BIOWASTE-DERIVED LIGNIN AND ITS USE FOR ADSORBING Fe(II) IONS FROM AQUEOUS ENVIRONMENTS

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Given the abundance of lignin in nature, its relatively accessible processing, and the minimal costs associated with it, this biomaterial has the potential to be exploited to a much greater extent. This research aim to explore the potential of lignin as an adsorbent for retaining of certain polluting species, with a particular focus on Fe(II) in aqueous environments. To achieve optimal adsorption, initial experimental tests were performed to determine the following parameters: the initial pH of the aqueous iron and lignin solution, the concentrations of Fe(II) in the aqueous solutions, the mass of the adsorbent, and the contact time between the involved phases in the adsorption process. To assess the efficiency of Sarkanda grass lignin adsorption, a series of analyses were carried out, with a particular emphasis on: the surface morphology, the state of chemical equilibrium elucidated through the interpretation of the adsorption isotherms using the Freundlich and Langmuir models, the kinetics of the process elucidated through the application of the Lagergren I and Ho-McKay II models, and biological stability assessed through the evaluation of the behavior of selected test biological species, represented by seeds germination of *Triticum aestivum* L, Glosa variety, incorporated in the adsorbent contaminated with Fe(II) and in the filtrates resulting from phase separation. The behavior of these biological species was then evaluated in the filtrates resulting from the phase separation. The experimental results indicate that Sarkanda grass lignin is a viable solution for the adsorption of Fe(II) from wastewater under the tested experimental conditions. This is evident from the results obtained from the mass ratio and contact time studies, specifically the lignin-Fe(II) system. Additionally, the simplicity of the work technique, the ecological character of the biomass fraction, and the economic benefit resulting from valorizing this waste further support the suitability of Sarkanda grass lignin as an effective adsorbent for the removal of Fe(II) from wastewater.

Keywords: Fe(II) ions, Sarkanda grass lignin, seed germination, biowaste, adsorption

INTRODUCTION

Heavy metal ions are regarded as high-risk contaminants because of the significant adverse effects they have on human health and the environment. These effects are largely attributed to their non-biodegradable nature and their capacity for bioaccumulation.[1]

The global production of iron is currently experiencing a period of sustained growth. In 2013, for instance, the output exceeded 500 million tons, with the recycling of iron contributing an additional 300 million tons.[2] One potential route of toxicity induced by particulate matter is through iron, the second most abundant metal in the atmosphere,[3] which is chemically active and capable of forming two major series of chemical compounds: ferrous (Fe^{2+}) and ferric (Fe^{3+}). There

is a distinction between water-soluble (Fe^{2+}) compounds and ferric compounds (Fe^{3+}) that are soluble only in acidic aqueous environments. However, these compounds can be readily reduced to (Fe^{2+}) and thus serve as sources of formation of harmful molecules in the case of free radicals.[2] It is the ferrous form that is responsible for the toxic phenomena, which can lead to pancreatic and hepatic dysfunctions when there is a vitamin E deficiency.[4] It is therefore essential to monitor and control the balance of iron in living systems, as its presence in various environmental matrices, including air, water, soil, and food, can pose a risk to plants, animals, and humans, particularly when it is in excess.[5]

The conventional techniques for the elimination of metal ions from aqueous solutions, including chemical precipitation, lime coagulation, membrane filtration, ion exchange, reverse osmosis, and solvent extraction, are constrained by shortcomings, particularly inadequate removal of the contaminating species.[6-11] Among the emerging methodologies, adsorption is regarded as a prospective approach for the remediation and recovery of metal ions from aqueous media, attributed to its simplicity, high removal efficiency across a broad pH range, and cost-effectiveness.[12, 13] It is equally important to implement readily available, inexpensive, and renewable adsorbents. The conversion of waste into value-added adsorbents aligns with the principles of the circular bioeconomy, offering an environmentally beneficial approach.[14] Furthermore, these bioadsorbents can be reused for multiple cycles, thereby increasing their cost-effectiveness and sustainability.[15,16] Despite these advances, further research is needed to optimize the performance of adsorbents or to explore new materials, gain deeper insights into the underlying mechanisms, and develop more cost-effective and sustainable methods for removing heavy metals from wastewater.[17]

Lignin is a biowaste-derived polymer, with a cross-linked structure, with a variety of functional groups present in the lignin structure, which are negatively charged as a result of deprotonation, allowing for the formation of complexes with metal ions, thereby facilitating the formation of relatively stable compounds.[17-25]

The efficiency of adsorption processes is evaluated by adsorption isotherms, which are subsequently interpreted using mathematical models. The most frequently used models are the Freundlich and Langmuir models.[21-26] The Langmuir model is applicable to solid-liquid systems, assuming that all sites on the adsorbent surface have equal chances of being occupied by heavy metals. In contrast, the Freundlich model characterizes a non-ideal process that occurs on heterogeneous surfaces, often involving the formation of multiple layers.[27] Both models take into account the amount of sorbate retained by the adsorbent under precisely known experimental conditions, including the adsorbent mass, initial pollutant concentration, adsorbent-adsorbate contact time, or initial pH of the aqueous medium.[21-25]

The kinetics of adsorption are described using mathematical models that are designed to reproduce the mechanism involved in the retention of pollutants in aqueous substrates as faithfully as possible. The first-order Lagergren model and the second-order Ho-McKay kinetic model are regarded as the most appropriate for elucidating the mechanism of diffusion of sorbate from the aqueous medium to the active centers on the adsorbent surface.[28]

