

# USE OF SARKANDA GRASS LIGNIN AS A POSSIBLE ADSORBENT FOR As (III) FROM AQUEOUS SOLUTIONS – KINETIC AND EQUILIBRIUM STUDIES

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Received May 6, 2022

Considering the negative effects of polluting species on the environment and human health, in particular heavy metals, and the need for efficient use of resources, the present study investigated the adsorption of As (III) from aqueous solutions under static conditions onto chemically unmodified Sarkanda grass lignin. In order to optimize the adsorption process, the retention of As (III) was tested under various experimental parameters (pH of the initial solution and adsorbent, concentration of aqueous solutions, adsorbent dose and contact time of the two phases). The experimental data obtained were interpreted based on the classical models of Freundlich and Langmuir isotherms, which was useful in establishing the equilibrium conditions and in evaluating the adsorption capacity for a solute. The adsorption dynamics was studied using the Lagergren pseudo-first order and the Ho and McKay pseudo-second order models. The analysis of the obtained experimental data recommends chemically unmodified Sarkanda grass lignin as a future alternative adsorbent for water remediation, taking into account its practical applicability in the retention of As (III) from aqueous solutions, in terms of both adsorbent and adsorbed doses, as well as the time required for adsorption.

**Keywords:** Sarkanda grass lignin, As (III), adsorption, equilibrium, kinetics

## INTRODUCTION

The use of resources, in particular renewable ones, along with the generation and treatment of wastes are some of the current concerns of the society, with direct impact on the environment, especially considering the stages of extraction, production, use, but also the end of the life cycle of products. Therefore, reducing the consumption of materials, the efficient use of resources, reducing the generation of wastes and their transformation into resources can be starting points for efficient solutions to these problems. The element arsenic is included in the category of

heavy metals, even though it belongs to the class of metalloids, according to the European Union legislation – EU-955/2014. There are about 300 substances that contain arsenic, either in the form of minerals or in the form of modified compounds: arsenides, arsenites, arsenates *etc.*<sup>1-5</sup> Therefore, arsenic can be released from a variety of natural (rocks) and anthropogenic sources (mining, glass processing, manufacture of insecticides, pesticides *etc.*), accumulating in soils and sediments. Literature shows that, in polluted areas, the total arsenic content can reach 314-3497

mg/kg in sediments, which is much higher than the maximum allowed in sediments (by 11 to 121 times).<sup>5-7</sup>

Lignin is one of the main fractions of biomass, and, at the same time, it can be a reusable vegetal resource, with high potential for valorisation, which is the objective of the current research.<sup>8,9</sup> Considered an amorphous cross-linked polymer, lignin shows the capacity of ionic exchange due to the presence of numerous functional groups (hydroxyl, carbonyl, methoxyl, carboxyl) in its structure, which are capable of interacting with organic or inorganic ionic species, forming relatively stable complex combinations.<sup>8</sup> Thus, lignin can act as a chemical substrate, where the functional groups are strongly associated with the skeleton, and can retain polluting species from solutions, by forming chemical bonds with metal ions. Considering this, lignin can be valorized in wastewater remediation processes for reducing environmental pollution, serving as an adsorbent for the removal of heavy metal ions, even though the mechanisms involved in the adsorption process are not completely elucidated.<sup>8</sup> Due to the complex structure of this biopolymer, it is possible to trigger activated adsorption through Coulombian attraction between ionic and neutral species or the dipoles of water.<sup>10-13</sup> The affinity of heavy metals and, implicitly, of arsenic towards lignin can also be attributed to its non-polar character, which can direct the diffusion of adsorbate molecules.<sup>14</sup> There are literature data that attest to the quantitative retention of metal ions on lignin.<sup>11,13,15</sup> Thus, this low-cost material can be a promising alternative in the context of diversification of raw materials for reducing the content of pollutants in industrial wastewaters.

The pH, dose and nature of the adsorbent, as well as the initial concentration of the polluting species and the contact time, are factors that control the adsorption process. In general, in order to highlight the role of pH, it is necessary to take into account the influence of H<sup>+</sup> and OH<sup>-</sup> ions in adjusting the electrical potential of the lignin surface. Literature data suggest that lignin has the best adsorption capacity in the pH range of 4.0-6.5.<sup>16,17</sup> Probably, the pH influences the adsorption by varying the degree of dissociation of the functional groups on the superficial binding sites of the adsorbent, which leads to the modification of the equilibrium characteristics of the adsorption process.

