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OPTIMIZATION AND MODELING OF Cr (VI) BIOSORPTION FROM AQUEOUS SOLUTION ON BIOSORBENT - SARKANDA GRASS LIGNIN

OPTIMIZAREA ȘI MODELAREA BIOSORBȚIEI Cr (VI) DIN SOLUȚIE APOASĂ PE BIOSORBENT- LIGNINĂ DIN IARBĂ SARKANDA

UNGUREANU Elena*[1]**, CHELARIU Elena Liliana*[1]*, TOFĂNICĂ B.I*[2]*,
***POPA V.I.*[2]*, JITĂREANU Carmenica Doina*[1]**
*Corresponding author e-mail: eungureanu@uaiasi.ro

***Abstract.** The negativ impact induced by the presence of heavy metals in the environment and on the health of living organisms is accentuated by their long-term persistence, as a result of their low solubility and mobility and in close connection with the sorption and complexation processes. In this study, the bioadsorption of Cr (VI) from aqueous solution onto unmodified Sarkanda Grass lignin was analyzed. Cr (VI) retention was tested at different experimental parameters (pH of initial solution and biosorbent, biosorbent dosage, aqueous solution concentration and contact time), in order to obtain optimal experimental conditions. The experimental results have been interpreted using the classic Langmuir and Freundlich isotherms models, as well as two kinetic models (the Lagergren pseudo-first order and the Ho-McKay pseudo-second order models). The experimental data recommend the unmodified Sarkanda Grass lignin as an efficience biosorbent in the retention of chromium ions from aqueous solution, both in terms of the amount of biosorbent and pollutant species retained, as well as in terms of adsorption time.*

Key words: Sarkanda Grass lignin, chromium ions, adsorption, equilibrium, kinetics.

***Rezumat.** Impactul negativ pe care îl induce prezența metalelor grele în mediul înconjurător și asupra sănătății organismelor vii este accentuat de persistența acestora pe termen lung, ca urmare a solubilității și mobilității lor scăzute și în strânsă legătură cu procesele de sorbție și complexare. În acest studiu, a fost analizată bioadsorbția Cr (VI) din soluția apoasă pe lignină nemodificată Sarkanda Grass. Retenția Cr (VI) a fost testată la diferiți parametri experimentali (pH-ul soluției inițiale și al biosorbentului, doza de biosorbent, concentrația soluției apoase și timpul de contact), pentru a obtine condiții experimentale optime. Rezultatele experimentale au fost interpretate folosind modelele clasice de izoterme Langmuir și Freundlich, precum și două modele cinetice (modelul Lagergren de ordinul întâi și modelul Ho-McKay de ordinul doi). Datele experimentale recomandă lignina Sarkanda Grass nemodificată ca biosorbent eficient în reținerea ionilor de crom din soluție apoasă, atât în ceea ce privește cantitatea de biosorbent și specie poluantă reținută, precum și din punct de vedere al timpului de adsorbție.*

Cuvinte cheie: lignină Sarkanda Grass, ioni de crom, adsorbție, echilibru, cinetică

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[1] "Ion Ionescu de la Brad" University of Life Sciences, Iasi, Romania
[2] "Gh. Asachi" Technical University of Iasi, Romania.

INTRODUCTION

Heavy metals accumulate in the body over time, depositing on tissues and vital organs, and their elimination is slow and difficult, because their presence is difficult to detect because they have no smell, taste or color. The existence of chromium in nature is highlighted by its combinations, mainly by the two stable forms: Cr (III) and Cr (VI). The literature presents exact data on the proportion of chromium in different rocks: granite -10 ppm, basalt - 185 ppm, oceanic clays - 90 ppm, schist clays - 100 ppm, limestone - 11 ppm and the maximum dose allowed according to the legislation: in the human body - 50 µg/L, in the soil - 30 mg/kg s.u. and in water - 0.05 mg/L. (Pavesi *et al*, 2022). Cr (III) is the most abundant form of chromium in the environment and the least toxic for living cells, precisely 500 - 1000 times less than the toxicity of Cr (VI), which can stop the development and growth of plants and cause allergies, lung tumors or dermatitis. (Pavesi *et al,* 2022).

