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# LIGNIN-BASED BIOMASS FRACTIONS FOR Cr(VI) ADSORPTION FROM AQUEOUS MEDIA – THERMODYNAMIC, SPECTRAL AND BIOLOGICAL ANALYSIS

BY

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**Abstract.** In the context of the complex valorisation of biomass and the absolute need to mitigate polluting sources, such as heavy metals, the present study proposes a renewable/strategic bioresource, Sarkanda grass (*Tripidium bengalense*) lignin, as a substrate for adsorption of the Cr(VI) ions from aqueous media under static conditions. Through a synthesis of thermodynamic, spectral, and biological considerations, the study demonstrates the efficacy of this natural aromatic polymer. The findings suggest potential applications in industrial wastewater treatment, offering a sustainable alternative to existing methods. This research contributes to the growing field of bio-based materials for environmental remediation, highlighting the value of agricultural waste in addressing water pollution challenges.

**Keywords:** Sarkanda grass lignin, *Tripidium bengalense*, Cr(VI) ions, adsorption, *Triticum aestivum* L.

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## 1. Introduction

Anthropogenic activities, such as: chroming, welding, galvanizing, paint and glass manufacturing, tanning, alloying, etc., reveal the economic importance of chromium. On the other hand, the wide range of practical applications contributes to its large-scale accumulation, with the effect harmful to soil, plants, food security and human health (Wani *et al*., 2022).

Researchers are making considerable efforts to limit chromium (VI) concentrations in soils, industrial waste streams and aqueous environments. They and are proposing different methods, including biosorption which is based on the capacity of specific types of bio-based materials to capture and concentrate heavy metals (Garg *et al*., 2008).

The variety of oxidation states, from 0 to + 6, imprints the chemical and toxicological properties of chromium, the Cr(VI) form known as being the most bioavailable and toxic, showing carcinogenic effects in humans (Khalid *et al*., 2021; Ungureanu *et al*., 2022).

While various methods exist for Cr(VI) removal, including chemical precipitation, ion exchange, and membrane filtration, many of these techniques are expensive, energy-intensive, or generate secondary waste (Armanu and Volf, 2022). Biosorption using bio-based materials offers a promising alternative due to its cost-effectiveness, sustainability, and high efficiency. Sarkanda grass, an abundant agricultural residue in many parts of Asia, represents an underutilized source of bio-based materials in general and lignin, in particular, with potential for environmental applications (Gîlcă *et al*., 2015).

The current study proposes as an adsorption substrate, lignin, which can be considered a strategic, non-toxic, cheap, renewable bioresource, being the second most widespread biopolymer in nature, after cellulose. (Ungureanu *et al*., 2024). The possibility of complexing lignin with heavy metal ions is favoured by the large number of functional groups, especially carboxyl and hydroxyl, that it possesses and by its porous structure, functions that propel it into of nano or biosorbents the category (Vasile *et al*., 2023).

This study aims to evaluate the adsorption capacity of Sarkanda grass lignin for Cr(VI) removal under static conditions, focusing on spectral, thermodynamic, and biological analyses, after a previous study which demonstrated the efficiency of the adsorbent through kinetic considerations (Ungureanu *et al*., 2022). Furthermore, this research explores the potential synergistic effects between the unique structural properties of Sarkanda grass lignin and its adsorption mechanisms, aiming to provide insights into optimizing lignin-based materials for enhanced Cr(VI) removal in various environmental conditions. By exploring this novel bio-based adsorbent, we seek to contribute to the development of sustainable solutions for heavy metal remediation in aqueous environments.

