggests that in the adsorption mechanism interactions of the type predominate electrostatic (ion exchange interactions or hydrogen bonds), and less so covalent or coordination (tab. 2). The (ΔH) values show that the process of adsorption of Cd (II) on lignin is endothermic, for both pH values the initial solution (tab. 2). The positive values of the entropy variation (ΔS) that characterize the process of adsorption of Cd (II) from aqueous solution on lignin, suggests that: the disorder of the system increases, most likely due to the decrease in the degree of ordering of water molecules around the surface functional groups of the adsorbent (tab. 2).

CONCLUSIONS

1. It seems that the retention of Cd (II) on lignin is active, because most likely, the degrees of freedom of Cd (II) are not very restricted with their adsorption on the surface of the biomass fraction.

2. Through the prism of the analysed thermodynamic parameters and under precisely established experimental conditions, the present study recommends the use of Sarkanda grass lignin in the retention of Cd (II) from aqueous medium, to replace more expensive conventional adsorbents.

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