This research aims to explore the potential of lignin as an adsorbent for retaining certain polluting species, with a particular focus on Fe(II) in aqueous environments. The thermokinetic and biological interpretation of the experimental results obtained regarding the retention of Fe(II) from aqueous media on Sarkanda grass lignin under static conditions indicates that the biomaterial is an efficient adsorbent of contaminants. These findings corroborate those of previous studies, which demonstrated the effective adsorption capacity of the bioresource for the recovery of Pb(II), Zn(II), As(III), Cd(II), Ni(II), and Co(II) from aqueous solutions.[21-25]

In light of these considerations, future research endeavors will be directed towards an investigation of the properties and the identification of the optimal operating conditions for the lignin regeneration process, in conjunction with desorption, with the objective of ensuring the comprehensive utilization and reuse of biowaste.

EXPERIMENTAL

Materials

The main chemical materials include: Sarkanda grass lignin offered by Granit Récherche Development S.A., Lausanne, Switzerland,[24] and $FeSO_4 \cdot 7H_2O$ supplied by ChimReactiv S.R.L., Bucharest. The biological material – *Triticum aestivum L* seeds (Glosa

variety) – was offered by "Ion Ionescu de la Brad" Iasi University of Life Sciences, Iasi, Romania.[24]

Adsorption experiments

The experimental conditions have a significant influence on the efficiency of many processes, including adsorption. In order to ascertain the optimal conditions for the adsorption process, preliminary tests were performed to determine the initial concentrations of Fe(II), the pH of the initial solution, the mass of Sarkanda grass lignin, and the contact times between the two phases involved. Based on the results of preliminary experimental analyses, a solution of 5 g lignin/L aqueous Fe(II) was selected, to ensure an adequate availability of active adsorption sites within the adsorbent structure,[24,29] and a weakly acidic to neutral environment pH.

The stock solutions of metal ion were prepared at a concentration of 0.001 mg/L by dissolving $FeSO_4 \cdot 7H_2O$ separately in distilled water. The working solutions were prepared by diluting the exact volume of the stock solutions with distilled water. The concentrations of metal ion in aqueous media (mg/mL) were as follows: 5.584, 11.168, 16.752, 22.336, 27.92, 33.504, 39.088, 44.672, 50.253, and 55.84. A total of 20 mL of $FeSO_4 \cdot 7H_2O$ was added to each lignin sample at the specified concentrations. The samples were then allowed to rest under laboratory conditions for three contact times: 30, 60, and 90 minutes. This was done to identify the optimal adsorption time of Fe(II) and, by extension, the state of chemical equilibrium.

Spectrophotometric determination of Fe(II)

The quantitative determination of the iron ion obtained after filtration from the aqueous media was carried out by analyzing a precise measured volume (2 mL) in accordance with the established experimental procedure. The concentration value for each sample was subsequently calculated from the regression equation of the calibration curve. The concentration of Fe(II) in the form of $FeSO_4 \cdot 7H_2O$ in the aqueous solutions resulting from the separation of the two phases was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). This method is appropriate for the analysis of heavy metals in various matrices, as recommended in the literature, due to its efficiency, speed, and precision, as well as its high sample throughput.[31,32]

For the spectrophotometric analysis, an inductively coupled plasma-optical emission spectrometer (Perkin Elmer, Model Optima 7000 DV, USA) was employed, with the absorption reading taken at 238.204 nm, which is specific to Fe(II).[33]

Isotherm models

Isotherm refers to the relationship between the equilibrium adsorbate concentrations in the liquid phase and the equilibrium adsorption amount on the solid phase at a given temperature. Therefore, equilibrium adsorption data can be modeled by isotherms and thus adsorption information, such as adsorption mechanisms, maximum adsorption capacity, and adsorbent properties can be investigated.[34] Langmuir and Freundlich isotherms are considered to be the optimal isotherms, being the most commonly adopted for the adsorption of metal ions, dyes, pharmaceuticals, and other types of organic pollutants on biosorbents and abiotic adsorbents.[34,35]

The adsorption capacity of lignin towards Fe(II) were determined according to the following Equation (1):[24,25]

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

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

The Langmuir and Freundlich isotherms provide information about the adsorption surface, whether it is homogeneous or heterogeneous.[36] The Langmuir equation can be written in the following linear form:[24,25]

$$C_e/q_e = 1/q_m \cdot k_L + C_e/q_m \quad (2)$$

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

The linear form of the Freundlich isotherm is as follows:[24,25]

$$\log q_e = \log k_F + 1/n \cdot \log C_e \quad (3)$$

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

The values of the correlation coefficient R^2, calculated with the least squares method, indicate the most appropriate model for interpreting the experimental data obtained.[37]

Kinetic models

The rate and mechanism of sorption processes are dependent on the kinetics of adsorption, which is a significant criterion for characterization. The classical models that describe this phenomenon are the first-order Lagergren model and the second-order Ho-McKay model, which are the most commonly used.[38,39,13]

The Lagergren model is applicable to liquid-solid adsorption and is mathematically represented by the following relationship:[24,25]

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

The equation of the Ho and McKay model reflects the adsorption capacity of the solid phase[21] and is expressed through the following relationship:[24,25]

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

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

By employing linear regression, the most appropriate kinetic model can be selected for the purpose of corroborating the experimental findings.

