RENEWABLE LIGNIN-BASED BIOMATERIALS FOR THE ADSORPTION OF Co(II) IONS FROM WASTEWATERS

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The current study examines the adsorptive potential of a biomaterial resulting from the extraction of cellulose, Sarkanda grass lignin, for the retention of Co(II) from aqueous medium under static conditions. The initial solution pH, initial concentration of Co(II), the adsorbent dose and the contact time between the adsorbent and the adsorbate were the main parameters preliminarily tested in order to accurately establish the optimal experimental conditions. The adsorption capacity of Sarkanda grass lignin was evaluated through surface analyses, the application of the Freundlich and Langmuir models to establish chemical equilibrium conditions, the Lagergren I and Ho-McKay II models for process kinetics, and biological stability analysis of specific indices. The number of germinated seeds or germination energy for the seeds of *Triticum aestivum* L, Glosa variety, introduced in the contaminated adsorbent and in the filtrates resulting from the phase separation was also evaluated. The results obtained through the aforementioned analysis methods indicate that Sarkanda grass lignin may be a promising solution for the adsorption of Co(II) from wastewater. This is evidenced by the observed adsorption capacity and the time required for the adsorption process.

Keywords: Co(II) ions, Sarkanda grass lignin, adsorption, *Triticum aestivum* L., environmental pollution

INTRODUCTION

The discharge of toxic pollutants, such as heavy metals, into biogeochemical circuits[1] is alarming, considering their potential to accumulate in natural and artificial ecosystems. This accumulation can subsequently lead to contaminating the food chain, thereby exposing humans to risk factors on a daily basis in modern society.[2]

Cobalt and its compounds are ubiquitous in nature and are integral to numerous anthropogenic activities.[3-5] The primary biological function of cobalt is as the metal component of vitamin B12. Cobalt compounds are of great technological importance through numerous industrial, medical, and military applications. The most common method of alloying with nickel is the production of stainless steel. Cobalt is found in a variety of applications, including airplane turbines, brake discs, dental implants, orthopedic prostheses, components of construction materials based on cement, metallic objects, such as buttons, zippers, and jewelry, binders in the hard metals industry, drying and coloring agents in paints and varnishes, glass ceramics, and cosmetics. The diverse range of practical applications, to which food sources rich in cobalt can also be added, such as fish, vegetables, drinking water, results in frequent exposure to cobalt compounds, which

can become toxic in excess.[6] The toxic salts mainly cause oxidative damage to DNA.[5] Cobalt compounds are described as toxic for the environment and the human body following excessive exposure.[7] Some health agencies[8] have listed them as probable or possible human carcinogens. The mitigation of these negative effects with serious consequences has become paramount.[9]

In addition to reducing the amount of pollutants, it is essential to identify potential avenues for the valorization of industrial waste and renewable resources. One such material is lignin, which has been explored as an adsorbent for the retention of some polluting species, represented by heavy metal ions. The literature presents several attempts to exploit this bioresource in this sense.[10-16] Lignin is considered the most abundant reservoir of natural aromatic units and the second most common biopolymer in nature, after cellulose. It is a natural protector of plants and is currently rarely used in high-end applications. However, if one considers its origin from renewable resources, its non-toxic nature and last but not least its low cost, it is clear that lignin has significant potential for high-end applications.[15-17] The presence of a large number of functional groups in its porous and branched structure enables lignin to form coordinative bonds with heavy metal ions,[18] thus creating stable ligno-complexes.[16] This property makes lignin an efficient substrate for the adsorption of these polluting species.[19]

The literature proposes that the efficiency of adsorption processes should be evaluated by obtaining and subsequently interpreting the experimental adsorption isotherms graphically. The most frequently used mathematical models[20] for this purpose are the Freundlich and Langmuir models,[14,16,21] which consider the amount of sorbate retained by the adsorbent under precise experimental conditions. These include the adsorbent mass, the initial concentration of the pollutant, the adsorbent-adsorbate contact time and the initial pH of the aqueous environment.[13,14,16] The adsorption kinetics is directly correlated with the actual retention and with the way the sorbate diffuses from the aqueous medium to the active centres on the surface of the adsorbent. This provides details about the nature of the process. Also, the first-order Lagergren model and the second-order Ho-McKay kinetic model are recommended by the

literature for this purpose, as they reproduce the mechanism involved in the retention of pollutants in aqueous substrates as faithfully as possible.[22,23]

The present study undertakes a comprehensive investigation into the adsorptive properties of Sarkanda grass lignin, derived from the extraction of cellulose,[11,12] specifically for retaining Co(II) ions from aqueous solutions. The experimental data of the present study, interpreted through thermokinetic and biological parameters, regarding the static adsorption of Co(II) from aqueous media onto Sarkanda grass lignin, indicate that the material is an effective adsorbent for this heavy metal pollutant. The results are corroborated by those obtained in a series of previous studies that tested the adsorption capacity of lignin for Pb(II), Zn(II), As(III), Co(II) and Ni(II) from wastewater,[11,12,14,16] indicating that lignin is a promising biosorbent. Additionally, the study introduces a novel approach by evaluating the biological stability of the adsorbent through seed germination assays, providing a unique assessment of the environmental impact and safety of the lignin-based adsorbent for potential agricultural applications.

