

Comparative analysis of nickel adsorption by natural sisal fiber and treated with citric acid

ABSTRACT

Introduction: Removing nickel from wastewater is complex and costly, requiring research into alternatives with technical and economic solutions. An alternative would be the use of plant biomass. In the Northeast region of Brazil, one of these alternatives, with a large cultivation area, is sisal (*Agave Sisaliana*), which may have greater yields for this purpose through surface chemical treatment with citric acid, which inserts carboxylic groups into the structure of the plant fiber. Thus, the objective was to analyze the ability to remove nickel in solution by sisal fibers. **Methodology:** For this purpose, part of the sisal fibers was cut into 0.5 cm, washed and dried; initially treated with NaOH (0.1 mol/L); washed with distilled water and treated with citric acid (1.2 mol/L). The fibers were identified by FTIR; XRD; XRF and SEM. Adsorption tests were carried out with nickel solution for the parameters: kinetics, balance, influence of pH and adsorbent mass. **Results:** The XRF analysis demonstrated a greater presence of NiO adhered to the treated fiber (55.74%); FTIR confirmed the presence of non-ionized carbonyl in the region from 1700 to 1750 cm^{-1} ; the adsorption kinetic test demonstrated greater effectiveness of the treated fiber > 80%; an ideal adsorbent mass was observed to be 0.1g; the ideal pH for removal was 5.0 while the equilibrium test has the best Langmuir isotherm, the uncontrolled fiber obtained $R^2 = 0.9810$ and the controlled fiber $R^2 = 0.9643$. **Conclusion.:** Therefore, it was observed that the treatment of sisal fiber with citric acid increases the removal efficiency of nickel ion in aqueous solution, presenting itself as a low-cost and widely available material.

Keywords: Sisal. Removal. Nickel. Citric acid.

1. INTRODUCTION

The expansion of urbanization in developing countries has contributed to the contamination of water resources by heavy metals, such as nickel, chromium, copper, gallium, aluminum and cadmium, which are sources of pollutants: industrial sectors textile, tanneries, metallurgical, microelectronics, mining and electroplating (EWECHAROEN et al, 2008; GHAEAA et al, 2012; SAMARGHANDI et al, 2011, VIEIRA et al, 2009; ZHENG et al, 2021). These metals can pose risks to human health, including exposure to nickel, ~~the object of study~~, allergic reactions (irritation of mucous membranes and skin), malaise (nausea, vomiting) and risks of carcinogenicity (SAMARGHANDI et al , 2011; MONFERRÁN et al, 2012; NORSUHAILIZAH et al, 2024).

Removing this heavy metal from wastewater is complex and costly, requiring research into alternatives with technical and economic viability. An alternative would be the use of plant biomass, with great availability and the possibility of regeneration through adsorption (RODRIGUES et al, 2006; LEYVA-RAMOS et al, 2012; ALHAWAS et al, 2013; VAKILI et al., 2021).

In the Northeast region of Brazil, one of these alternatives, with a large cultivation area, is sisal (*Agave Sisaliana*). This plant, native to Mexico, was introduced to the country in the 20th century and is currently used for manufacturing ropes, automotive coatings and handicrafts (SANTOS et al, 2011; MARTIN et al, 2009; LEITE et al., 2022). Being chosen as a vegetable fiber for Ni (II) removal tests from natural and chemically treated aqueous solutions.

Surface modification is, in general, a resource that enables the evolution of a certain characteristic, leaving the material with greater affinity, consequently improving its performance (CHEE et al, 2008; RENMIN et al, 2006; WARTELLE & MARSHALL, 2000; WANG et al, 2016). There are several types of surface modification, ranging from bleaching, cationization, to the insertion of chemical groups.

Among the forms of surface chemical treatment to improve the removal of metal ions is the use of citric acid, which inserts carboxylic groups into the structure of the plant fiber (RENMIN et al, 2006; LEVYA-RAMOS et al, 2012; HOANG et al., 2021). Thus, in an aqueous medium, the OH of the carboxylic group dissociates, forming negative charges, which will be binding points for metal ions in solution (Me^+). Therefore, the efficiency of sisal fiber would be greater for removing Ni (II) from aqueous solutions after carrying out this chemical treatment (RENMIN et al, 2006; LEVYA-RAMOS et al, 2012; HOANG et al., 2021).