## 2. Material and Method

The following materials have been utilised in this study:

- Sarkanda Grass lignin (extracted industrially from *Tripidium bengalense*), supplied by Granit Recherche Development S.A. Lausanne, Switzerland and $K_2Cr_2O_7$ supplied by ChimReactiv S.R.L., Bucharest (Ungureanu *et al*., 2022).
- *Triticum aestivum* L seeds (Glosa variety) offered by "Ion Ionescu de la Brad" Iasi University of Life Sciences, Iasi, Romania (Ungureanu *et al*., 2024).
- Stock solutions were prepared by dissolving $K_2Cr_2O_7$ in distilled water until a concentration of 0.001 mg/L was achieved. The working solutions were prepared by diluting a precisely measured aliquot of the stock solution in distilled water. The chromium concentrations in the aqueous media (mg/mL) are presented as: 5.2, 10.04, 15.6, 20.08, 26, 31.5, 36.4, 41.6, 46.8, and 52 mg/mL. Over 5 g of lignin, 20 mL of $K_2Cr_2O_7$ were added in the previously specified concentrations, after which the samples were left to rest (20 ± 0.5°C) at three contact times: 30, 60 and 90 minutes.

Work procedure: The concentration of Cr(VI) was determined using the diphenylcarbazide method, with the absorption value at 545 nm (Ungureanu *et al*., 2022). The quantitative determination of the metal ion obtained after filtration from the aqueous solutions was conducted by analysing an accurately 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.

For the spectrophotometric analysis, we used a Visible Spectrophotometer for laboratory, model VS-721N, 300-1000 nm, manufacturer JKI, Shanghai, China. Scanning electron microscopy (SEM) was performed using a Quanta 200 SEM (5 kV) (Brno, Czech Republic). Contaminated and uncontaminated samples were metallized with Pt for better contrast, resulting in Pt in both types of samples. The thermodynamic behavior of Cr(VI) adsorption on lignin was characterized by calculating the thermodynamic parameters: variation of free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), using van't Hoff laws (Chong *et al*., 1995).

Biological tests: germination tests were performed on seeds of *Triticum aestivum* L., Glosa variety, both on lignin contaminated with aqueous chromium solutions, in the concentration range studied (5.2-52 mg/mL), at the three contact times, and on the filtrate. As control samples, distilled water was used for the filtrates, and uninfected adsorbent for the contaminated lignin. The experiment took place for seven days, according to the procedure described by Ungureanu et al. (Ungureanu *et al*., 2024).

## 3. Results and Discussions

In order to characterize the thermodynamic properties of the adsorption process, the following parameters were employed: Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) (Table 1).

It can be posited that the retention of Cr(VI) from aqueous solutions on lignin is spontaneous, given that the variation of Gibbs free energy (ΔG) demonstrates negative values at both pH values. A change of Gibbs free energy value greater than -30 kJ/mol suggests the occurrence of charge transfer between the metal ion and the adsorbent surface.

For the adsorption of chromium (VI) ions onto lignin at both initial solution pH values, the experimentally derived Gibbs free energy values range from -26.08 kJ/mol to -38.14 kJ/mol. This indicates that electrostatic interactions play a predominant role in the adsorption mechanism (Table 1).

**Table 1**
*The thermodynamic parameters for the adsorption of chromium ions on Sarkanda grass lignin*

| pH | Time (minutes) | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/mol K |
|---|---|---|---|---|
| 2.09 | 30 | - 26.08 | 12.96 | 98.17 |
| | 60 | - 27.94 | 11.37 | 88.72 |
| | 90 | - 28.82 | 11.82 | 93.14 |
| 5.0 | 30 | - 30.76 | 15.34 | 111.02 |
| | 60 | - 35.41 | 14.25 | 132.24 |
| | 90 | - 38.14 | 15,01 | 124.38 |

The enthalpy values (ΔH) show that the process of adsorption of chromium (VI) on Sarkanda grass lignin is endothermic, for both pH values the initial solution (Table 1). The positive values of the entropy (ΔS) suggest that the degrees of freedom of Cr(VI) are partially restricted with its adsorption on the lignin surface (Table 1), and the state of disorder is favored by the decrease in the degree of ordering of the nearby solvent molecules functional groups of the adsorbent.