EXPERIMENTAL
Materials and methods

Sarkanda grass lignin was offered by Granit Récherche Development S.A., Lausanne, Switzerland,[14] and $Co(NO_3)_2 \cdot 6H_2O$ was supplied by ChimReactiv S.R.L., Bucharest. *Triticum aestivum L* seeds (Glosa variety) were provided by the "Ion Ionescu de la Brad" University of Life Sciences, Iasi, Romania.[16]

Adsorption experiments

The preliminary stage of the experiments comprised a series of tests designed to ascertain the optimal conditions for the adsorption process. These tests focused on the initial concentration of Co(II), the pH of the initial solution, the mass of Sarkanda grass lignin and the contact time between the two phases involved. The experimental tests concluded that 5 grams of lignin in 1 liter of an aqueous Co(II) solution (0.001 mg Co(II) per liter of distilled water) provided an optimal adsorbent-to-adsorbate ratio, ensuring a sufficient number of active adsorption sites within the lignin structure.[14,16] The hydrophilic functional groups, particularly carboxyl and hydroxyl, on the lignin surface dissociate and deprotonate, becoming negatively charged, thus enabling them to associate with the positive ions of Co(II) present in the aqueous substrate. This results in the formation of relatively

stable lignin complexes, due to the appearance of coordinative bonds.[13] Following the experimental tests, a slightly acidic environment with a pH of 5 was chosen, as this proved to be optimal in other systems, such as those involving lignin and the following metals: Pb(II), Zn(II), As(III), Cd(II) and Ni(II).[11-14,16]

The stock solutions of metal ions in a concentration of 0.001 mg/L were prepared by dissolving separately $Co(NO_3)_2 \cdot 6H_2O$ in distilled water. The working solutions were prepared by diluting an exact volume of the stock solutions with distilled water, and the concentrations of metal ions in aqueous media (mg/mL) were determined to be as follows: 5.8933, 11.3933, 17.6799, 23.5972, 29.4965, 35.3958, 41.2951, 47.1944, 53.0937, 58.993. Twenty millilitres of $Co(NO_3)_2 \cdot 6H_2O$ were added to the lignin powder in concentrations previously specified. The samples were then left to rest under laboratory conditions at three different contact times. The optimal adsorption time of Co(II) was identified by measuring the adsorption capacity at 30, 60 and 90 minutes. This is in direct correlation with the state of saturation/chemical balance and with the kinetics of the process.

Spectrophotometric determination of Co (II)

In order to determine the concentration of Co(II), rubeanic acid was employed, with a maximum absorption observed at 580 nm. The rubeanic acid solution was prepared by dissolving 0.05 g of the solid reagent in 100 mL of 96% ethanol. The quantitative determination of the cobalt ion was conducted by filtering the solution from the aqueous media and analysing a precise measured volume (2 mL) according to the experimental procedure. The concentration value for each sample was calculated from the regression equation of the calibration curve.[24] For the spectrophotometric analysis, a Visible Spectrophotometer for laboratory use, model VS-721N, with a wavelength range of 300-1000 nm, manufactured by JKI in Shanghai, China, was employed.

Isotherm models

The degree of accuracy achieved through adsorption processes is significantly influenced by the successful modelling and interpretation of adsorption isotherms,[25] which represent the effective distribution of metallic ions between the two phases of the adsorption system.[13] Analytical isotherm equations, such as Langmuir and Freundlich isotherms, are commonly employed for the modelling of adsorption data.[26]

The adsorption capacities of Co(II) were determined according to the following Equation (1):[16]

$$q = (C_i - C_e)V/m, \text{ (mg/g)} \tag{1}$$

where C_i – initial concentration (mg/mL); C_e – equilibrium concentration (mg/L); V – volume of cobalt ion solution (L); m – mass of lignin (g).

The Langmuir-Freundlich isotherm includes the knowledge of adsorption heterogeneous surfaces, such as the lignin surface. It describes the distribution of adsorption energy onto the heterogeneous surface of the adsorbent.[16,27]

The Langmuir equation can be written in the following linear form:[16]

$$C_e/q_e = 1/q_m \cdot k_L + C_e/q_m \tag{2}$$

where q_e is the amount of cobalt ions adsorbed per unit of mass of lignin (mg/g) at equilibrium; q_m is the maximum amount of cobalt ions retained on the absorbent after saturation (mg/g); K_L is the Langmuir constant (L/mg); C_e is the equilibrium concentration of cobalt ions in solution (mg/L).

The linear form of the Freundlich isotherm is as follows:[16]

$$\log q_e = \log k_F + 1/n \cdot \log C_e \tag{3}$$

where k_F – Freundlich constant, indicating adsorption capacity; n – constant characterizing the affinity of cobalt ions to the lignin sorbent; q_e – amount of cobalt ions adsorbed per unit of weight of lignin (mg/g) at equilibrium; C_e – concentration at the equilibrium of cobalt ions in solution (mg/L).

The most suitable model for the optimal interpretation of the experimental data was selected according to the values of the correlation coefficient R^2, calculated with the least squares method.[16,25]

Kinetic models

By kinetic modelling, the solute uptake rate is described, which in turn controls the residence time of sorbate uptake at the solid–solution interface.[16,28] The kinetics of adsorption can be described using classical models, the most frequently employed of which are the first-order Lagergren model and the second-order Ho-McKay model.[29]

The Lagergren model is applicable to liquid-solid adsorption and can be mathematically reproduced by the following relation (4):[16]

$$\ln [q_e/(q_e - q)] = k_1 \cdot t \tag{4}$$

The equation of the Ho and McKay model reflects the adsorption capacity of the solid phase[11] and is expressed through the following relationship:[16]

$$t/q_t = (1/k_2 \cdot q_e^2) + t/q_e \tag{5}$$

where k_1, k_2 – constant adsorption rates for models 1 and 2; q_e, q_t – adsorption capacity at equilibrium and at time t, respectively.

The use of linear regression enabled the identification of the most appropriate kinetic model for the verification of the experimental results.