Surface analyses

Scanning electron microscopy (SEM) was conducted using the Quanta 200 (5 kV) scanning electron microscope (SEM) (Brno, Czech Republic), an effective technique for examining organic and mineral substances at the nanometer (nm) to micrometer (μm) scale.[40]

Biological experiments

The biological approach is based upon a fundamental premise: if the adsorbent has retained the pollutant species, it will become toxic to any living system. Consequently, the adsorption capacity of Sarkanda grass lignin for Fe(II) from aqueous media was assessed through germination tests on *Triticum aestivum* L. seeds, variety Glosa,[24] conducted on both the lignin itself, which had been contaminated with Fe(II), and on the filtrates obtained following phase separation. Distilled water was utilized as a control sample for comparison with the filtrates, while the initial adsorbent was employed as a control for the contaminated lignin. The experiment was carried out over a seven-day period in a laboratory setting (20 °C ± 1, 15 hours of light and 9 hours of dark), with three repetitions and 20 seeds per batch.

The seeds were previously disinfected for five minutes with 5% NaClO and subsequently washed three times with MilliQ ultrapure water. The seeds were introduced into test tubes (180 x 18 mm) for the purpose of soaking with the filtrate/distilled water for one hour, with intermittent shaking, and subsequently distributed uniformly in Petri dishes (90 x 15 cm), which were covered with two overlapping filter paper discs.[24,25,41] In accordance with previously described methodology,[42,43] the seeds that exhibited swelling, rot or mold growth at the end of the germination period were classified as ungerminated. The toxicity level of the filtrates and lignin contaminated with aqueous solutions of Fe(II), in the concentration range studied (5.584-55.840 mg/mL), at the three contact times between the phases (30, 60, and 90 min), was assessed. The germination energy and germination capacity were assessed using relations (6) and (7):[24,25,43]

$$E_g = (a/n) \cdot 100 \quad (6)$$

$$C_g = (b/n) \cdot 100 \quad (7)$$

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 Fe(II) adsorption onto Sarkanda grass lignin

Initial concentration of Fe(II)

To assess the efficiency of the adsorption process, the amount of Fe(II) retained per unit of lignin mass (q, mg/g) was quantified. Given the observed increase in the ratio between the initial number of moles of Fe(II) and the number of accessible adsorption sites on the lignin fraction, it is reasonable to conclude that, with increasing concentration, adsorption will also intensify until saturation is reached. Figure 1 illustrates an increase in lignin adsorption capacity, from 1.2989 mg/g at a concentration of 5.584 mg/L to 12.3779 mg/g at a concentration of 55.85 mg/L, for a contact time between phases of 60 minutes, with increasing Fe(II) concentration in the studied concentration range. This confirms the anticipatory hypothesis.

Dose of Sarkanda grass lignin

The adsorbent dose represents a crucial factor influencing the adsorption process,[44] allowing to evaluate the performance of a material with prospective adsorbent properties[34] based on the available binding sites for eliminating a pollutant species at a specific concentration.[45,21-25] Prior tests performed to optimize the adsorption process were conducted within the range of 4-40 g Sarkanda grass lignin/L aqueous Fe(II) solution, a range proposed by the literature.[21-15,46] As illustrated in Figure 2, increasing the dose of Sarkanda grass lignin does not result in an enhanced adsorption capacity. Instead, it is observed that the amount of Fe(II) retained per unit mass of biosorbent decreases. This is attributed to the strong affinity between the hydrophilic functional groups in the lignin structure and Fe(II), as well as the probable complexation in the initial stage of adsorption. Subsequently, when the adsorption sites on the surface of the adsorbent become partially or totally inaccessible, reaching saturation, the migration of Fe(II) to the unreacted functional groups within the lignin is attenuated. Thus, it was concluded that the optimum dose of Sarkanda grass lignin is 5 g/L Fe(II) aqueous solution.

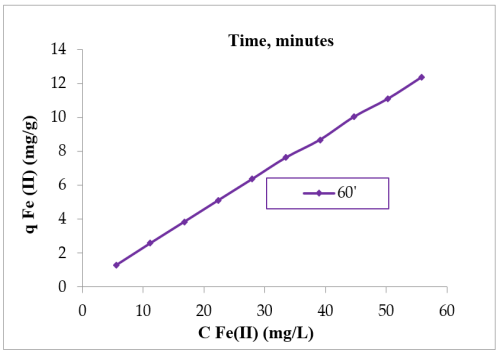

Figure 1: Adsorption capacity of Sarkanda grass lignin (contact time of 60 min, pH of 6.5)

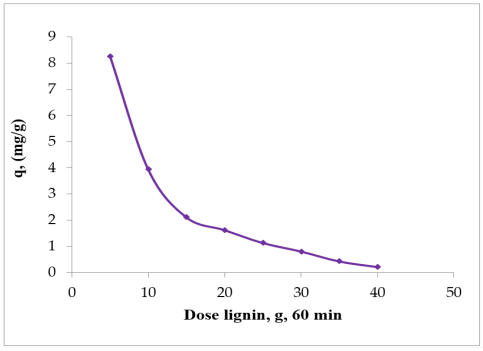

Figure 2: Effect of adsorbent dose on Fe(II) adsorption (Fe(II) concentration 55.84 mg/L, contact time 60 min, pH 6.5)