Figure 1 shows the morphology of Sarkanda grass lignin before and after Cr(VI) adsorption at a concentration of 52 mg/L and an interfacial contact time of 60 minutes obtained by scanning electron microscopy (SEM) and can be seen in the micrograph SEM of the uncontaminated lignin shows an agglomeration of micrometric particles well separated in relation to the surface morphology of the lignin contaminated with Cr(VI), a fact that confirms the contact between the two phases followed by the diffusion and adsorption of the metal ion in the lignin capillaries.

Chromium can have a toxic effect on plant growth and development, causing changes in the germination process. Considering this aspect, the biological stability of the caryopses of *Triticum aestivum* L., in contact with the samples contaminated with Cr(VI) was monitored for seven days.

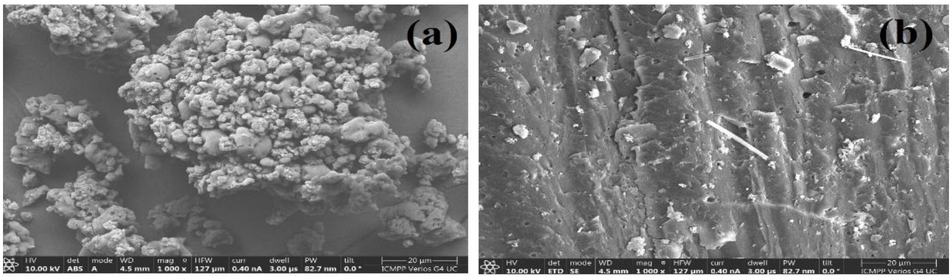


Fig. 1 − The SEM images for Sarkanda grass lignin before adsorption (a) and after Cr(VI) adsorption (b), contact time of 60 minutes.

The Fig. 2 (a, b and c) shows the average number after three repetitions of wheat seeds germinated at 3 days for the samples contaminated with Cr(VI), respectively the average number after three repetitions of germinated seeds at 3 and 7 days for the filtrates result from the retention of Cr(VI) at the three contact times. From Fig. 2 (a, b and c) it can be seen that with the increase in the concentration of Cr(VI) and the contact time between the phases, the number of *Triticum aestivum* L. seeds decreases, from the concentration of 41.6 mg/L, this being null.

From the total of 20 seeds used, 19-20 germinated in lignin and 20 in distilled water. In the case of the filtrates, the number of germinated seeds after 3 days, but also the number of seedlings after 7 days from germination, these are close to the one obtained in the case of the control, at the times of 60 and 90 minutes, but lower at the contact time of 30 minutes, which shows an adsorption non-equilibrium and imposes a longer interphase contact time, which is in agreement with the conclusions drawn from the interpretation of the thermodynamic parameters, which consider the optimal contact time of 60 minutes.

At 7 days after germination, in the case of all contaminated lignin samples, regardless of the contact times and the Cr(VI) concentration, no seeds germinated, and the existing seedlings died, which demonstrates the fixation of Cr(VI) ions in the pores Sarkanda grass lignin.