Even though the removal of heavy metals can be successfully achieved by adsorption on activated carbon, this procedure is expensive and cannot be applied on an industrial scale. For this reason, an adsorbent available in large quantities, environmentally friendly and cheap is advisable. (Ungureanu *et al*, 2021, 2022).

Lignin is a polyaromatic and cross-linked biopolymer, with three-dimensional branched amorphous structure, made up of thousands of monomeric phenylpropane 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 mechanisms involved in the adsorption of metal ions on lignin are still under debate. (Crist *et al,* 2008; Ungureanu *et al*, 2021, 2022).

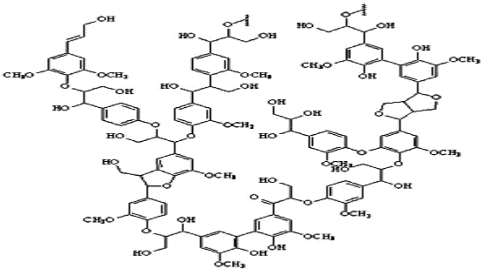

Fig. 1 - Fragment from the structure of lignin (Lignin-American Chemical Society)

Some studies have concluded that the ion exchange mechanisms (Crist *et al,* 2008) may be responsible for the adsorption of metal ions onto lignin, while others suggested that the retention of metal ions on lignin by adsorption is the result of combining several mechanisms, such as ion exchange, adsorption and complexation. (Guo *et al*, 2008). The retention of the pollutant species is influenced by: the nature and dose of the adsorbent/adsorbate, the contact time or the pH, whose role is directed by H_3O^+ and HO^- essential in regulating the electrokinetic potential as a result of the appearance of the electrical double layer between the lignin surface and the ion metallic. Most probably, pH influences both the speciation and solubility of metal ions and the dissociation of functional groups, which leads to the modification of the equilibrium characteristics of the adsorption process.

The adsorption isotherms obtained and interpreted with the help of the classic Freundlich and Langmuir models elucidate the equilibrium conditions in the case of adsorption processes, according to the literature recommendations. In order to predict the kinetics and mechanism of adsorption, two mathematical models are applied: Lagergren of pseudo-first order and Ho-McKay of pseudo-second order, which categorizes adsorption as a diffusion of the sorbate from the solution, around, on the surface and in the internal pores of the adsorbent, followed by its association with the active centers. (Crist *et al*, 2008).

The present experiment tests the adsorption capacity under static conditions of Cr (VI) from aqueous solutions on a unmodified Sarkanda Grass lignin substrate, successfully used for the retention of Pb (II), Zn (II) and As (III). (Ungureanu *et al,* 2021, 2022).

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 (Ungureanu E. et al, 2021, 2022).
- The stock solution of metal ion at a concentration of 0.001 mg/L was prepared by dissolving the $K_2Cr_2O_7$ 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 copper in aqueous solutions are shown in Table 1.

Work procedure*:*

Spectrophotometric determination of Cr (VI) - by the diphenylcarbazide method. VIS Spectrophotometer V1000 SN was used: YA07151909217, 1 cm glass tub, 20 ± 0.5° C.

In acidic solutions, diphenylcarbazide forms a red-violet coloration in the presence of chromate ions, which can be determined spectrophotometric (λ = 545 nm) by the calibration curve method. Quantitative determination of the metal ions 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 the concentration value for each sample was calculated from the regression equation of the calibration curve.

Adsorption experiments: 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 $K_2Cr_2O_7$ were added over the lignin substrate in different concentrations (tab. 1).

Subsequent, the samples were left to stand 30, 60 and 120 minutes to achieve the state of equilibrium and to capture the optimal retention time of the solution, thus obtaining information about the mechanism of adsorption and to be able to interpret kinetic data. After each rest period, phase separations with were performed by filtration to determine concentration of polluting specie.