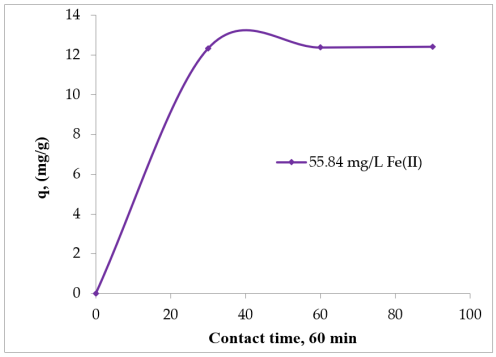

Figure 3: Effect of contact time on adsorption of Fe(II) on Sarkanda grass lignin (pH 6.5)

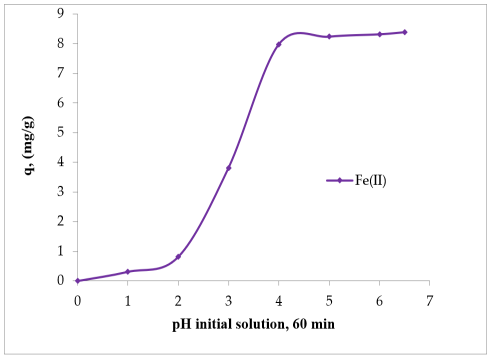

Figure 4: Effect of initial solution pH on Fe(II) adsorption on Sarkanda grass lignin

Contact time

The existing literature recommends that the contact time between the adsorbate and the adsorbent should be longer in order to accurately characterise the kinetics and to achieve interphase equilibrium.[47] The experimental data were analyzed, and it was found that an increase in the contact time between Sarkanda grass lignin and the aqueous iron solution resulted in a more pronounced increase in the amount of Fe(II) retained in the initial stage. Subsequently, the adsorption rate slowed down, reaching a maximum at 60 minutes, which is considered optimal for reaching the equilibrium state (Fig. 3). Notably, at the contact time of 90 minutes, there were negligible variations in the adsorption capacity compared to the values recorded at 60 minutes.

Initial solution pH

The preliminary tests conducted on the variation of the adsorption capacity of Sarkanda grass lignin depending on the initial pH of the aqueous solution of Fe(II) targeted the acidic range of 0-7, as this is the range in which Fe(II) is ordered and can precipitate as hydroxide in alkaline environments (pH 9-11). This can result in a reduction or even a blockage of the adsorption process.[30] As illustrated in Figure 4, the degree of adsorption of Sarkanda grass lignin for Fe(II) increases with the initial pH of the solution. The maximum adsorption capacity (8.39 mg/g) was observed at pH 6.5, which is considered the optimal pH. This can be attributed to the predominance of ferrous species. In acidic environments,[44] the presence of $[Fe(H_2O)_6]^{2+}$ and $[Fe(OH)(H_2O)5]^{+}$ ions and the deprotonation of functional groups on the lignin surface, which become negatively charged, facilitate the chelation of Fe(II) from the aqueous environment. Therefore, strongly acidic environments are not conducive to this process, as the excess of hydronium ions can compete with iron ions for active binding sites on lignin.[46]

Adsorption isotherms

Mathematical models were employed to interpret the experimentally obtained adsorption data,[48] with the most commonly utilized models being the Langmuir and the Freundlich isotherms.[49] These are particularly useful for the study of adsorption equilibrium. The Langmuir isotherm postulates monolayer adsorption on a

homogeneous surface, with a finite number of adsorption sites and with uniform adsorption strategies, precluding the transmigration of the adsorbate in the surface plane.[50,21-25] The linear form of the Freundlich isotherm assumes monolayer or multilayer adsorption on a heterogeneous surface, with a non-uniform distribution of adsorption energy on the surface.[51,21-25] The suitability of isotherm models for the study of adsorption is evaluated based on the values of the R^2 correlation coefficients, which are calculated following the linear representation of the regression equations for both models. Consequently, the higher the R^2 value, the more accurately the model describes the adsorption process.[49,21-25] Figure 5 (a and b) depicts the linear representation of the Freundlich and Langmuir models for the adsorption of Fe(II) from aqueous media onto Sarkanda grass lignin under experimental conditions considered optimal: contact time (60 min) and pH 6.5 at room temperature (20 ± 0.1 °C). Table 1 presents the specific parameters of the Freundlich (R^2, 1/n, k_F) and Langmuir (R^2, q_m, K_L) models.

The correlation coefficients (R^2) for the Langmuir model fall within the range of 0.7852 to 0.8712, which is below the correlation coefficients (R^2) for the Freundlich model, which fall within the range of 0.9656 to 0.9789 (Table 1). This indicates that the experimental data is more consistent with the Freundlich model, which is better suited to describe the adsorption of Fe(II) on Sarkanda grass lignin. The relatively low values of K_L (0.0641-0.0693) suggest that the surface of Sarkanda grass lignin may be heterogeneous, and that the retention of Fe(II) may occur in a polylayer. As evidenced in Table 1, the values of K_L and 1/n are relatively low. The values of K_L range from 1.9902 to 2.0327, while those of 1/n span from 0.9142 to 0.9411. This observation highlights the potential influence of ion exchange interactions or the formation of a surface complexation on the observed adsorption phenomenon. However, without further insight, it remains challenging to ascertain whether the predominant mechanism is physical adsorption or chemisorption. Consequently, a kinetic interpretation is essential to elucidate the underlying adsorption process.