The study of adsorption equilibrium is very important to determine the retention capacity of

the adsorbent and establish the basic physico-chemical parameters of the adsorption process.<sup>13</sup> In order to establish the equilibrium conditions for an adsorption process, the adsorption isotherms represented by the two classical models – those of Freundlich and Langmuir – are used.<sup>16</sup> The kinetic approach deals with the adsorption as a cumulation of three successive diffusion processes consisting of the migration of the adsorbate from the solution mass to the solution layer around the adsorbent, the diffusion of the adsorbent from the solution layer around the adsorbent to its surface, and the diffusion of the adsorbent on the surface into the internal pores of the adsorbent, followed by its binding to the active sites. The Lagergren pseudo-first order kinetic model and the Ho and McKay pseudo-second order kinetic model describe as faithfully as possible the kinetics and mechanism of the adsorption process.<sup>18</sup>

With these considerations, the present study investigates the adsorption capacity of a chemically unmodified Sarkanda grass lignin substrate towards As (III) in aqueous solution under static conditions. This work has been motivated by the findings of our previous study, which have demonstrated Sarkanda grass lignin as an efficient adsorbent for Pb (II) and Zn (II).<sup>13</sup>

## EXPERIMENTAL

### Materials and methods

Unmodified Sarkanda grass lignin (Sarkanda grass-100SA-140) was supplied by Granit Recherche Développement S.A. Lausanne, Switzerland, and was used as an adsorbent (Table 1).

A stock solution of arsenic ion with the concentration 0.001 mg/L was prepared by dissolving sodium arsenite (NaAsO<sub>2</sub>) in distilled water. The working solutions were prepared by diluting with distilled water an exact measured volume of the stock solution. The concentration of the metal ion in the aqueous solutions is presented in Table 2.

### *Spectrophotometric determination of As (III)*

A specific and selective, linear and precise spectrophotometric analysis method was chosen for determining the concentration of As (III) in the form of sodium arsenite in aqueous solutions resulted from the separation of the two phases – optical emission spectrometry with inductively coupled plasma with hydride generation (HG-ICP-OES). This method has the detection and quantification limits appropriate for the intended purpose in this study, ensuring accuracy of determinations. An inductively coupled plasma optical emission spectrometer was used (iCAP 7400 ICP-OES), with dual vision, using plasma generated at

atmospheric pressure, with a radio frequency field in the presence of argon, as a source of ions.

According to the method described in the literature, a solution of 10% HCl was used to generate arsenic hydride, as well as 0.6% NaBH<sub>4</sub> in 0.5% NaOH used as a reducing agent, thus yielding a stable system, with maximum absorption at 189.042 nm.<sup>5-7,9,19,20</sup>

According to the experimental procedure, the quantity of As (III) obtained after filtration from the aqueous solutions was determined by analyzing an exactly measured volume (2 mL) and the concentration for each sample was calculated from the regression equation of the calibration curve.

Table 1  
Properties of unmodified Sarkanda grass lignin<sup>13</sup>

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

#### Adsorption experiments

For determining the optimal conditions for the adsorption process, some preliminary experimental tests were made, focusing on the initial concentrations of As (III), the pH of the initial solution, the doses of the adsorbent, and the contact times between the two phases. The influence of temperature was not taken into account, as literature data have proved that the impact of this parameter on retention is negligible.<sup>21</sup>

The experiment was carried at 20 (±0.5 °C), using an adsorbent dose of 5 g of lignin per liter of As (III) aqueous solution, to ensure an acceptable number of adsorption sites available for retention.<sup>22</sup> Considering data reported in the literature, according to which the removal of arsenic is achieved with maximum efficiency in the pH range of 6-9,<sup>23</sup> and the fact that in our previous study, a weak acid to neutral medium proved to be adequate for the adsorption of Pb (II) and Zn (II) onto the lignin substrate,<sup>13</sup> the experiments in the present work were performed at pH 6.