Some studies point to efficiency in this process, including: functionalization of activated carbon to remove copper (PAUL CHEN (RENMIN et al, 2006), modified agricultural residues to remove copper (WARTELLE & MARSHALL, 2000), modified

coconut fiber for copper removal (LEYVA-RAMOS et al, 2012); plant bark (*Ceiba pentandra*) for nickel removal (RAMANA et al, 2012) and sugarcane bagasse for lead adsorption (HOANG et al, 2021). The main objective of this work was to compare the nickel adsorption performance using sisal fiber modified with citric acid and unmodified sisal fiber.

2. MATERIAL AND METHODS

2.1 Fibers collection and preparation

The sisal fibers from Embrapa in Campina Grande – PB, Brazil, were first cut to a size similar to 0.5 cm, washed with non-ionic detergent for 60 minutes to remove impurities and undesirable dirt that accompanied the fiber during its collection. Subsequently, the fibers were properly dried in an oven (Forced Convection Oven, BIOFOCO BF2 ECF 64) at a temperature of 115°C.

2.2 Chemical treatment of fibers

The sisal fibers were previously immersed in a sodium hydroxide solution (0.1 mol/L) with a fiber/solution ratio of 1g:40ml, where they were stirred for 2 hours. They were then washed with distilled water until the solution reached a pH between 6 – 7. Drying at 55°C for 24h was carried out before the next step.

The dried fibers were immersed in a citric acid solution (1.2 mol/L) in a proportion of 1g/20ml, stirred for 30 minutes and then dried for 24h at 55°C. To complete the treatment, the temperature was increased to 120°C for 90 min. A final drying at 55°C for 24h was carried out (RODRIGUES et al, 2006).

2.3 Biomass characterization

Sisal fibers chemically treated and untreated sisal fibers were characterized by:

- FTIR - Spectroscopy in the Infrared Region (FTIR) to characterize the chemical and molecular nature of samples (resolution of 4 cm⁻¹ and 32 scans) - NEXUS - 470 - FTIR;

- XRD – X-ray diffraction for analysis of the crystalline phases of samples (fast detector, type D, operating at 30 kV and 15mA, copper anode K α = 0.1542 nm and Nickel filter) XRD-7000 X-RAY DIFFRACTOMETER;
- FRX - X-ray fluorescence spectrometry that determines and quantifies which chemical elements are present in the fiber in percentage - EDX720 SHIMADZU ENERGY DISPERSIVE X-RAY SPECTROMETER;
- SEM – Scanning Electron Microscopy (Voltage 20-30 kV and magnification between 75 x and 30,000 x) - TM 3000 – TABLETOP MICROSCOPE – HITACHE).

2.4 Adsorption tests

To carry out the adsorption tests, solutions containing nickel and sisal fibers were used under stirring. In order to define the best processing conditions for adsorption, the following parameters were analyzed: kinetics, balance, influence of pH, where it was adjusted when necessary with solutions of sodium hydroxide (NaOH) and sulfuric acid, influence of mass of the adsorbent, where the time, rotation and volume of the solution remained constant, but with mass variation. The samples, after being collected, were filtered and stored under refrigeration for later analysis.

The essential calculations for the adsorption analysis were based on the studies by SHRESTHA, et al (2013), Ma et al (2014) and YADAVA et al (2014) The metal removal capacity per gram of biosorbent (q_e (mg/g)) was calculated using the expression:

$$q_e = \frac{V(C_o - C_e)}{M} \quad (1)$$

Where C_o and C_e are the initial and final concentration of the metal in solution (mg/L), V the volume of the solution (L) and M the adsorbent mass (g). The determination of the percentage removal rate (R%) of Ni (II) was calculated by the expression:

$$R\% = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

a. Kinetics adsorption

This test was carried out to analyze the behavior of the adsorption process as a result of contact time. For this test, sisal fibers without chemical treatment and with chemical treatment were used. The pH was adjusted with NaOH (Sodium Hydroxide) or H₂SO₄ (Sulfuric Acid) when necessary to 5.0 using the MS TECNOPON pH meter.