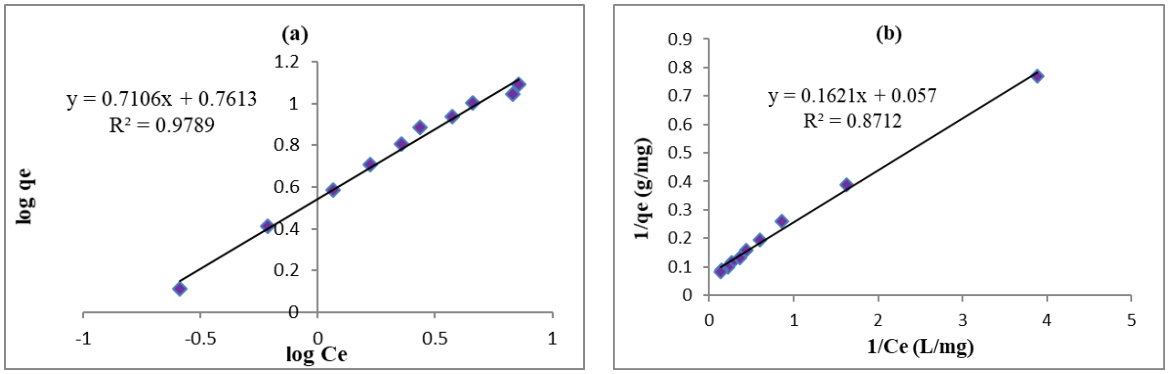

Figure 5: Freundlich adsorption model (a) and Langmuir adsorption model (b) for Fe(II) adsorption onto Sarkanda grass lignin after 60 min

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

Time (min)	Freundlich model			Langmuir model		
	R^2	1/n	k_F	R^2	q_m (mg/g)	K_L
30	0.9656	0.9142	2.0327	0.7852	12.8821	0.0693
60	0.9789	0.9242	1.9856	0.8712	13.6117	0.0687
90	0.9684	0.9411	1.9902	0.7931	13.7002	0.0641

Kinetic modeling

Two mathematical models are frequently applied to describe the adsorption kinetics, as recommended by the literature. The first is the pseudo-first order Lagergren model, which is specific to liquid-solid adsorption. The second is the pseudo-second order Ho-McKay model, which indicates the adsorption capacity of the solid phase.

These models have been described in detail previously.[38,39] Figure 6 (a and b) illustrates the linear correlation between the two models for interpreting the adsorption of Fe(II) from aqueous media onto Sarkanda grass lignin, at a normalized initial concentration of 100 mg/mL. Table 2 presents the specific kinetic parameters, calculated from the slopes and ordinate intercepts of the linear dependencies obtained for each kinetic model. The correlation coefficients (R^2) were obtained through linear regression.

As illustrated in Table 2, the correlation coefficients (R^2) calculated using the pseudo-first order Lagergren kinetic model fall below 0.9, with a range of 0.6798 to 0.8817. The probability of triggering electrostatic interactions between Fe(II) and free functional groups on the lignin surface is increased, with the predominance of active chemical adsorption over physical adsorption. However, this phenomenon is not explained by the Lagergren model, limiting its use for the kinetic interpretation of Fe(II) adsorption from aqueous media on Sarkanda grass lignin. This finding aligns with a series of previous studies.[23,25]

The correlation coefficients (R^2) calculated according to the Ho-McKay kinetic model present unitary values in all cases (Table 2), as do the other parameters. The positive affinity of Fe(II) as a pollutant agent with Sarkanda grass lignin as a biosorbent, indicated by q_e and K_2, is also accompanied by the probability of chelation. This is facilitated by the availability of lignin functional groups that can be involved in donor-acceptor exchanges and the formation of relatively stable lignocomplexes following active adsorption of Fe(II). Accordingly, the Ho-McKay model, by virtue of its superior accuracy, is of greater relevance than the Lagergren model. This leads to the conclusion that the rate-determining step of Fe(II) adsorption on Sarkanda grass lignin is governed by the chemical interaction between Fe(II) and the functional groups in the lignin structure.

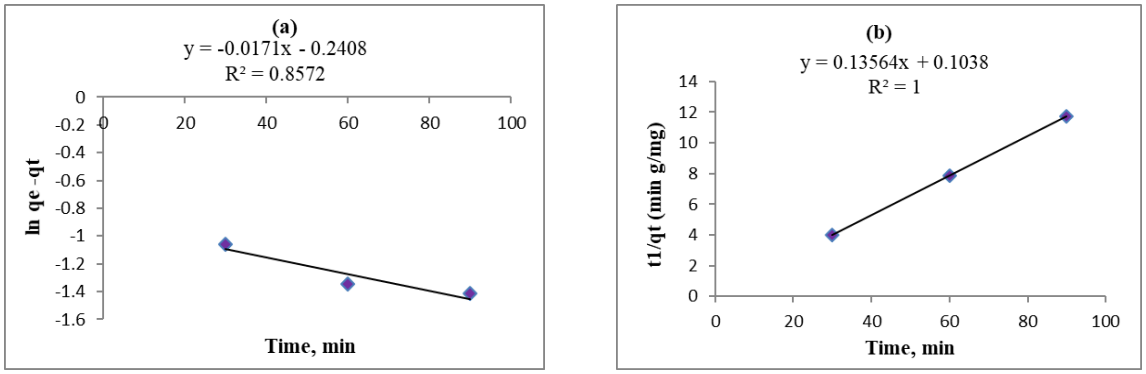

Figure 6: Linear representation of the Lagergren pseudo-I order model (a) and Ho-McKay pseudo-II order model (b) for adsorption of Fe(II) onto Sarkanda grass lignin after 60 min