Thus, 20 mL of sodium arsenite solution with different concentrations (Table 2) were added to the lignin adsorbent. The solutions were left at rest for different times: 10, 20, 30, 40, 50, 60 and 120 minutes, to allow them to reach the state of equilibrium and to determine the optimal retention time of the polluting species. Then, the As (III) concentration was determined by HG-ICP-OES spectrophotometry for each resting time, following the separation of the phases by simple filtration.

#### Isotherm models

The adsorption efficiency of the Sarkanda grass lignin towards As<sup>3+</sup> was evaluated by determining the amounts of metal ion retained per unit mass of the adsorbent (q, mg/g) by Equation (1):<sup>13</sup>

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

where C<sub>i</sub> – initial concentration (mg/mL); C<sub>e</sub> – equilibrium concentration (mg/L); V – volume of metal ion solution (L); m – mass of adsorbent (g).

The experimental data obtained were analyzed based on the two most commonly used models in the literature – the Freundlich and Langmuir isotherms. They are widely used for establishing equilibrium conditions and the way in which metal ions are fixed on the surface of the adsorbent during the adsorption process.<sup>13,16</sup> The Langmuir model describes the adsorption in monolayer and admits that the adsorbate molecules are retained on energy-equivalent (homogeneous) sites, and that saturation corresponds to the complete occupation of these sites. On the other hand, the Freundlich model considers that the adsorption process takes place on relatively inhomogeneous surfaces and in several layers, represented by the functional groups of the adsorbent, with different affinities for a given metal ion.

The Langmuir isotherm is expressed by Equation (2):<sup>13</sup>

$$q_e = q_{\max} (k_L \cdot c_e / 1 + k_L \cdot c_e) \quad (2)$$

where K<sub>L</sub> – Langmuir constant related to free energy adsorption (L/mg); q<sub>max</sub> – maximum amount of metal ion retained on the adsorbent after complete saturation; (mg/g); q<sub>e</sub> – amount of metal ions adsorbed per unit of mass of adsorbent (mg/g) at equilibrium; c<sub>e</sub> – equilibrium concentration (mg/L).

The Freundlich isotherm is expressed by the empirical relationship in Equation (3):<sup>13</sup>

$$q_e = k_F \cdot c_e^{1/n} \quad (3)$$

where k<sub>F</sub> – Freundlich constant, indicating adsorption capacity; n – constant characterizing the affinity of metal ions to sorbent; q<sub>e</sub> – amount of metal ions adsorbed per unit of mass of adsorbent (mg/g) at equilibrium; c<sub>e</sub> – concentration at the equilibrium of metal ions in solution (mg/L).

Considering the values of the correlation coefficients ( $R^2$ ) obtained for the linear representation of each model, the most appropriate model to describe the experimental data was chosen.

#### Kinetic models

The Lagergren pseudo-first-order and the Ho and McKay pseudo-second-order models allow determining the kinetic parameters of the adsorption process of As (III) from aqueous solution onto lignin, from the slopes and the intercept of the linear dependencies  $\lg(q_e - q_t)$  and  $t$ , respectively  $t/q_t$  and  $t$ .

The Lagergren model for adsorption in a liquid-solid system is expressed by the equation:<sup>13</sup>

$$\lg(q_e - q_t) = \lg q_e - (k_1/2.303) t \text{ (linear shape)} \quad (4)$$

The Ho and McKay model reflects the adsorption capacity of the solid phase and is expressed by the following relationship:<sup>13</sup>

$$t/q_t = (1/k_2 \cdot q_e^2) + t/q_e \text{ (linear shape)} \quad (5)$$

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

## RESULTS AND DISCUSSION

### Effects of experimental parameters on As (III) adsorption onto Sarkanda grass lignin

Considering the nature of lignin, with its branched polyaromatic structure and thousands of monomer units of phenylpropane,<sup>1</sup> and the known affinity between its functional groups and metal ions, it was expected that, once in contact with the aqueous solution of  $As^{3+}$ , it would allow, through

the functional groups present in its structure, activated adsorption by the dissociation and interaction with the metal ion.