In this experiment, 0.1g of fiber was stirred with 40ml of nickel solution at a concentration of 90mgL⁻¹, in contact times ranging from 1 min to 24h (1 min, 2 min, 5 min, 10 min, 30 min, 60 min, 120 min, 240 min, 480 min, 960 min and 24h). The procedure was carried out in duplicate, on a CERTOMAT MO shaker, at a speed of 150 rpm. The resulting concentration after adsorption was determined.

b. Equilibrium adsorption

In this study, the influence of nickel concentration on its adsorption by sisal fibers with and without chemical treatment with citric acid was evaluated. The tests were carried out using 40ml of nickel solutions at concentrations of 10 to 300 mg/L, with a pH equal to 5.0, adjusted when necessary with NaOH (Sodium Hydroxide) or H₂SO₄ (Sulfuric Acid), in which they were left under stirring, with sisal fibers for 4 hours, at a speed of 150 rpm.

c. Influence of pH

The influence of pH evaluates the ideal pH condition for greater metal adsorption. The tests were carried out in duplicate batches with 40 ml of 90mg/L nickel solution and pH varying from 2.0 to 6.0, adjusted with NaOH (Sodium Hydroxide) or H₂SO₄ (Sulfuric Acid), under agitation with the sisal fibers at a speed 150 rpm for 8h.

d. Influence of mass

This test was carried out to analyze the influence of the amount of sisal used in adsorption. 0.05g and 0.15g of adsorbent mass were placed in contact with 40ml of 90mgL⁻¹ nickel solution and kept stirring for 6h. The procedure was performed in duplicate, at a speed of 150 rpm. After adsorption, the samples were filtered and the final concentration of the solutions was determined (YADAVA et al, 2014).

3. RESULTS AND DISCUSSIONS

3.1 Fiber characterization

a. XRD

The comparative XRD analysis between the two fibers showed that the chemical treatment exposed the crystalline phase of the cellulose of the treated fiber, a fact that justifies a higher intensity profile for the treated fiber, illustrated in the figure below. Mainly at the level of 22° , the highest intensity peak, typical of ligno-cellulosic materials (SARKIA et al, 2011; MARTINS et al, 2009).

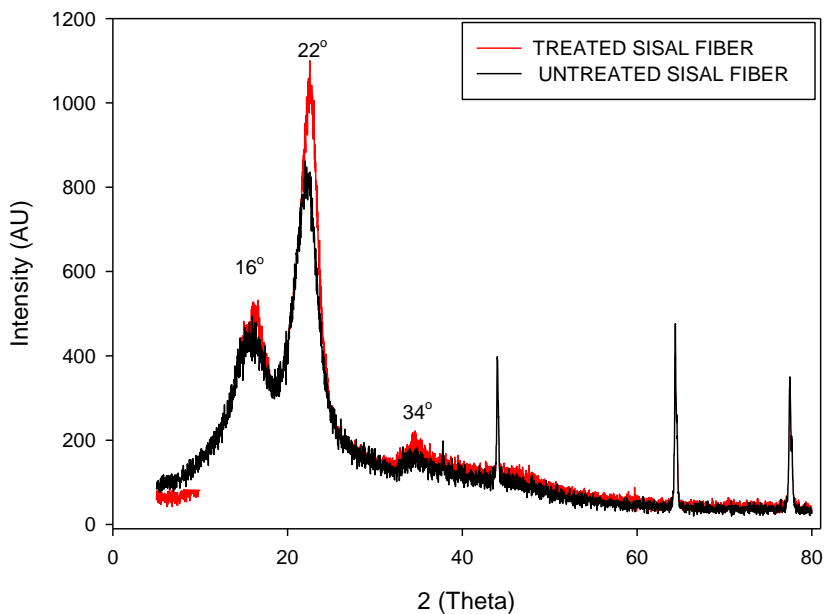


Figure 01 – X-ray diffraction analysis (XRD) of natural sisal fiber treated with citric acid. Source: Authors, 2024..

b. XRF

The sisal fibers used in this study were evaluated by XRF after being exposed to a nickel solution. It is possible to observe that the metal is adhered to the surface of the fiber in large percentages, compared to other chemical elements, thus confirming the adsorption and retention capacity of the metal in solution (MWAIKAMBO et al, 2002; MARTIN et al, 2009). As shown in table 01, there was a higher concentration in chemically treated sisal fiber.