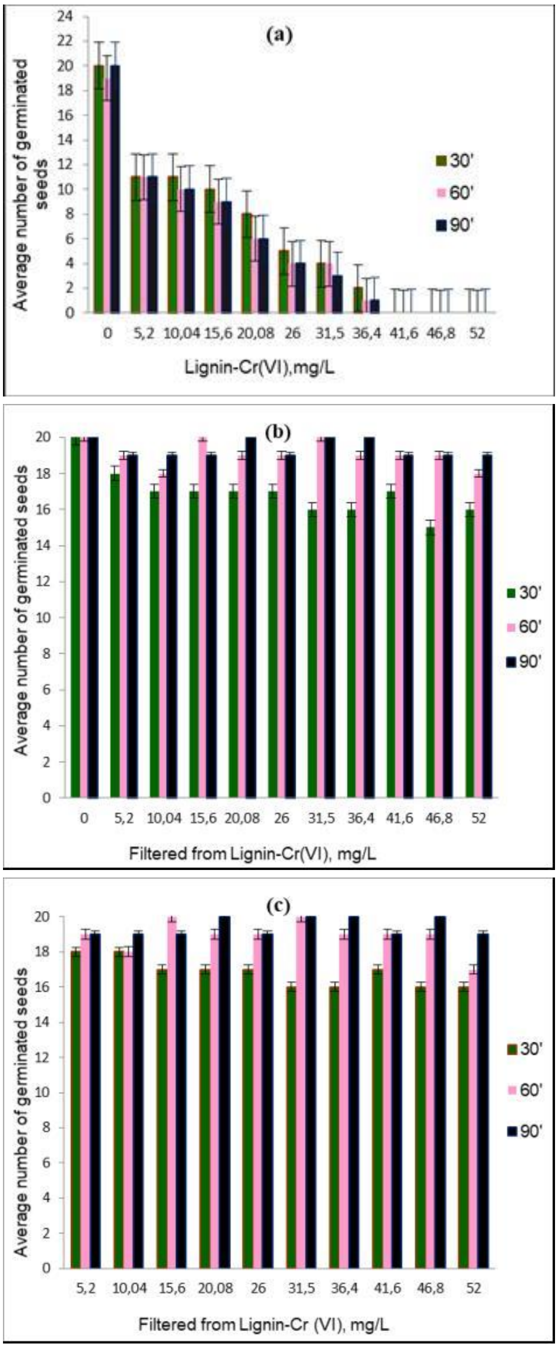


Fig. 2 − The average number of *Triticum aestivum* L. caryopses germinated at 3 days for the contaminated samples (a) and for the filtrates resulting from Cr(VI) adsorption at 3 days (b) and 7 days (c).

The observations of the surface analysis combined with the thermodynamic and biological data obtained, suggest the use of Sarkanda grass lignin, under precisely established experimental conditions, as an efficient adsorption substrate for Cr(VI) from aqueous media, a function supported by good chelation capacity between the aromatic units of the fraction biomass and Cr(VI).

## 4. Conclusions

This study demonstrates the efficacy of Sarkanda grass lignin as an adsorbent for Cr(VI) ions from aqueous media, offering a promising perspective for applications in industrial wastewater treatment.

Thermodynamic parameter values indicate the occurrence of active adsorption of Cr(VI) from aqueous media on Sarkanda grass lignin, which is correlated with the extended relative distribution of degrees of freedom with respect to the adsorption centres of the biomass adsorbent, as evidenced by SEM.

Biological analyses have demonstrated that Cr(VI) is retained on Sarkanda grass lignin through its toxic effect on the germination of *Triticum aestivum* L. seeds. This is due to the action of Cr(VI) as an oxidising agent, as well as the formation of free radicals during the reduction of Cr(VI) to Cr(III).

This research adds valuable knowledge to the growing field of bio-based materials for environmental remediation, offering new insights into heavy metal adsorption mechanisms. The findings suggest promising applications not only in industrial wastewater treatment but also in other areas of environmental remediation where heavy metal removal is necessary. Future studies could explore process optimization, scalability, and applicability in real wastewater treatment conditions.

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## FRACȚIUNI BIOMASICE PE BAZĂ DE LIGNINĂ PENTRU ADSORBȚIA Cr(VI) DIN MEDII APOASE – ANALIZE TERMODINAMICE, SPECTRALE ȘI BIOLOGICE

(Rezumat)

În contextul valorificării complexe a biomasei și a necesității absolute de atenuare a sursele poluante, precum metalele grele, prezentul studiu propune ca substrat de adsorbție în condiții statice a ionului Cr(VI) din medii apoase, o bioresursă regenerabilă/strategică, lignina Sarkanda grass, demonstrând prin considerente termodinamice, spectrale și biologice eficiența acestui polimer natural aromatic. Rezultatele sugerează potențiale aplicații în tratarea apelor uzate industriale, oferind o alternativă durabilă la metodele existente. Această cercetare contribuie la domeniul în creștere al materialelor bio-bazate pentru remedierea mediului, evidențiind valoarea deșeurilor agricole în abordarea provocărilor legate de poluarea apei.