When optimizing the experimental conditions for As (III) adsorption, a smaller dose of lignin was intended to be used for economic reasons. The literature data recommend a dose of lignocellulosic adsorbent in the range of 4-40 g/L.<sup>21</sup> In our previous experiments, we found the optimal dose to be of 5 g of Sarkanda grass lignin per L of Pb (II) and Zn (II) aqueous solutions.<sup>13</sup> Taking into account these data, experimental tests were performed and led to the same result, confirming that the most efficient retention of As (III) was recorded at a dose of 5 g of lignin adsorbent per L of aqueous solution of the pollutant.

### Initial concentration of As (III)

To estimate the efficiency of adsorption, the amount of As (III) retained per unit of lignin mass ( $q$ , mg/g) was calculated. Increasing the initial concentration of As (III), while maintaining the other parameters constant, leads to an increase in the adsorption capacity of lignin, until saturation, when most of the functional groups of lignin associate with the metal ion, and the diffusion to the unreacted (free) functional groups inside the lignin particles will probably be blocked.

Table 2  
Quantity of  $As^{3+}$  retained per unit mass of Sarkanda grass lignin ( $q$ , mg/g)

$c_{As^{3+}}$ (mg/L)	$q_{As^{3+}}$ (mg/g)						
	Time (min)						
	10	20	30	40	50	60	120
7.4920	1.3325	1.3329	1.3331	1.3331	1.3332	1.3332	1.3332
14.9840	2.6651	2.6655	2.6658	2.6659	2.6660	2.6660	2.6660
22.4760	3.9978	3.9981	3.9985	3.9986	3.9987	3.9987	3.9987
29.9680	5.3305	5.3308	5.3311	5.3313	5.3314	5.3314	5.3314
34.4600	6.6631	6.6634	6.6637	6.6638	6.6639	6.6640	6.6640
44.9520	7.9957	7.9960	7.9963	7.9964	7.9965	7.9965	7.9965
52.4440	9.3283	9.3286	9.3289	9.3291	9.3291	9.3291	9.3291
59.9360	10.6608	10.6611	10.6614	10.6616	10.6616	10.6616	10.6616
67.4280	11.9933	11.9937	11.9940	11.9941	11.9942	11.9942	11.9942
74.9200	13.3259	13.3263	13.3265	13.3267	13.3267	13.3267	13.3267

### Initial solution pH

The literature specifies that the ionic species of As (V) is predominant at  $pH > 3$ , and in solutions containing As (III) the neutral species prevails at  $pH < 9$ , so that the removal of arsenic is achieved with maximum efficiency in the pH range of 6-

9.<sup>23</sup> As the pH increases, the carboxyl and hydroxyl functional groups on the lignin surface probably suffer a deprotonation process, becoming negatively charged and active in establishing covalent coordination bonds with  $As^{3+}$  in the aqueous solution. Moreover, at

moderately alkaline pH (9-11),  $\text{As}^{3+}$  is ordered and can precipitate as hydroxide, thus, the adsorption can be weaker or even stopped. Thus, the pH value of 6 was chosen as the optimal value at which arsenic exists in the form of a trivalent ion. This is also in accordance with literature recommendations.<sup>13,22</sup>

#### Contact time

The complex structure of lignin can cause a differentiated migration of  $\text{As}^{3+}$  to the internal functional groups and, therefore, the contact time between the two phases necessary to reach the adsorption equilibrium is important. In order to establish the optimal contact time for the adsorption, the adsorption behaviour was observed during 7 different contact times (10, 20, 30, 40, 50, 60 and 120 min). Overall, it was established that an increase in the contact time between the two phases of the adsorption system leads to an increase in the amount of  $\text{As}^{3+}$  retained on the lignin adsorbent. This increase is more pronounced in the initial stage, and then the process slows down, the maximum adsorption being reached at 60 min (probably at saturation). Therefore, it can be considered that 60 minutes is the optimal contact time, since it is sufficient to achieve adsorption equilibrium in the case of As (III). In a previous study<sup>13</sup> examining the adsorption of Pb (II) and Zn (II) ions from aqueous solutions on lignin, the most suitable contact time was also found to be 60 minutes. Thus, the findings corroborate our earlier experimental data and conclusions, confirming their reproducibility.

#### Adsorption isotherms

Adsorption isotherms allow obtaining information on the nature of the interactions during the retention process, the mechanism of the adsorption process and the practical applicability and efficiency of the adsorbent.