Surface analyses

A scanning electron microscope (SEM) was employed to perform scanning electron microscopy (SEM), an effective method for analysing organic and inorganic materials from the nanometre (nm) to

micrometre (μm) scale.[30] The Quanta 200 (Brno, Czech Republic) at 5 kV was utilised.

Biological experiments

The adsorption capacity of Sarkanda grass lignin for Co(II) from aqueous media was also analysed from a biological point of view by performing germination tests on *Triticum aestivum* L., Glosa[16] variety seeds, both on contaminated lignin and on filtrates – the liquid that remains after the solid adsorbent has been separated from the solution, leaving behind the clear liquid (filtrate) that is then analysed. Distilled water was used as control sample for the filtrates, and a clean adsorbent served as control sample for the contaminated lignin. The experiment was conducted over a seven-day period under laboratory conditions (24 °C ±1, 16 hours of light and 8 hours of darkness), with three repetitions and a total of 20 seeds per batch. The seeds were previously disinfected for five minutes with 5% sodium hypochlorite (NaClO), and then washed three times with MilliQ ultrapure water[31] until the specific smell disappeared. The seeds were incubated in test tubes (180 x 18 mm) for one hour, with intermittent shaking to facilitate imbibition with the filtrate or distilled water. They were then distributed uniformly in Petri dishes (90 x 15 cm),[14] to which two overlapping rounds of filter paper were attached. Seeds that exhibited swelling, rot, or mould growth at the conclusion of the germination period were deemed non-germinated in accordance with the methodology.[32] The toxicity of filtrates and lignin contaminated with cobalt aqueous solutions was estimated in the studied concentration range (5.8933-53.0937 mg/mL) at the three interphase contact times. The germination energy and germination capacity were determined at 30, 60, and 90 minutes, with the aid of the following relations:[14,16,32]

$$E_g = (a/n) \cdot 100 \qquad (6)$$
$$C_g = (a/n) \cdot 100 \qquad (7)$$

where a is the number of seeds germinated after three days, n is the total number of seeds analyzed, b is the number of seeds germinated at the end of the period (seven days).

RESULTS AND DISCUSSION
Effects of experimental parameters on the adsorbtion of cobalt (II) on Sarkanda grass lignin
Initial concentration of Co(II)

In order to estimate the efficiency of adsorption, the amount of Co(II) retained per unit of lignin mass (q, mg/g) was calculated. As illustrated in Figure 1, the elevated concentration of Co(II) within the studied concentration range is indicative of an augmented adsorption capacity of lignin. The capacity in question displays an increase from a Co(II) concentration of 1.5615 mg/g to a maximum concentration of 58.993 mg/L, respectively, for an interphase contact time of 60 minutes. This phenomenon can be attributed to the rise in the ratio between the initial number of moles of Co(II) and the number of accessible adsorption centers on the lignin fraction.

Dose of Sarkanda grass lignin

The adsorption process is influenced by the quantity of adsorptive substrate employed, offering credible hypotheses regarding the adsorptive potential of a material.

This is primarily achieved through the association centres available for the elimination of a pollutant species at a certain concentration.[33] In order to optimise the experimental conditions, a series of preliminary tests were carried out in the range of 4-40 g lignin/L Co(II) aqueous solution, a range suggested by the available literature.[11-14,16] The data obtained, as can be seen in Figure 2, indicate that the ideal dose of Sarkanda grass lignin should be 5 g/L Co(II) aqueous substrate.
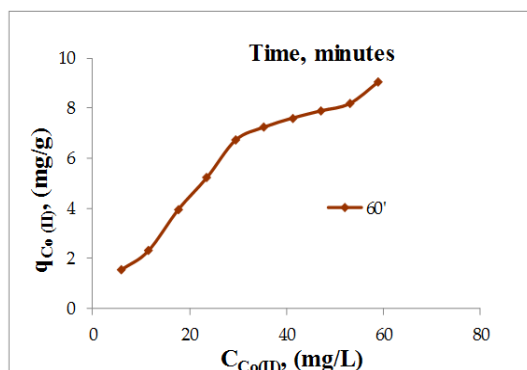

Figure 1: Adsorption capacity of Sarkanda grass lignin for contact time of 60 min, pH 5
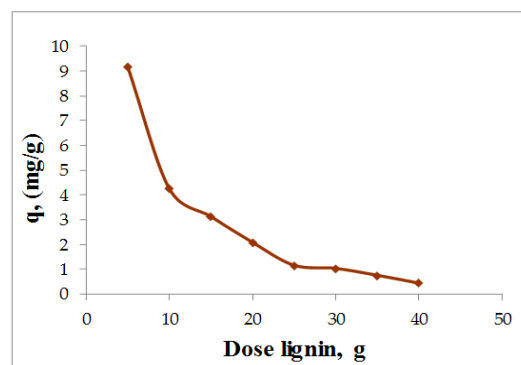

Figure 2: Effect of Sarkanda grass lignin dose on Co(II) adsorption at a concentration of 58.993 mg/L, contact time of 60 min, pH 5
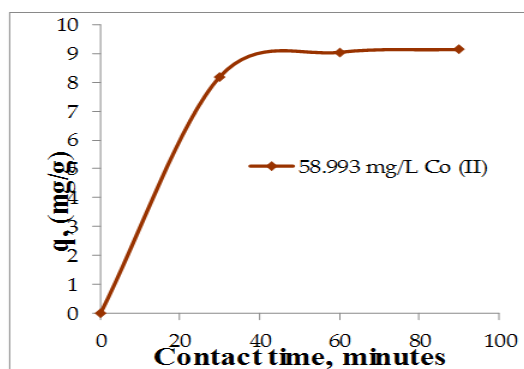
Figure 3: Influence of contact time on adsorption of Co(II) on Sarkanda grass lignin, pH 5

Figure 4: Influence of initial solution pH on Co(II) adsorption on Sarkanda grass lignin

Figure 2 illustrates that an increase in the dose of Sarkanda grass lignin does not result in an increase in the degree of adsorption. Instead, it is observed that there is a decrease in the amount of Co(II) retained per unit mass of biosorbent. This phenomenon can be attributed to the strong affinity between the hydrophilic functional groups in the lignin structure and Co(II) and the probable formation of a complex in the initial stage of adsorption. As the adsorbent pores become partially or totally inaccessible and reach saturation, the diffusion of Co(II) towards the groups that have not undergone reaction within the lignin is diminished.