Table 01: XRF analysis (untreated and chemically treated sisal) after the Ni (II) adsorption test in aqueous solution.

Analyte	Untreated fiber	Treated fiber
NiO	47.233 %	55.740 %
CaO	27.974 %	31.591 %
Other components	24.793 %	12.669%

c. SEM

The superficial analysis of the sisal samples by electron microscopy (SEM) made it possible to confirm the effectiveness of the chemical treatment of the fibers, by removing impurities and undesirable dirt that accompanied the fiber during its collection. Figure 2 – B illustrates the surface of chemically treated sisal fiber free of impurities.

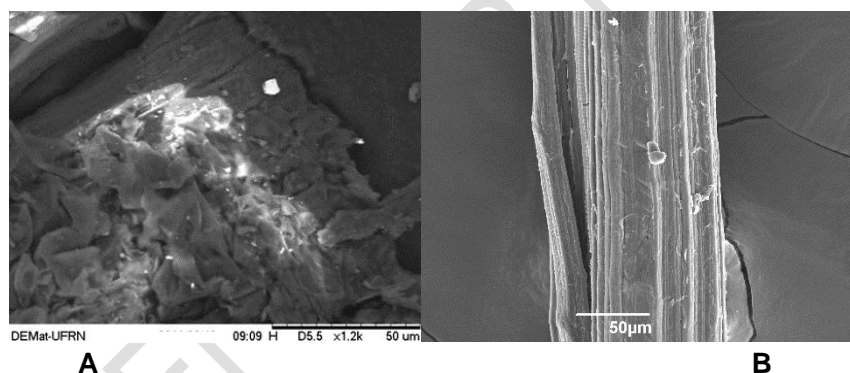


Figure 02: SEM analysis of sisal fibers: Untreated fiber (A) and Chemically treated (B)

c. FTIR

Figure 3 illustrates the FTIR analyzes of sisal samples, describing characteristic vibrations of chemical groups of these samples at: 3000-3500 cm^{-1} (hydroxyl groups - OH), 1010 and 1040 cm^{-1} (CO and CH), 1650 and 1750 cm^{-1} (carbonyl group). More specifically, the carbonyl belonging to a non-ionized COOH group has an absorption band in the region of 1700 to 1750 cm^{-1} , with specific addition of these groups confirmed by FTIR. EZEKIELA et al, 2011; NETO et al (2011).

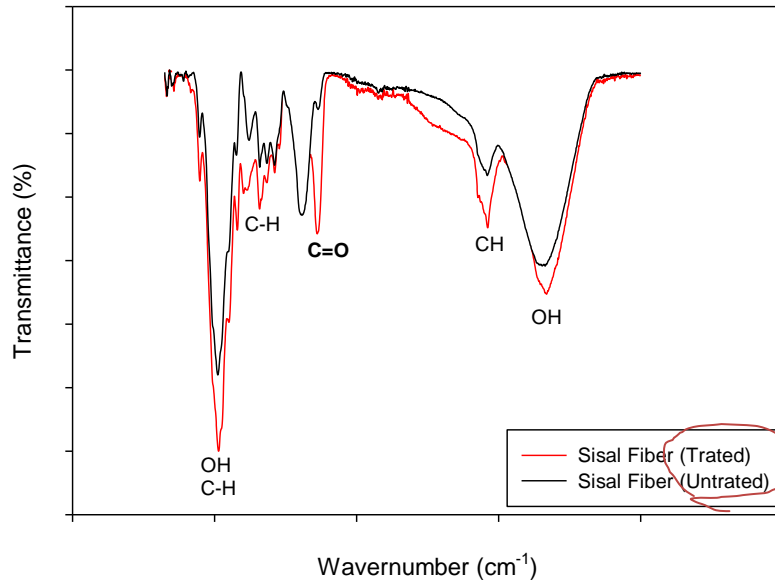


Figure 03: FTIR analysis of sisal fibers: Untreated fiber (A) and chemically treated (B)

3.1 Adsorption tests

A. kinetics

The kinetic study aimed to evaluate the progress of the adsorption process until reaching the concentration limit of Nickel ions adsorbed on the fiber surface under the influence of time. It was possible to verify that the ability to remove this metal occurs quickly in both sisal samples, being, however, more efficient for the treated sisal fiber. Thus demonstrating that the insertion of carboxyl groups would increase the reactive surface area of this sample for capturing the nickel ion in solution.