The distribution profile of As (III) was captured by using the adsorption isotherms, obtained by the graphic representation of  $q$  (mg/g) in relation to the equilibrium concentration values of the polluting species in the aqueous solution ( $c$ , mg/L). The isotherms are nonlinear in the studied concentration range, and their form is a typical one, as mentioned in the specialized literature for the adsorption of most metal ions onto different adsorbent materials.<sup>13,15,24</sup>

The experimental data were fit to the most widely used isotherms – the Freundlich and the Langmuir models, which can provide an insight

into the nature of the adsorption of As (III) onto the lignin adsorbent. The correlation coefficients ( $R^2$ ) were calculated for each model from the regression equations resulting from the linear representation of each model. Figures 1 and 2 show the linear representation of the Freundlich and Langmuir models for the adsorption of As (III) from aqueous solutions onto unmodified Sarkanda grass lignin, under optimal experimental conditions (temperature:  $20 \pm 0.5$  °C, contact time: 60 min, pH 6), and Table 3 shows the characteristic parameters of the Freundlich ( $R^2$ ,  $1/n$ ,  $K_F$ ) and Langmuir ( $R^2$ ,  $q_{\max}$ ,  $K_L$ ) models under the same working conditions.

From Table 3, the values of the correlation coefficients ( $R^2$ ) obtained for the Langmuir model are noted to be in the range of 0.8251-0.9791. These values are slightly lower than those of the correlation coefficients ( $R^2$ ) for the Freundlich model (0.9719-0.9930), which suggests that the Langmuir model would be less suitable to describe the process of adsorption of As (III) on Sarkanda grass lignin compared to the Freundlich model. Moreover, the values of the Langmuir  $K_L$  show that the adsorption could not occur as a monolayer process, and the surface of the Sarkanda grass lignin would not be perfectly homogeneous.

The Freundlich constants ( $n$  and  $K_F$ ) are a measure of the degree of adsorption, indicating the mechanism of the process. Thus, the values of these parameters in the range between 0 and 1 indicate a favorable adsorption process.<sup>25</sup> The higher the values of  $K_F$  and  $1/n$ , the stronger the interactions between the metal ions in the aqueous solution and the functional groups of the adsorbent are.<sup>25</sup> This was confirmed in the present work, where the values of  $K_F$  fell within the range of 0.1840-1.0960, and those of  $1/n$  – in the range of 0.2320-1.1024, reflecting the existence of an adsorption binding energy as a result of ionic exchange interactions or superficial complexation.

The contact time of 60 minutes was confirmed as the optimal adsorption time. At 120 minutes, the analyzed parameters vary very little, which is attributed to saturation, when the concentration gradient and adsorption rate decrease. Analyzing the correlation coefficients obtained in the case of the two models, it is not possible to establish with certainty whether the adsorption is physical or chemical, which will most likely be clarified with the help of kinetic models, although the data confirm the Sarkanda grass lignin as a potent adsorbent for As (III).

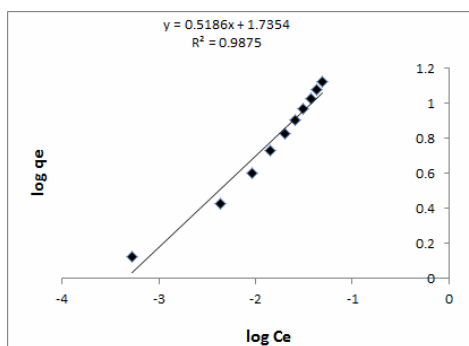


Figure 1: Freundlich adsorption model for As (III) removal by unmodified Sarkanda grass lignin for 60 min

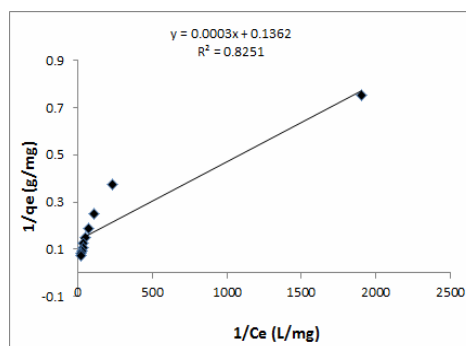


Figure 2: Langmuir adsorption model for As (III) removal by unmodified Sarkanda grass lignin for 60 min