Contact time

As indicated in the literature, the contact time between the phases must be longer in order to obtain clear indications regarding the interphase kinetics and equilibrium.[34] The experimental data demonstrate that an increase in the contact time between the Sarkanda grass lignin and the cobalt aqueous solution results in a more pronounced increase in the amount of Co(II) retained in the initial stage. Subsequently, the adsorption rate slows down, reaching a maximum at 60 minutes, while it is considered optimal for reaching the equilibrium state (Fig. 3). The contact time of 90 minutes was excluded from further analysis because there were insignificant variations in the adsorption capacity compared to the values recorded at 60 minutes.

Initial solution pH

Figure 4 illustrates that the degree of adsorption of Co(II) onto Sarkanda grass lignin increases with the initial pH of the solution. 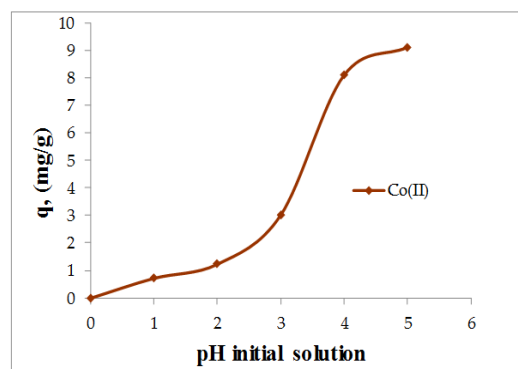This phenomenon can be attributed to the deprotonation of the functional groups on the surface of the lignin, which become negatively charged and can be chelated with Co(II) from the aqueous substrate. The donor-acceptor bond allows for the avoidance of strongly acidic environments, as the excess of hydronium ions can compete with cobalt ions for the active binding centres on lignin. In strongly alkaline environments, the precipitation of Co(II) in the form of hydroxide may occur, which would reduce the adsorption efficiency.[13] The preliminary tests conducted in the current study indicate that an optimal pH of 5 is associated with the highest values of Co(II) adsorption capacity of Sarkanda grass lignin.

Adsorption isotherms

The interactions between the adsorbent and adsorbate are analysed by means of experimental adsorption isotherms, which are interpreted with the help of mathematical models. These include[11-14,16] the Freundlich isotherm, which is applicable for mono/multilayer adsorption on heterogeneous surfaces, and the Langmuir one, which is useful for monolayer adsorption on homogeneous surfaces. Subsequently, the linear representation of the regression equations for both was employed to calculate the correlation coefficients (R^2), which enabled the identification of the most appropriate model for describing the adsorption process. Figure 5 (a and b) presents the linear representation of the Freundlich and Langmuir models for Co(II) adsorption from aqueous media on Sarkanda grass lignin under experimental conditions considered to be optimal: temperature (24 ± 0.5 °C), contact time (60 min), pH of 5. The selection of the optimal temperature as 24 °C for the adsorption process is justified by its alignment

with standard laboratory conditions, making the experimental setup energy-efficient and easily replicable in real-world applications. Table 1 provides the specific parameters of the Freundlich (R^2, 1/n, k_F) and Langmuir (R^2, q_m, k_L) models.
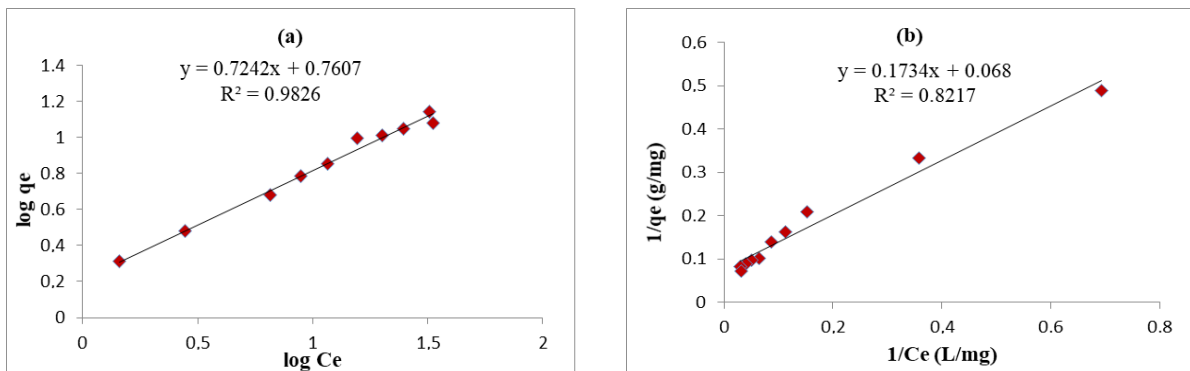

Figure 5: Freundlich adsorption model (a) and Langmuir adsorption model (b) for Co(II) adsorption onto Sarkanda grass lignin for 60 min

Table 1
Characteristic parameters of Freundlich and Langmuir models, obtained for
Co(II) adsorption on Sarkanda grass lignin