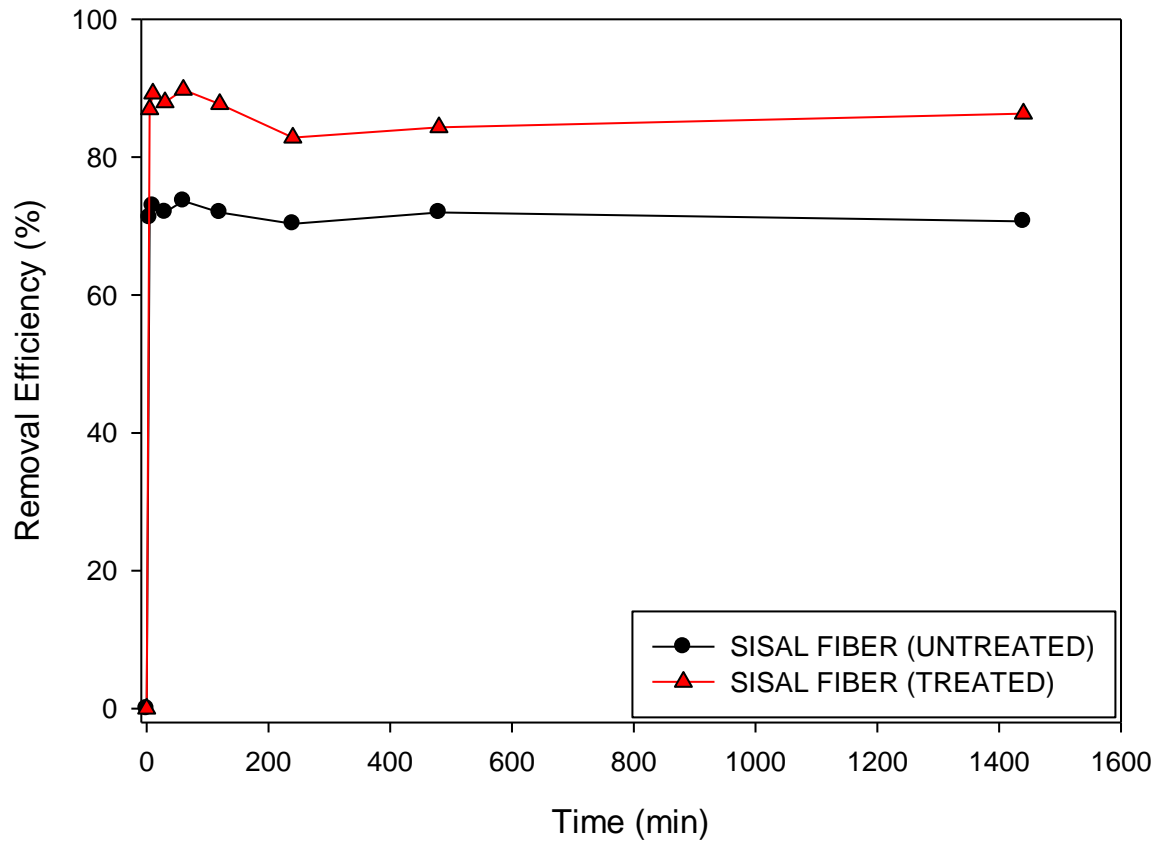


Figure 04: Effect of time on Ni (II) removal by chemically treated and untreated sisal fiber.

Fiber Treated

Fiber Untreated

Conclusion of time adsorption profile? Minimum time needed for the adsorption?

b. Influence of mass

The investigation of the effect of the amount of biomass on the removal of metal ions was carried out using 0.05, 0.1 and 0.15g, in contact with 40ml of a solution containing 90mg/L of nickel for 6 hours. It is possible to determine an ideal sample in 0.1g.