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

c_i	Lagergren model			Ho-McKay model		
(mg/mL)	R^2	q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg·min)
10	0.6798	1.6231	-0.0021	1	1.8721	2.5541
20	0.8062	1.9886	-0.0019	1	2.9118	1.7094
30	0.8601	3.0004	-0.0022	1	4.9312	3.1154
40	0.8435	4.5561	-0.0019	1	8.0901	3.0059
50	0.7149	6.4091	-0.0017	1	9.6951	2.0073
60	0.8572	7.3491	-0.0019	1	10.8906	0.0621
70	0.6871	8.0021	-0.0020	1	11.8983	1.2843
80	0.7736	9.0734	-0.0018	1	12.4762	3.0592
90	0.8817	9.4001	-0.0018	1	13.9571	1.5555
100	0.8634	10.1937	-0.0019	1	14.8363	1.2980

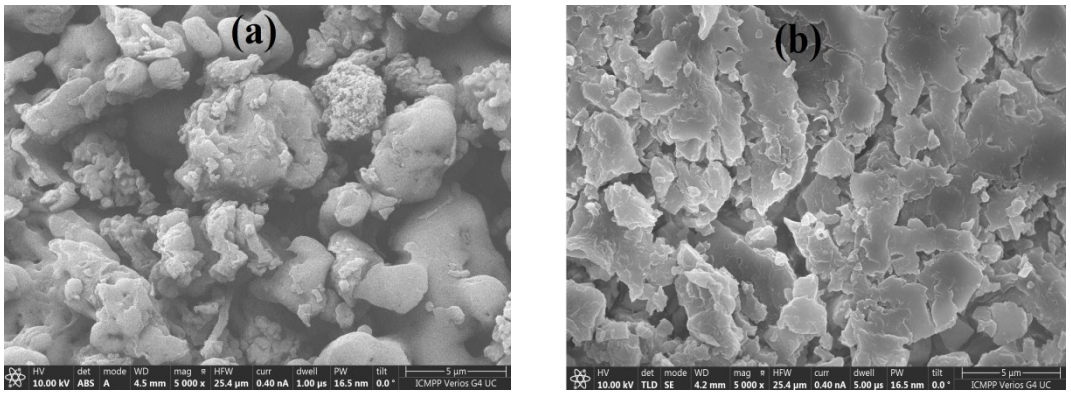

Figure 7: SEM images of Sarkanda grass lignin before adsorption (a) and after Fe(II) adsorption (b), contact time of 60 min

Surface morphology

In order to perform scanning electron microscopy (SEM), the prepared sample was metallized with platinum (Pt) in order to improve contrast. Figure 7 depicts the morphology of Sarkanda grass lignin prior to and following Fe(II) adsorption at a concentration of 55.84 mg/L and a contact time between phases of 60 minutes. Figure 7(a) depicts the SEM micrograph of the uncontaminated lignin, which exhibits an agglomeration of well-separated particles of approximately 4 μm. This morphology differs significantly from that of the Fe(II) contaminated lignin, as shown in Figure 7(b), which illustrates the contact of Fe(II) from aqueous media with the lignin, followed by its migration and adsorption onto the biomaterial.

Biological toxicity study

Iron plays a dual role both as an acceptor and a donor, participating in the transfer of electrons in the processes of photosynthesis and respiration. The phenomenon of iron toxicity in plants is contingent upon elevated concentration of Fe^{2+} ions present in the roots and their subsequent transport to the leaves. The presence of excess Fe^{2+} has been demonstrated to result in the production of free radicals, which can lead to irreversible damage to cellular structures and components, such as membranes, DNA, and proteins. Ferritin, a protein that plays a crucial role in iron metabolism, has been shown to bind with Fe(II) and facilitate the transfer of this metal ion to plastids within the cytoplasm through the use of specialized transit peptides.[52]

In light of this, the development of the caryopsis of *Triticum aestivum* L., the Glosa variety, was monitored for seven days in the presence of samples contaminated with Fe(II). Figure 8 depicts the mean number of wheat seeds germinated after contact with the contaminated lignin samples or with the filtrates resulting from Fe(II) retention at the three contact times.

The experimental data (Fig. 8) indicate that the presence of Fe(II) has a negative impact on the germination of *Triticum aestivum* L. seeds, particularly when the concentration of the metal ion is increased and when the contact time between the phases is extended. Of the total number of seeds (n = 20) included in the study, the average germination rate was 96.65% in the control lignin samples and 100% in distilled water. In the case of the filtrates, the number of germinated seeds after three days and the number of seedlings developed after seven days from germination were similar to those obtained in the distilled water control, at times of 60 and 90 minutes. However, at the 30-minute contact time, the number of germinated seeds was lower, indicating that the adsorption equilibrium was not reached at this interphase time.

This finding supports the hypothesis that a longer contact time is necessary to achieve equilibrium. This conclusion is in line with the thermokinetic data interpretation, which recommends 60 minutes as the optimal contact time. In contaminated lignin, at a contact time of 30 minutes and at low concentrations of Fe(II), the highest number of germinated seeds appears after 3 days. Conversely, from a concentration of 44.672 mg/L Fe(II), the number of germinated caryopses is zero at all three contact times. This demonstrates that increasing the concentration of Fe(II) and the interphase contact time results in a decrease in the germination capacity of the seeds. This is due to the negative effect triggered by the polluting species.