Table 3  
Characteristic parameters of Freundlich and Langmuir models for As (III) adsorption on unmodified Sarkanda grass lignin

Freundlich model			
Time (min)	R <sup>2</sup>	1/n	K <sub>F</sub>
10	0.9719	1.1024	0.1840
20	0.9755	0.4610	0.6415
30	0.9930	0.3387	0.8645
40	0.9825	0.2925	0.9700
50	0.9875	0.2360	1.0836
60	0.9875	0.2323	1.0949
120	0.9888	0.2320	1.0960
Langmuir model			
Time (min)	R <sup>2</sup>	q <sub>max</sub> (mg/g)	K <sub>L</sub>
10	0.9791	2.6336	0.0194
20	0.8645	2.4313	0.1532
30	0.8951	2.7070	0.2296
40	0.8446	2.7708	0.2742
50	0.8274	2.7901	0.3124
60	0.8251	2.8042	0.3145
120	0.8287	2.8145	0.3134

### Kinetic studies

The kinetics of the adsorption process depends both on the retention process and on the diffusion stages that direct the transfer of the solute from the solution to the active sites on the surface of the adsorbent. In order to be able to interpret the experimental data from a kinetic point of view, it was necessary to obtain the correlation coefficients calculated by linear regression of the Lagergren pseudo-first order kinetic model, specific to the adsorption in a liquid-solid system,

and of the Ho and McKay pseudo-second order model derived on the basis of the adsorption capacity of the solid phase.

Figures 3 and 4 illustrate the linear dependencies obtained for each kinetic model, for the adsorption of As (III) ions from aqueous solutions on Sarkanda grass lignin, at the initial normalized concentration of 10 mg/mL. Tables 4 and 5 present the characteristic kinetic parameters, calculated from the slopes and the ordered intercept of these dependencies.

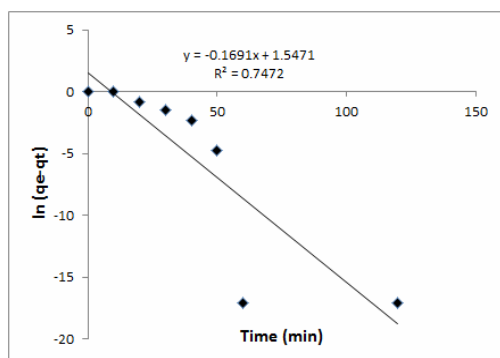


Figure 3: Linear representation of the Lagergren model for adsorption of As (III) ions on unmodified Sarkanda grass lignin

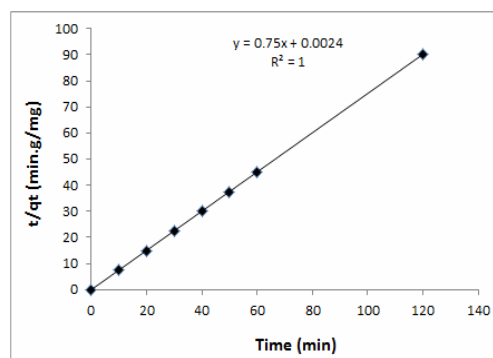


Figure 4: Linear representation of the Ho and McKay model for adsorption of As (III) on unmodified Sarkanda grass lignin

Table 4

Kinetic parameters of the Lagergren pseudo-first order model for adsorption of As (III) on unmodified Sarkanda grass lignin

$c_i$ , mg/mL	$R^2$	$q_e$ , mg/g	$K_1$ , $\text{min}^{-1}$
10	0.7472	4.6978	-0.0014
20	0.9406	8.3086	-0.0010
30	0.7399	5.2299	-0.0012
40	0.9694	3.4431	-0.0007
50	0.9220	1.6561	-0.0004
60	0.9692	3.0128	-0.0007
70	0.7770	2.4200	-0.0009
80	0.9127	12.8211	-0.0012
90	0.7460	4.5398	-0.0012
100	0.7596	3.6302	-0.0012

Table 5

Kinetic parameters of the Ho and McKay pseudo-second order model for adsorption of As (III) on unmodified Sarkanda grass lignin

