ADSORPTION OF Cu (II) FROM AQUEOUS SOLUTION ON SARKANDA GRASS LIGNIN: EQUILIBRIUM AND KINETIC STUDIES

ADSORBȚIA Cu (II) DIN SOLUȚIE APOASĂ PE LIGNINĂ DIN IARBĂ SARKANDA: STUDII CINETICE ȘI DE ECHILIBRU

UNGUREANU Elena[1]*, JITĂREANU Carmenica Doina[1], TROFIN Alina[1], UNGUREANU O.C.[2],* FORTUNĂ *Maria Emiliana[3], ARITON Adina-Mirela[4], , TRINCĂ Lucia Carmen[1], POPA V.I.[5]

*Corresponding author e-mail: eungureanu@uaiasi.ro

Abstract. *In this study, the adsorption of copper ions from aqueous solution onto lignin obtained from unmodified Sarkanda Grass was analyzed. To ensure optimal reaction conditions, the retention of copper ions was tested at different experimental parameters (pH of the initial solution and adsorbent, the dose of adsorbent, the concentration of aqueous solution and contact time). 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). Based on the analysis of the experimental data, it has been concluded that unmodified Sarkanda Grass lignin can be recommended as an efficient alternative, considering its practical applicability, in the retention of copper ions from aqueous solution, both in terms of the amount of adsorbent and pollutant specie retained, as well as in terms of adsorption time.*

Key words: Sarkanda Grass lignin, copper ions, adsorption, equilibrium, kinetics

Rezumat. *În acest studiu, a fost analizată adsorbția ionilor de cupru din soluție apoasă pe lignină obținută din Iarbă Sarkanda nemodificată. Pentru a asigura condiții optime de reacție, retenția ionilor de cupru a fost testată la diferiți parametri experimentali (pH-ul soluției inițiale și al adsorbantului, doza de adsorbant, concentrația soluției apoase și timpul de contact). 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). Pe baza analizei datelor experimentale, s-a ajuns la concluzia că lignina Sarkanda Grass nemodificată poate fi recomandată ca alternativă eficientă, având în vedere aplicabilitatea sa practică, în reținerea ionilor de cupru din soluție apoasă, atât din punct de vedere al cantității de adsorbant și de specie poluantă reținută, precum și în ceea ce privește timpul de adsorbție.*

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

[1]"Ion Ionescu de la Brad" University of Life Sciences, Iasi, Romania
[2] "V. Goldis" West University of Arad, Romania
[3] "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania
[4]Research and Development Center for Cattle Breeding Dancu, Iasi, Romania
[5] "Gh. Asachi" Technical University of Iasi, Romania.

INTRODUCTION

At present, biomass can be defined as matter that derives directly or indirectly from plants, being used as energy or raw material.

The main fractions selected from biomass can be grouped into three categories: lignocellulosic materials or woody biomass (extracted from the ineligible part of biomass: corn cobs, grass, wood, coal), amorphous sugars (starch, glucose) and triglycerides (vegetable oils). (Popa, 2018).

The compounds of renewable vegetable resources, such as lignin, can be considered as a strategic resource that can provide viable products, qualitatively and quantitatively, to sectors dependent on external factors (fuel, chemicals, electricity), also offering numerous advantages for the sustainable development of society. (Ungureanu *et al,* 2021).

The literature on the reduction of environmental pollution has shown that a number of materials, which have a porous structure and a relatively large number of superficial functional groups can be used effectively to remove some pollutants from aqueous solutions. (Bailey *et al*, 1999; Ungureanu *et al*, 2021).

The presence in its structure of numerous functional groups capable of forming chemical bonds with metal ions gives lignin a cation exchange capacity and provides it with the potential to be used as an adsorbent for the removal of heavy metal ions from wastewater.

Moreover, there is literature evidence of the quantitative retention of metal ions on lignin. (Le Digabel *et al*, 2006; *Crist et al*, 2008; Ungureanu *et al*, 2021).

Currently, the mechanisms involved in the adsorption of metal ions onto lignin are still under debate.

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 study of adsorption equilibrium is very important to determine the retention capacity of the adsorbent and establish the basic physicochemical parameters of the adsorption process.

The Langmuir and Freundlich models are most commonly used for establishing the equilibrium conditions in adsorption processes and are considered classic models of adsorption isotherms. (Ungureanu *et al*, 2021).

The kinetics of the adsorption process depends both on the retention process itself and on the diffusion stages that lead to the transfer of ions from the solution to the active sites on the surface of the adsorbent.

The most commonly used kinetic models applicable to the adsorption of pollutants from aqueous solutions are the pseudo-first order Lagergren kinetic model, the pseudo-second order Ho-McKay kinetic model and the intra-particle diffusion model. (Ungureanu *et al*, 2021).