Isotherm models: Adsorption equilibrium modeling consists in experimentally obtaining adsorption isotherms, which are analyzed using mathematical models. The Langmuir model describes monolayer adsorption onto homogeneous surfaces, while the Freundlich model considers that the adsorption process takes place on relatively nonhomogeneous surfaces. The choice of the most appropriate model to describe the experimental data was made on the basis of the correlation coefficients (R^2) obtained for the linear representation of each model. (Ungureanu *et al,* 2021, 2022).

Kinetic models: The kinetics of the adsorption process depends both on the retention process itself and on the diffusion stages that direct the transfer of the solut from the solution to the active centers on the surface of the adsorbent. With the help of the kinetic models of Lagergren and Ho-McKay, the kinetic parameters of the adsorption process of Cr (VI) ions onto lignin can be determined from the slopes and the orderly intercept of linear dependencies lg (q_e-q_t) and t, respectively, t/q_t and t. (q_e, q_t = adsorption capacity at equilibrium and at time t, respectively). (Ungureanu *et al*, 2021, 2022).

RESULTS AND DISCUSSIONS

Lignin dose: During the optimization of the experimental conditions of Cr^{6+} adsorption, it was aimed to use a lower dose of lignin, which is especially advantageous from an economic point of view. The experimental tests have established that, at 5 g lignin/L aqueous solution of metal ion, the most efficient retention of the pollutant specie studied is recorded.

Initial concentration of $Cr^{6+}$and initial solution pH: In order to obtain the most conclusive information about the adsorption efficiency, the quantity of Cr^{6+} retained on the unit of mass of lignin (q, mg/g) was calculated. A pH = 5 was chosen, a value at which the probability of Cr (VI) precipitation does not appear.

Table 1

Quantity of Cr^{6+} retained per unit mass of lignin (q, mg/g)

C_{Cr}^{6+} (mg/L)	**q_{Cr}^{6+} (mg/g)**		
	Time (minutes)		
	30	**60**	**120**
5.2	1.3329	1.3329	1.3330
10.04	2.6653	2.6649	2.6651
15.6	3.9973	3.9977	3.9977
20.08	5.3299	5.3301	5.3301
26	6.6619	6.6626	6.6626
31.5	7.9943	7.9945	7.9948
36.4	9.3263	9.3264	9.3264
41.6	10.6586	10.6587	10.6587
46.8	11.9910	11.9916	11.9917
52	13.3235	13.3236	13.3236

Increasing the initial concentration of Cr (VI) and the contact time between the two phases, involve an increase of the adsorption capacity of lignin until saturation, when most of the functional groups of lignin associate with the metal ion, and the diffusion to the unreacted/free functional groups inside the lignin particles will probably likely be blocked. This increase is more intense in the initial stage, then the biosorption becomes slower, reaching a maximum after 60 minutes. At this point, saturation is probably reached, which is understandable considering that adsorption is a surface process. The contact time of 60 minutes can be considered as the optimum value because it is sufficient to reach the equilibrium in the retention of Cr (VI) from the aqueous solution on the unmodified Sarkanda Grass lignin.

Adsorption isotherms: Characteristic parameters of Freundlich and Langmuir models obtained by adsorption of Cr (VI) of aqueous solution on lignin at 20 ± 0.5° C and at different contact times are shown in Table 2. 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. Lignin seems to be a good thing alternative as a potential biosorbent application in Cr (VI) retention (fig. 2).

Table 2

Characteristic parameters of the Freundlich and Langmuir models

Pollutant	**Time (minutes)**	**Freundlich model**			**Langmuir model**		
		R^2	1/n	k_F	R^2	q_{max}.(mg/g)	K_L
Cr^{6+}	30	0.9930	0.9387	0.8645	0.8951	2.7070	0.2296
	60	0.9875	0.9423	1.0949	0.8251	2.8042	0.3145
	120	0.9888	0.9112	1.0960	0.8287	2.8450	0.3134

R^2 correlation coefficients; n = constant characterizing the affinity of metal ions to sorbent; k_F = Freundich constant; q_{max} = maximum amount of metal ion retained on the absorbent after total saturation; K_L = Langmuir constant.