Time	Freundlich model			Langmuir model		
(min)	R^2	1/n	k_F	R^2	q_m (mg/g)	K_L
30	0.9743	0.9014	2.1732	0.9061	13.2187	0.0703
60	0.9826	0.9124	1.9342	0.8217	14.0061	0.0690
90	0.9632	0.9281	1.9382	0.7324	14.1398	0.0651

In the case of the Langmuir model, the values of the correlation coefficients (R^2) fall within the range of 0.7324-0.9061 and are slightly lower than the values of the correlation coefficients (R^2) obtained in the case of the Freundlich model, which are in the range of 0.9014-0.9281 (Table 1). This indicates that the experimental data better verifies the Freundlich model in describing the adsorption of Co(II) on Sarkanda grass lignin. Additionally, the low values of k_L, ranging from 0.0651 to 0.0703, indicate that the surface of the Sarkanda grass lignin exhibits asperities and is not homogeneous, suggesting that Co(II) retention is not a monolayer process. A review of the data presented in Table 1 reveals that the values of k_F and *1/n* are relatively low: k_F falls within the range 1.9382-2.1732, while those of *1/n* are included in the range 0.9014-0.9281. This suggests the presence of energy in the bond due to adsorption, possibly as a result of ion exchange interactions or superficial complexation. However, it is not possible to determine the predominant type of adsorption, whether physical or chemical, without further kinetic modelling.

Kinetic modeling

The most frequently cited literature recommends two mathematical models for describing the kinetics of adsorption. The Lagergren model, which is specific to liquid-solid adsorption, and the Ho-McKay model, which indicates the adsorption capacity of the solid phase, are two mathematical models that have been developed to describe the kinetics of adsorption.[29]

Figure 6 (a and b) illustrates the linear dependence of the two models for the interpretation of Co(II) adsorption from aqueous substrates on Sarkanda grass lignin, at a normalized initial concentration of 100 mg/mL. Table 2 presents the specific kinetic parameters, calculated from the slopes and the intercept with the ordinate of the linear dependencies obtained for each kinetic model. The correlation coefficients (R^2) were obtained by linear regression.

As illustrated in Table 2, the correlation coefficients (R^2) calculated using the pseudo-I order Lagergren kinetic model fall within the

922

range from 0.6407 to 0.8967, with values below 1. These findings suggest the occurrence of electrostatic interactions between Co(II) and the functional groups on the lignin surface, as well as the predominance of chemisorption at the expense of physical adsorption. However, the Lagergren model is unable to explain these observations, which limits the applicability of this model for the kinetic interpretation of the adsorption of Co(II) ions from aqueous media on Sarkanda grass lignin. These results are consistent with previous research.[11,12,14,15]

(a)
$y = -0.0174x - 0.2491$
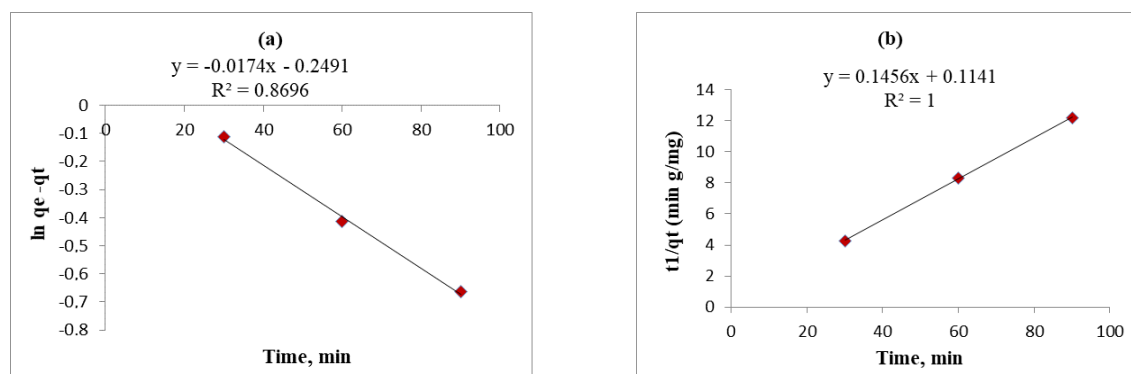$R^2 = 0.8696$

(b)
$y = 0.1456x + 0.1141$
$R^2 = 1$

Figure 6: Linear representation of the Lagergren pseudo-I order model (a) and Ho-McKay pseudo-II order model (b) for adsorption of Co(II) onto Sarkanda grass lignin

Table 2
Kinetic parameters of the Lagergren and Ho-McKay models for Co(II) adsorption on Sarkanda grass lignin

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)
10	0.7834	1.7253	-0.0020	1	1.9451	2.7954
20	0.8126	2.0863	-0.0018	1	3.0197	1.8409
30	0.7146	3.2544	-0.0017	1	5.2193	2.7810
40	0.8173	4.7289	-0.0019	1	8.2701	3.1759
50	0.6549	6.1832	-0.0018	1	9.8934	1.9276
60	0.8696	7.4921	-0.0017	1	11.0345	0.0564
70	0.6407	8.0587	-0.0021	1	12.0735	1.2472
80	0.7606	9.1517	-0.0016	1	13.2012	2.7324
90	0.8967	9.3201	-0.0018	1	14.2754	1.4869
100	0.8414	10.2661	-0.0017	1	15.7294	1.1548