Seven days after germination, in all cases where contaminated lignin samples were used, regardless

of the contact times and Fe(II) concentration, no further germination occurred and the existing seedlings died. This confirms the efficiency of Sarkanda grass lignin as an adsorbent for Fe(II), a conclusion supported by the thermodynamic and kinetic experimental results. Figure 9 illustrates the germination of *Triticum aestivum* L. seeds, over a seven-day period. The seeds were denoted as follows: reference/uncontaminated lignin (R/UL), lignin contaminated with Fe(II) (CL), reference/distilled water (R/DW), and the filtrate (F) obtained after adsorption for 60 minutes at a concentration of 55.84 mg/L Fe(II).

Table 3 presents the experimental results for germination energy and ability, which are directly correlated with the number of germinated seeds after contact with the filtrates or the Fe(II)-contaminated lignin samples.

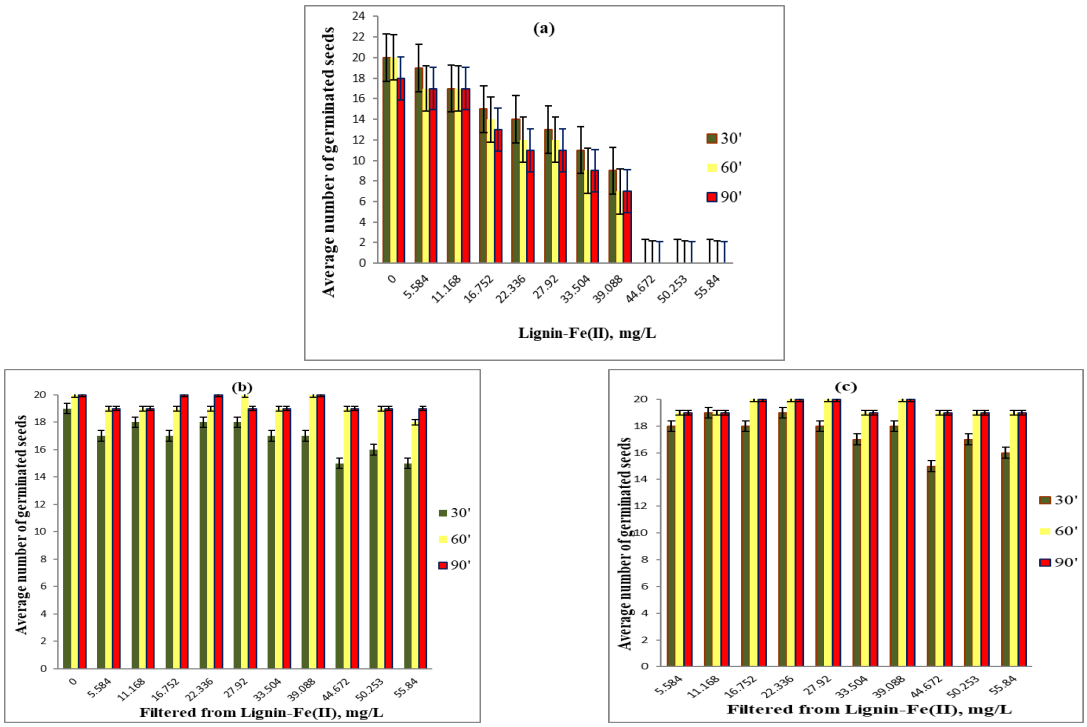

Figure 8: Average number of *Triticum aestivum L.* cariopses germinated after 3 days of contact with the contaminated adsorbent (a), and after 3 days (b) and 7 days (c) of contact with the filtrates resulting from Fe(II) adsorption

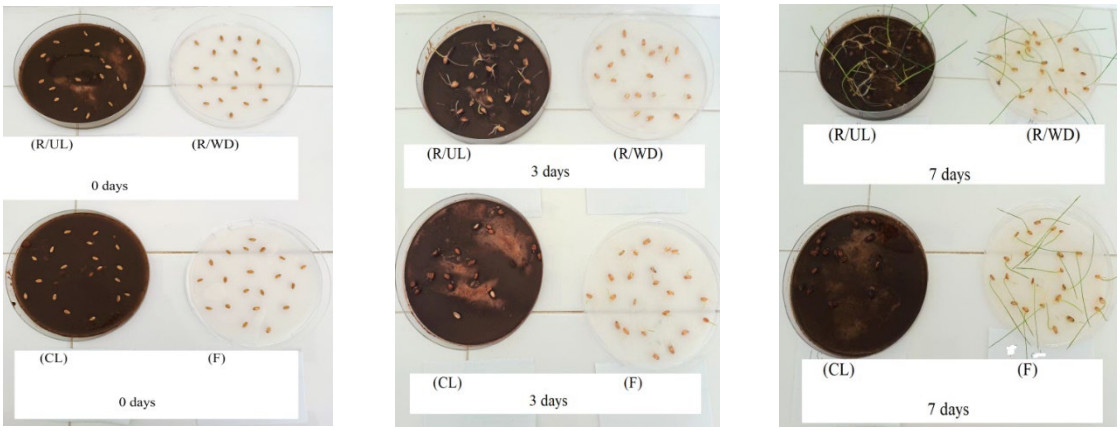

Figure 9: Germination of *Triticum aestivum L.* seeds over a period of 7 days on the loaded adsorbent used for an adsorption time of 60 min and Fe(II) concentration of 55.84 mg/L