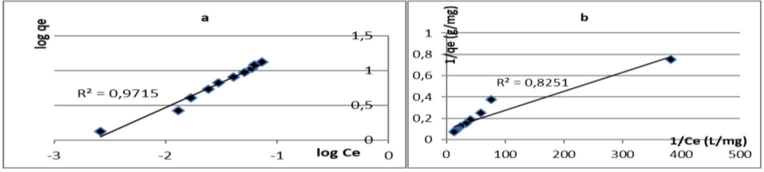

Fig. 2 - Freundlich model (a) and Langmuir model (b) for adsorption of Cr (VI) onto unmodified Sarkanda Grass lignin for 60 minutes

Characteristic kinetic parameters, calculated from slopes and orderly interception of these dependencies, are summarized in Table 3.

Table 3

Kinetic parameters of the Lagergren and Ho-McKay models

Pollutant	**c_i mg/mL**	**Lagergren model**			**Ho-McKay model**		
		R^2	q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg·min)
Cr^{6+}	10	0.9820	1.1042	-0.0037	1	0.9821	17.0000
	20	0.9462	5.6462	-0.0008	0,9997	3.4397	12.6130
	30	0.8327	8.2672	-0.0007	0.9998	3.5014	8.2198
	40	0.9765	12.0661	-0.0007	1	5.9376	7.9801
	50	0.9380	12.2374	-0.0005	0.9996	6.5073	5.9161
	60	0.9782	18.2269	-0.0005	1	8.4328	4.0946
	70	0.8687	17.8821	-0.0004	1	8.6243	3.4128
	80	0.9151	12.6936	-0.0003	0.9999	8.6802	2.1794
	90	0.7344	10.1036	-0.0002	1	8.7198	0.9231
	100	0.7388	7.2950	-0.0001	1	8.9309	0.3604

k_1, k_2 = constant adsorption rates for model 1 (Lagergren) and 2 (Ho-McKay).

Kinetic studies: Figure 3 illustrates linear dependencies obtained for the Lagergren and Ho-McKay kinetic models at adsorption Cr (VI) aqueous solution on lignin in optimal conditions at the initial concentration of 60 mg/mL.

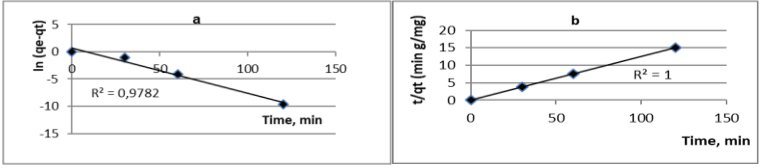

Fig. 3 - Lagergren model (a) and Ho-McKay model (b) for adsorption of Cr (VI) onto unmodified Sarkanda Grass lignin for 60 mg/mL

Experimental data show that the Lagergren model is less suitable for describing the chromium adsorption process on lignin, which is why the Ho-McKay model was used. The obtained results show that pseudo-second order Ho-McKay the kinetic model is best suited for describes the adsorption of Cr (VI) on lignin, providing conclusive details on the electrostatic nature of the interactions between the two partners and the triggering of an activated chemosorption as a result of the good complexation capacity between the involved species.

CONCLUSIONS

1. Modeling of Freundlich and Langmuir adsorption isotherms by analysis of correlation coefficients did not clarify the physical or chemical character of adsorption, for which Lagergren and Ho-McKey kinetic models were used. Adsorption of chromium from aqueous solution onto Sarkanda Grass lignin is best described by the Ho-McKay model, with reference to the chemical interaction between chromium and lignin functional groups.

2. Sarkanda Grass lignin seems to be an efficience alternative in retention Cr (VI), in precise experimental conditions (20 ± 0.5 °C, acid pH, biosorbent dose of 5 g/L pollutant, in the concentration domain studied (tab. 1) for a contact time of 60 minutes).

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