On the other hand, the correlation coefficients (R^2) calculated according to the Ho-McKay kinetic model exhibit unitary values in all situations (Table 2), as do the other parameters: The values of q_e and k_2 indicate high affinity of Co(II) in the role of polluting agent towards Sarkanda grass lignin, which serves as an adsorption support. Furthermore, the high probability of forming lignocomplexes following an active adsorption is supported by the availability of the functional groups of lignin to associate with the metal ion. The Ho-McKay model therefore demonstrates greater accuracy than the Lagergren model, as it is able to illustrate the fact that the rate-limiting step of adsorpti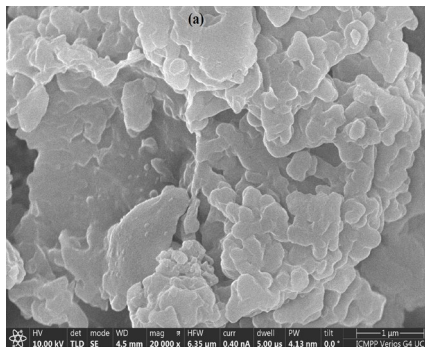on coincides with the chemical interaction between Co(II) and the functional groups, especially carboxyl and hydroxyl of lignin.

Surface morphology

Figure 7 illustrates the morphology of Sarkanda grass lignin before and after Co(II) adsorption at a concentration of 58.993 mg/L and a contact time between phases of 60 minutes, as observed by scanning electron microscopy (SEM).

In order to perform the SEM analysis, the samples were metallised with Pt to improve the contrast, thus resulting in Pt being present in both samples. Figure 7(a) depicts the SEM micrograph of the untreated lignin, which exhibits an agglomeration of well-separated particles of approximately 4 μm. This morphology differs

923

from that observed in Figure 7(b), which depicts the surface morphology of the lignin contaminated with Co(II). This figure confirms the contact between the two phases, followed by the diffusion and adsorption of Co(II) in the lignin pores.
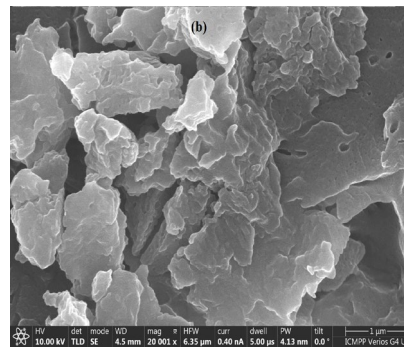

Figure 7: SEM images of Sarkanda grass lignin before adsorption (a) and after Co(II) adsorption (b), contact time of 60 min

Biological stability

Plants are regarded as living adsorbents, and the indirect toxic effect of Co(II) could result in metabolic dysfunctions that may affect stomatal opening, photosynthesis, respiration, growth and development.[35] In light of this, the biological stability of the caryopsis of *Triticum aestivum* L., Glosa variety, in contact with samples contaminated with Co(II) was monitored for seven days. Figure 8 (a, b and c) illustrates the mean number of germinated wheat seeds after 3 days for the contaminated samples, while Figure 8 (d, e and f) depicts the mean number of germinated seeds after 3 and 7 days for the filtrates resulting from Co(II) retention at the three contact times between the phases.

Figure 8 (a, b and c) illustrates the detrimental impact of Co(II) on the germination of *Triticum aestivum* L. caryopses, which is further exacerbated by the rise in metal ion concentration and the duration of contact between the phases. In the control samples, a total of 19 seeds germinated in the presence of lignin, while 20 seeds germinated in distilled water. In the case of the filtrates, the number of germinated seeds after 3 days and the number of seedlings after 7 days of germination are comparable to those obtained in the control, at the times of 60 and 90 minutes. However, they are lower at the contact time of 30 minutes, which indicates adsorption non-equilibrium and a longer interphase contact time. This agrees with the conclusions drawn from the interpretation of the adsorption isotherms and the kinetic parameters, which consider the optimal contact time of 60 minutes. In the presence of contaminated lignin, at a contact time of 30 minutes and at low concentrations of Co(II), the highest number of germinated seeds is recorded after 3 days. From a concentration of 41.2951 mg/L, the number of germinated seeds at a contact time of 30 minutes is 11 out of a total of 20. For contact times of 60 and 90 minutes, there were no germinated seeds. From a concentration of 47.1944 mg/L Co(II), the seeds did not germinate. This highlights the harmful effect of cobalt on the germination capacity of the seeds with the increase in concentration and duration of contact. Following germination, all contaminated lignin samples exhibited a lack of seed germination and the death of existing seedlings. This outcome was observed regardless of contact times and Co(II) concentration. These findings confirm the good adsorption capacity of Sarkanda grass lignin for Co(II), as demonstrated by the obtained thermokinetic results.