Table 3
Mean values of germination energy and capacity of seeds after contact with the contaminated adsorbent and the filtrates resulting from Fe(II) adsorption for different contact times between phases

Lignin/Fe(II) (mg/L)	Contact time (min)						Lignin/Fe(II) (mg/L) filtered	Contact time (min)					
	30	60	90	30	60	90		30	60	90	30	60	90
	Eg, %			Cg, %				Eg, %			Cg, %		
0	100	100	90	95	95	95	0	95	100	100	100	100	100
5.584	95	85	85	0	0	0	5.584	85	95	95	90	95	95
11.168	85	85	85	0	0	0	11.168	90	95	95	95	95	95
16.752	75	70	65	0	0	0	16.752	85	95	100	90	100	100
22.336	70	60	55	0	0	0	22.336	90	95	100	95	100	100
27.92	65	60	55	0	0	0	27.92	90	100	95	90	100	100
33.504	55	45	45	0	0	0	33.504	85	95	95	85	95	95
39.088	45	35	35	0	0	0	39.088	85	100	100	90	100	100
44.672	0	0	0	0	0	0	44.672	75	95	95	75	95	95
50.253	0	0	0	0	0	0	50.253	80	95	95	85	95	95
55.84	0	0	0	0	0	0	55.84	75	90	95	80	95	95

At a contact time of 30 minutes and, implicitly, at a state of chemical non-equilibrium, the filtrates are more concentrated and the germination energy is low. However, at 60 and 90 minutes, the germination energy is higher due to the dilution of the filtrates resulting from the retention of Fe(II) on the lignin adsorbent. For contaminated lignin, the increase in iron concentration and contact time results in a reduction of the germination energy to zero values, at all three contact times, within the concentration range of 47.674-55.84 mg/L Fe(II), as illustrated in Table 3.

For lignin contaminated with Fe(II), the germination capacity is zero in all situations. In contrast, for filtrates, the germination capacity varies proportionally with the germination energy, exhibiting values close to those obtained in the control sample. This remains the case regardless of the Fe(II) concentration, with insignificant variations at times of 60 and 90 minutes. This indicates the efficient adsorption of Fe(II) on Sarkanda grass lignin at the contact time of 60 minutes. This is considered optimal also based on thermokinetic data. This ensures good reproducibility of the experimental results.

Based on the findings of the present study, which were derived from the analysis of the surface properties of Sarkanda grass lignin in conjunction with data pertaining to its adsorption efficiency, it can be concluded that lignin can be considered as an effective adsorbent for the retention of Fe(II) under static conditions from aqueous solutions. The objective of the subsequent research will be to identify potential applications and optimize the regeneration conditions of the lignin adsorbent, with a view to subsequently testing its resorption capacity. The research will also seek to ascertain whether it is possible to generate zero waste.

CONCLUSION

Sarkanda grass lignin, a biowaste-derived product, can be considered a promising substrate with favorable adsorption functions for the retention of Fe(II) in static conditions from aqueous media under precise experimental conditions. The optimum conditions established in this study are: solution pH of 6.5, and a dose of 5 g adsorbent/L pollutant solution at room temperature (20 ± 0.1 °C). The equilibrium time for the interphase was found to be 60 minutes, with a Fe(II) concentration range of 5.584-55.84 mg/L.

The experimental adsorption isotherms were interpreted through the Freundlich and Langmuir models, with the R^2 correlation coefficients responsible for estimating the efficiency of an adsorbent from a practical point of view. However, these models did not clarify the nature of the adsorption. Instead, they indicated a higher probability of chemisorption, as the Freundlich model is more appropriate for describing the retention of Fe(II) in the polylayer on the non-uniform and capillary-pervaded surface of the lignin, as shown by the SEM surface analysis.

The pseudo-first order Lagergren and pseudo-second order Ho-McKay models, employed for the kinetic interpretation of practical data, facilitated the acquisition of coherent information regarding the electrostatic nature of the interactions between the species involved. This was achieved through the values of the calculated specific parameters, as represented by the Ho-McKay model. This

characterization is particularly compelling insofar as it pertains to the static retention of Fe(II) from aqueous media on Sarkanda grass lignin. Moreover, it is in accordance with the Freundlich model, which offers a pertinent prediction regarding the probability of chemisorption. This is attributed to the appearance of the donor–acceptor bond between lignin and Fe(II), which subsequently leads to the formation of relatively stable lignocomplexes.

Bioassays were performed on *Triticum aestivum* L. caryopses introduced into the lignin adsorbent loaded with Fe(II) and into the filtrates resulting from the separation of the two phases after the adsorption process. The adsorption capacity of the lignin waste for Fe(II) from aqueous media was confirmed by the results obtained for interphase contact times of 30, 60, and 90 minutes, which reflected the inhibitory effect generated by the presence of Fe(II) on the biological dynamics of wheat seeds/seedlings.

In the context of sustainable recovery, with zero waste generation, the experimental results obtained on the adsorption of Fe(II) from aqueous solutions on Sarkanda grass lignin indicate that biomass waste derived lignin may be a feasible and efficient adsorbent from several points of view. These include the natural abundance and renewability of biomass, from which it is derived, its relatively easy processing and environmental compatibility, but also its aromatic structure, which possesses functional groups capable of participating in ion exchange or chelation processes with metal ions.

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