$c_i$ , mg/mL	$R^2$	$q_e$ , mg/g	$K_2$ , g/mg·min
10	1	1.5669	15.1358
20	1	2.0859	11.2485
30	1	2.4050	8.6127
40	1	2.6434	8.1901
50	1	2.8628	5.5170
60	1	2.9691	3.5602
70	1	3.2071	2.6531
80	1	3.2873	1.2999
90	1	3.4566	0.6232
100	1	3.5997	0.0264

It can be observed that in the case of the Lagergren pseudo-first order model, the correlation coefficients ( $R^2$ ) are lower than 0.96, varying in the range of 0.7399-0.9694. This suggests the probability of the existence of electrostatic chemical interactions between the metal ion and the functional groups on the surface of the adsorbent, chemisorption being favored at

the expense of the van der Waals physical adsorption, which cannot be explained by the Lagergren model. Also, the fact that  $R^2$  has sub-unit values suggests that this model has limited applicability for the kinetic description of the adsorption of As (III) ions from aqueous solutions on lignin, and confirms the experimental results and the conclusions obtained in our previous

study.<sup>13</sup> Consequently, it can be concluded that the Lagergren pseudo-first order model is less suitable for describing this adsorption processes.

Therefore, the Ho and McKay pseudo-second order model was used, starting from the hypothesis that the rate-determining step of the adsorption process is the chemical interaction between the metal ion in the aqueous solution and the functional groups of the adsorbent.<sup>21,26</sup> The compatibility of the experimental data with this kinetic model indicates that such interactions have occurred.

The correlation coefficients ( $R^2$ ) present unity values in all situations, and the  $q_e$  and  $K_2$  parameters reveal the good affinity of the unmodified Sarkanda grass lignin as an adsorbent for the As (III) pollutant, suggesting active adsorption of As (III), especially due to the availability of functional groups of lignin. It seems that the Ho and McKay pseudo-second order model successfully describes the adsorption of As (III) ions on lignin, which has also been the case in other previous studies,<sup>11,13,21</sup> providing pertinent and plausible information regarding the electrostatic nature of the interactions between the two phases.

Also, in correlation with the parameters obtained in the case of the Freundlich and the Langmuir models, it appears that the assumption that the chemical adsorption predominates at the expense of the physical one, and that the active sites located on the surface of the lignin are accessible for As (III) in aqueous solution seems to be confirmed. Moreover, the idea of adsorption that unfolds differently is outlined, as in the initial stage, the process unfolds faster as a result of more intense interactions, and towards the end, it takes place more slowly, and intraparticle diffusion becomes predominant in the retention of the metal ion in the pores of the lignin.

Consequently, the present study confirms the potential of lignin as an efficient adsorbent that could be suitable for reducing environmental pollution. Considering the fact that lignin can be extracted with relatively low costs from grasses and agricultural residues, which are renewable and widely available in significant amounts, it can prove to be a feasible solution for wastewater remediation.

## CONCLUSION

In light of the data obtained, the present study demonstrates that chemically unmodified Sarkanda grass lignin can be an efficient

adsorbent in terms of As (III) retention, under optimal experimental conditions – room temperature 20 °C ( $\pm 0.5$  °C), acidic to neutral pH (pH 6), a dose of 5 g adsorbent/L pollutant, within the studied concentration range (Table 2), and contact time necessary to achieve equilibrium of 60 minutes. From the kinetic point of view, the adsorption of As (III) ions from aqueous solutions on Sarkanda Grass lignin was analyzed with the Lagergren pseudo-first order and the Ho and McKay pseudo-second order models. It was remarked that the Ho and McKay model best describes the adsorption of As (III) on the lignin adsorbent, providing conclusive details regarding the electrostatic nature of the interactions between the two phases and suggesting an activated chemical adsorption.

Thus, it can be concluded that unmodified Sarkanda grass lignin can be an alternative solution for wastewater remediation, to reduce environmental pollution, given its adsorbent properties arising from the presence of functional groups in its structure, which make possible the retention of various pollutants through ion exchange or complexation processes. Also, it can be economically advantageous, due to the wide availability of the required raw materials at a global level. Moreover, its regeneration after use should be considered, which would make it an even more attractive low-cost adsorbent.

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