Figure 9 illustrates the germination of the caryopsis of *Triticum aestivum* L. Glosa variety over a seven-day period. The four experimental groups are as follows: control/uncontaminated lignin (R/UL), lignin contaminated with Co(II) (CL), control/distilled water (R/DW) and the filtrate (F) obtained after adsorption for 60 minutes at a concentration of 58.993 mg/L Co(II).
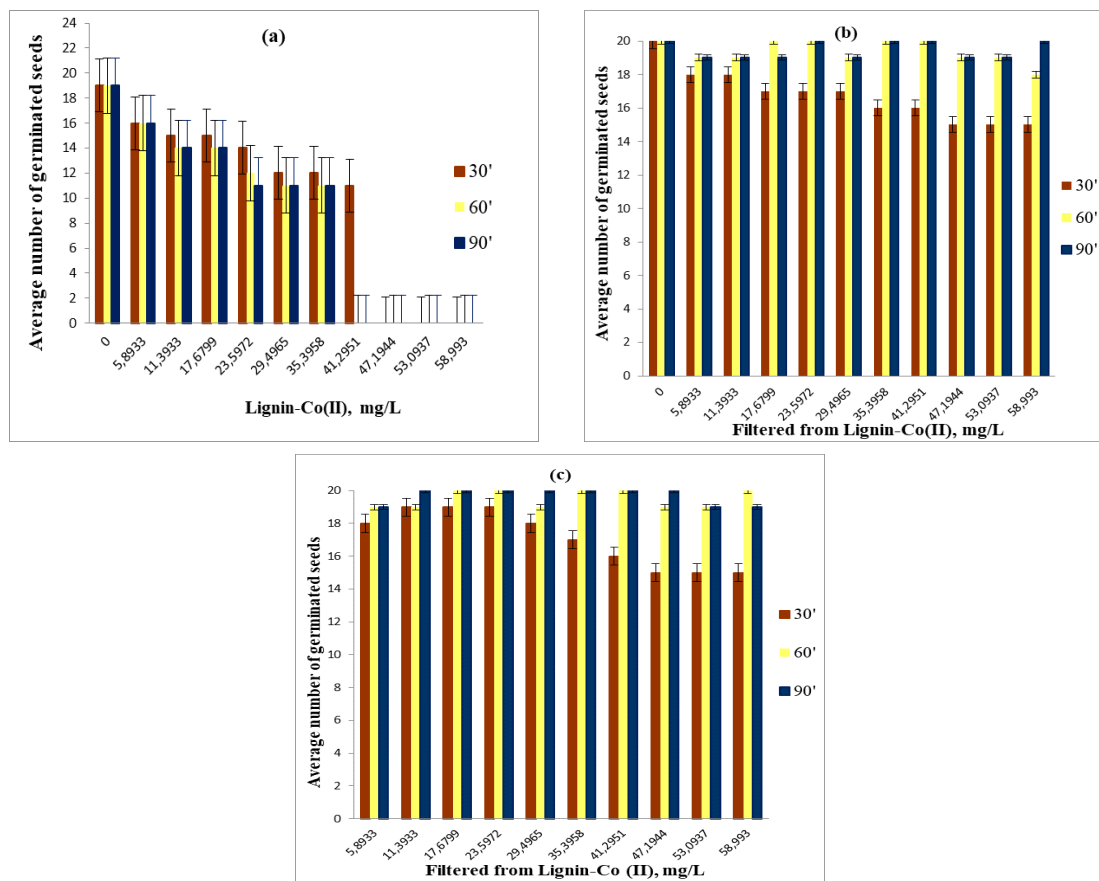
Figure 8: Average number of *Triticum aestivum L.* cariopses germinated after 3 days on contaminated samples (a) and on filtrates resulting from Co(II) adsorption after 3 days (b) and 7 days (c)
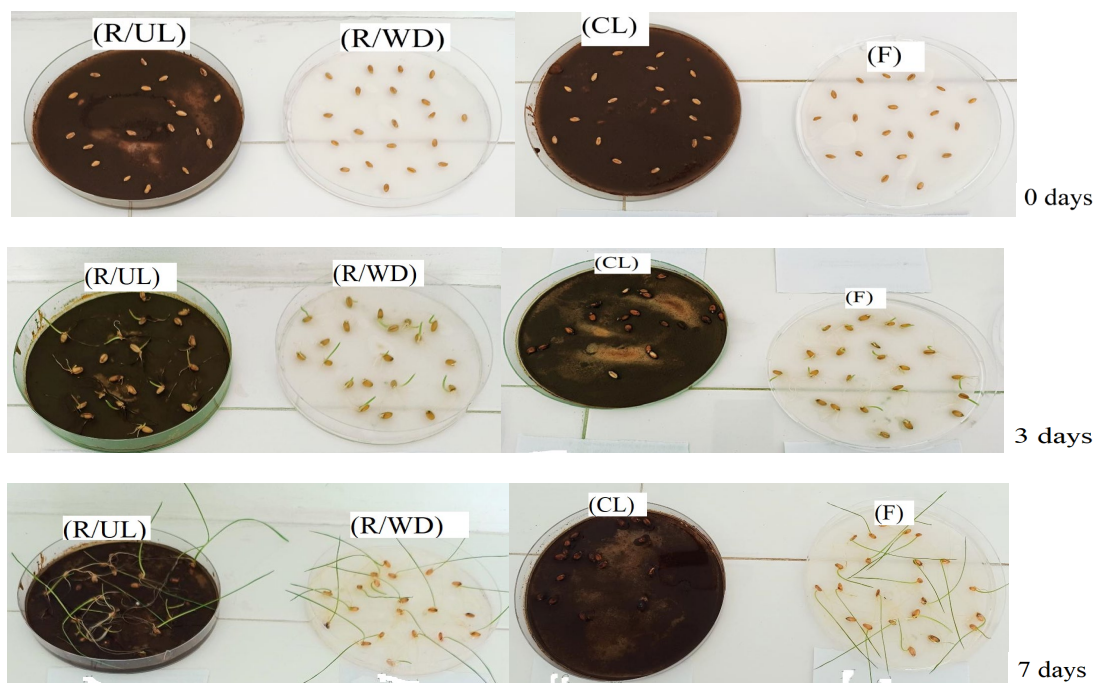

Figure 9: Germination of *Triticum aestivum L.* seeds over a period of 7 days, on contaminated lignin during an adsorption time of 60 min, using a concentration of 58.993 mg/L Co(II)

Table 3
Experimental data for the energy and germination capacity of *Triticum aestivum L.* seeds