MATERIAL AND METHOD

The following materials have been used:

- Unmodified Sarkanda Grass lignin, supplied by Granit Recherche Development S.A. Lausanne, Switzerland, was used as an adsorbent substrate, with the following characteristics presented in table 1;

Table 1

Properties of unmodified Sarkanda Grass lignin (Ungureanu *et al,* 2021).

Characteristics of substrate	Unmodified Sarkanda grass lignin
Lignin insoluble in acids, %	87
Lignin soluble in acids, %	2
Nitrogen, %	1.2
COOH, mmol/g	3.3
Aromatic OH, mmol/g	1.7
Ash, %	2.2
T (softening), °C	160

- The stock solution of metal ion at a concentration of 0.001 mg/L was prepared by dissolving the $CuSO_4$ salt 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 2.

Work procedure*:*

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

Cu (II) ions from aqueous solutions reacts with rubeanic acid (pH=4.5-5.0, acetate buffer) and forms a water-soluble olive-green complex that can be determined spectrophotometric (λ=390 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 room temperature (20 ± 0.5° C), use 5 g lignin as adsorption substrate/L of aqueous solution metal ion. 20 mL of copper sulphate were added over the lignin substrate in different concentrations (Table 2). Subsequent, the samples were left to stand for a period of time (30, 60 and 90 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 species.

Isotherm models: The starting point in the modeling the adsorption equilibrium is to obtain experimentally adsorption isotherms, which are then analyzed using mathematical models. Mathematical models have been used to shape the adsorption isotherms to clearly determine the adsorption mechanism. 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.

Kinetic models: With the help of the kinetic models of Lagergren and Ho-McKay, the kinetic parameters of the adsorption process of Cu (II) 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).

RESULTS AND DISCUSSIONS

Lignin dose: During the optimization of the experimental conditions of Cu^{2+} 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 ions, the most efficient retention of the pollutant species studied is recorded.

Initial concentration of Cu^{2+} and initial solution pH: In order to obtain the most conclusive information about the adsorption efficiency, the quantity of Cu^{2+} retained on the unit of mass of lignin (q, mg/g) was calculated. A pH = 5 was chosen, a value at which copper exists as a divalent ion and does not precipitate as a hydroxide.

Table 2

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

C_{Cu2+} (mg/L)	q_{Cu2}^{+} (mg/g)		
	Time (minutes)		
	30	60	90
6.355	2.7364	2.7413	2.7403
12.71	5.4431	5.4602	5.4633
19.065	7.9711	8.0981	8.1002
25.42	9.8992	10.0108	10.1302
32.665	13.5870	13.6000	13.6011
38.13	16.3154	16.3321	16.3320
44.485	18.9912	19.0077	19.0165
50.84	21.1253	21.2109	21.2121
57.195	24.4328	24.9572	24.9677
63.55	27.0015	27.1458	27.1503

As expected, the increase in the initial concentration of metal ion and the contact time between the two phases causes an increase in the adsorption capacity of lignin until most functional groups of lignin are fully occupied. At this point, the diffusion to the unreacted functional groups (free), which are found inside lignin particles, will most likely be hampered. This increase is more pronounced in the initial stage, for both metal ions studied, then the process becomes slower, reaching a maximum after 60 minutes. At this point, saturation is probably reached and thus, the adsorption process respects Le Châtelier's principle of mobile equilibrium. Under these circumstances, the contact time of 60 minutes can be considered as the optimal value, as it is sufficient to achieve equilibrium in the retention of Cu (II) ions from aqueous solution onto the unmodified Sarkanda Grass lignin.

Adsorption isotherms: Characteristic parameters of Freundlich and Langmuir models obtained by adsorption of Cu (II) of aqueous solution on lignin at 20 ± 0.5° C and at different contact times are shown in Table 3. 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 adsorbent application in Cu (II) retention (fig.1).

Table 3

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
Cu^{2+}	30	0.9969	0.9020	2.1421	0.9820	13.0204	0.0643
	60	0.9971	0.9394	2.0001	0.9854	13.1122	0.0638
	90	0.9982	0.9500	1.9643	0.9882	13.1872	0.0631

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 complete saturation; K_L = Langmuir constant.

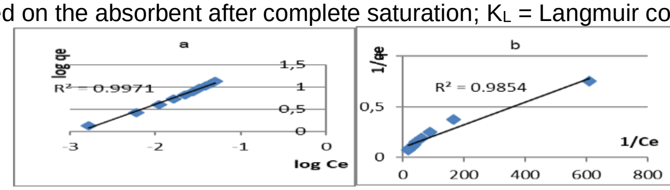

Fig. 1 - Freundlich model (a) and Langmuir model (b) for adsorption of Cu (II) onto unmodified Sarkanda Grass lignin for 60 minutes

Kinetic studies: Figure 2 illustrates linear dependencies obtained for the Lagergren and Ho-McKay kinetic models at adsorption Cu (II) aqueous solution on lignin in optimal conditions at the initial concentration of 10 mg/mL.

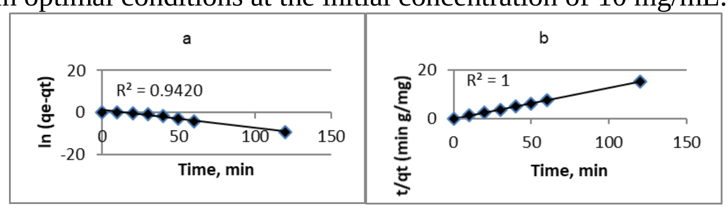

Fig. 2 - Lagergren model (a) and Ho-McKay model (b) for adsorption of Cu(II) onto unmodified Sarkanda Grass lignin for 10 mg/mL

Experimental data show that the Lagergren model is less suitable for describing the process of copper adsorption on lignin and the Ho-McKay model was later used.

Characteristic kinetic parameters, calculated from slopes and orderly interception of these dependencies, are summarized in Table 4.

Experimental data show that pseudo-second order Ho-McKay the kinetic model is best suited for describes the adsorption of Cu (II) on lignin, probably suggesting its chemical nature by forming complexes according to availability of lignin functional groups.

Table 4

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)
Cu^{2+}	10	0.9420	1.5071	-0.0019	1	1.3246	18.4702
	20	0.9303	1.8160	-0.0018	1	2.6383	5.2412
	30	0.8793	2.2472	-0.0017	1	3.8607	4.3220
	40	0.8312	5.2777	-0.0022	1	5.0740	3.2528
	50	0.8745	3.3081	-0.0019	1	6.5073	4.6921
	60	0.9000	2.3908	-0.0017	1	7.7966	3.8002
	70	0.8508	5.0234	-0.0021	1	9.1062	2.2539
	80	0.9014	3.5948	-0.0020	1	10.4038	3.3752
	90	0.8977	3.1354	-0.0019	1	11.7042	2,7532
	100	0.8704	4.3009	-0.0019	1	13.0302	1.6536

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

CONCLUSIONS

1. Under precise experimental conditions (20 ± 0.5 °C, weak acid pH, adsorbent dose of 5 g/L pollutant, in concentration range studied (Table 2) during a contact time of 60 minutes), Sarkanda Grass lignin appears to be an effective adsorbent for Cu (II) retention.

2. Modeling of Freundlich and Langmuir adsorption isotherms by the analysis of the correlation coefficients could not be proved if the adsorption was physical or chemistry, aspect clarified with the help of Lagergren and Ho-McKey kinetic models.

3. From a kinetic point of view, the adsorption of copper ion from aqueous solution on Sarkanda Grass lignin is well described by the Ho-McKay model, with reference to the chemical interaction between copper and lignin functional groups.

4. Sarkanda Grass lignin seems to be an effective and advantageous adsorbent for control of water pollution, especially in countries, where lignocellulosic waste is found in large quantities.

REFERENCES

1. **Bailey S.E., Olin T.J., Bricka M.R., Adrian D.D.,1999 -** *A review of potentially low cost sorbents for heavy metals,* Water Research, 33 (11), pp. 2469 – 2479.
2. **Crist R.H., Martin J.R., Crist D.R., 2004 -** *Use of a novel formulation of kraft lignin for toxic metal removal from process waters*, Sep. Sci. Technol., 39, pp.1535–1545.
3. **Guo X.Y., Zhang A.Z., Shan X.Q., 2008 -** *Adsorption of metal ions on lignin*, Journal of Haz. Mat., 151, pp.134–142.
4. **LeDigabel F., Avérous AL., 2006 -** *Effects of lignin content on the properties of lignocellulose-based biocomposites,* Carbohydr Polym., 66 (4), pp. 537-545.
5. **Popa V.I., 2018 -** *Biomass as renewable raw material to obtain bioproducts of high-tech value*, Elsevier, pp. 37.
6. **Ungureanu Elena, Trofin Alina Elena, Trincă Lucia Carmen, Ariton Adina-Mirela, Ungureanu O.C., Fortună Maria Emiliana, Jităreanu Carmenica Doina, Popa V.I., 2021 -** *Studies on kinetics and adsorption equilibrium of lead and zinc ions from aqueous solutions on Sarkanda Grass lignin,* Cellulose Chem. Technol., 55 (7-8), pp. 939-948.