Lignin/Co(II) (mg/L)	Contact time (min)						Lignin/Co(II) (mg/L) filtered	Contact time (min)					
	30	60	90	30	60	90		30	60	90	30	60	90
	Eg,%			Cg,%				Eg,%			Cg,%		
0	95	95	95	95	95	95	0	100	100	100	100	100	100
5.8933	80	80	85	0	0	0	5.8933	90	95	95	90	95	95
11.3933	75	45	40	0	0	0	11.3933	90	95	95	95	95	100
17.6799	75	70	70	0	0	0	17.6799	85	100	95	95	100	100
23.5972	75	70	70	0	0	0	23.5972	85	100	100	95	100	100
29.4965	70	60	60	0	0	0	29.4965	85	95	95	90	95	100
35.3958	70	60	60	0	0	0	35.3958	80	100	100	85	100	100
41.2951	60	0	0	0	0	0	41.2951	80	100	100	80	100	100
47.1944	0	0	0	0	0	0	47.1944	75	95	95	75	95	100
53.0937	0	0	0	0	0	0	53.0937	75	95	95	75	95	95
58.993	0	0	0	0	0	0	58.993	75	90	100	75	100	95

Table 3 presents the mean values of germination energy and capacity, obtained following three repetitions for the contaminated samples and for the filtrates resulting from Co(II) adsorption at the three contact times between phases. The experimental data were found to be correlated with the number of germinated seeds in both the case of filtrates and the case of samples of lignin contaminated with Co(II).

It was concluded that at 30 minutes of contact time between phases, the adsorption equilibrium was not reached, with the filtrates being more concentrated and the germination energy low. However, at 60 and 90 minutes, the germination energy was higher, due to the filtrates being more diluted than would be expected given the good adsorption capacity of lignin. For the contaminated lignin, an increase in cobalt concentration and contact time results in a reduction in germination energy to zero values at all three contact times, within the concentration range of 47.1944 to 58.993 mg/L Co(II), as illustrated in Table 3. In the case of contaminated lignin, the germination capacity is zero in all situations. In the filtered sample, the germination energy varies proportionally with the germination capacity, with values close to those recorded in the control sample, regardless of the Co(II) concentration. There are negligible differences for contact times of 60 and 90 minutes, which confirms the efficient adsorption of Co(II) on Sarkanda grass lignin at the contact time of 60 minutes, which was considered optimal, following the interpretation of the thermodynamic and kinetic results. This ensures the reproducibility of the experimental data obtained.

The findings underscore the significant potential of utilizing Sarkanda grass lignin as an adsorbent for Co(II) removal from aqueous substrates, aligning with the principles of circular economy. By upcycling lignin, a renewable bioresource and waste product, for effective metal ion adsorption, this study highlights a sustainable approach to waste valorization and resource utilization. The utilization of lignin in this manner not only addresses environmental challenges associated with lignin waste, but also contributes to the development of cost-effective and eco-friendly solutions for water treatment. This research exemplifies the circular economy concept by transforming a waste material into a valuable resource with practical applications in environmental remediation.

CONCLUSION

Sarkanda grass lignin has been demonstrated to possess excellent adsorption properties for the retention of Co(II) from aqueous media under precisely established experimental conditions. These conditions include a temperature of 24 ± 0.5 °C, a moderately acidic pH of 5, and a dose of 5 g adsorbent per litre of pollutant solution. The concentration range studied was 5.8933-58.993 mg/L Co(II), with an interphase contact time of 60 minutes.

The Freundlich and Langmuir models, employed to interpret the adsorption isotherms by means of the R^2 correlation coefficients, were unable to elucidate the type of adsorption. However, they did suggest that chemical adsorption was a more probable phenomenon than physical adsorption. The Freundlich model was

particularly useful in demonstrating the retention of Co(II) in the heterogeneous and porous surface of the biomass fraction, a conclusion that was confirmed by SEM surface analysis.

The kinetic interpretation of the experimental data using the Lagergren and the Ho-McKay models enabled the acquisition of pertinent information regarding the electrostatic nature of the interactions between the two species under investigation. The Ho-McKay model, in particular, provided insight into the interactions through the parameter values that could be calculated. This model provides the best description of Co(II) adsorption from aqueous media on grass lignin and is in correlation with the Freundlich model, which outlines the probability of a chemisorption as a direct consequence of the good lignin-Co(II) complexation.

The excellent adsorption capacity of Sarkanda grass lignin for Co(II) from aqueous substrates is also corroborated by the biological analyses performed on the seeds of *Triticum aestivum* L., Glosa variety incorporated in lignin contaminated with Co(II) in the studied concentration range. The concentration of Co(II) in the filtrates resulting from the separation of the two phases after retention was found to be 58.993 mg/L. It was determined that the inhibitory effect generated by the presence of Co(II) on the biological dynamics of caryopses/wheat seedlings is evident for 30, 60 and 90 min contact times.

The thermodynamic, kinetic and biological interpretation of the experimental data regarding Co(II) adsorption from aqueous substrates on Sarkanda grass lignin provides compelling evidence that the biomass fraction exhibits excellent adsorptive properties. This makes it a promising candidate for future use as a biosorbent, given its other advantages, including its renewability and abundance in nature, being a biowaste and low-cost material, a reservoir of aromatic units and superficial functional groups, its branched, porous and heterogeneous structure, which is favourable for ion exchange processes or complexation with metal ions.

In addition to its good capacity for adsorbing Co(II) from aqueous media, lignin derived from Sarkanda grass holds immense promise for driving circular economy principles forward. Serving as a renewable bioresource, lignin assumes an important role in sustainable material cycles, presenting avenues for repurposing and valorization across diverse sectors. Consequently, initiatives within the circular economy framework are inherently aligned with goals of enhancing resource efficiency, minimizing waste generation, and promoting sustainable development. Making use of the versatility and renewability of lignin enables us to propel towards the realization of more sustainable and resilient societies.

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