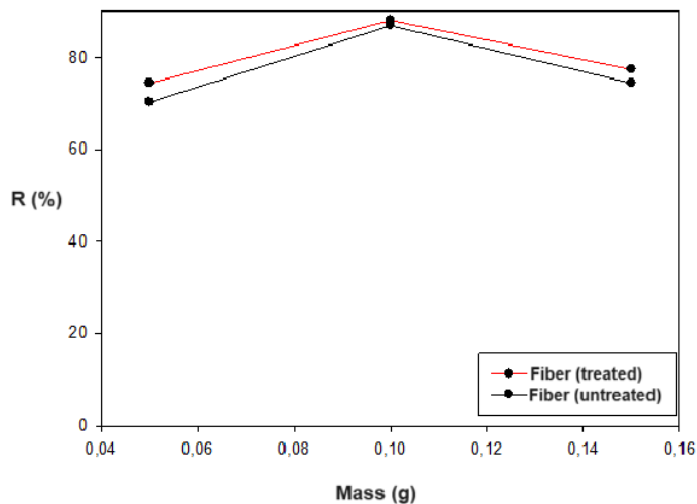


Image 01: Influence of the adsorbent mass (sisal) on the adsorption of nickel (II) in solution.

According to the illustration above, it can be seen that the main adsorption range is 0.1g. The justification for the lower adsorption in ranges below 0.1g of biomass would be the few options for adsorption sites, affecting its efficiency. However, for larger amounts of biomass there is no significant variation. This can be explained by the fact that active sites overlap with a higher amount of biomass (YADAVA et al, 2013). ?

c. Influence of pH

The pH of the solution is an important parameter to be analyzed as it directly influences the adsorption efficiency. To verify an optimal pH for adsorption of metal ions, a study was carried out with different pH values, shown in figure 05.

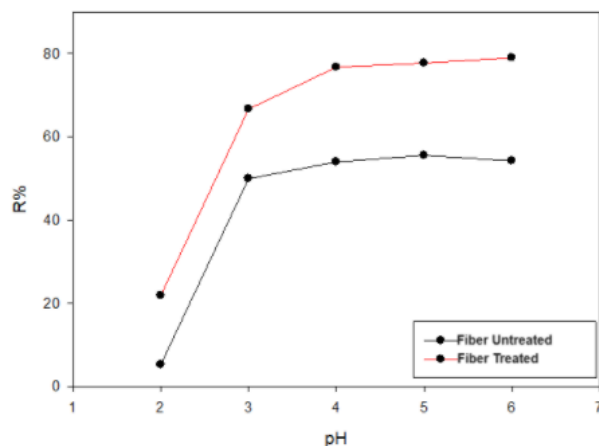


Figura 05: Influencia do pH na adsorção do níquel por fibras de sisal.

At this stage, it is observed that for very acidic pH values, such as the range between 2.0 and 4.0, there is little efficiency in the adsorption of metal ions. It is possible to find in the literature that low pH values correspond to a higher concentration of free H⁺ ions in the solution. As the pH increases, this concentration decreases. In the ion exchange process, the more acidic the solution, the greater the competition for H⁺ ions and metals to be adsorbed, making their adsorption more difficult.

d. Equilibrium

In the equilibrium study and obtaining adsorption isotherms, experiments were carried out varying the Ni (II) concentration (10 to 180 mg/L). The models evaluated were those of Langmuir and Freundlich (SHERESTHA et al, 2013; ALHAWAS et al, 2013). The Langmuir model was determined using the equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

Where q_e is the equilibrium sorbate absorption (mg/g), q_m is the maximum binding capacity (mg/g), C_e is the equilibrium concentration of sorbate in solution (mg/L) and K_L is the equilibrium constant apparent (L/mg).

The Freundlich isothermal model can be written as indicated in Eq.(4):

$$q_e = K_f C_e^{1/n} \quad (4)$$

Where q_e is the amount of adsorbed metal (mg/g), C_e is the equilibrium concentration in the solution (mg/L), k_f is a constant related to the adsorption capacity (mg/g) and $1/n$ the adsorption intensity.

Figure 6 illustrates the **Langmuir** and Freundlich isotherm for a chemically untreated sisal sample. The second model ($R^2 = 0.9810$) being considered a better correlation with the experimental and calculated data, the **Langmuir** model. The other parameters of this model were calculated at $K_{pf} = 3.1268$ and $n = 0.5477$.

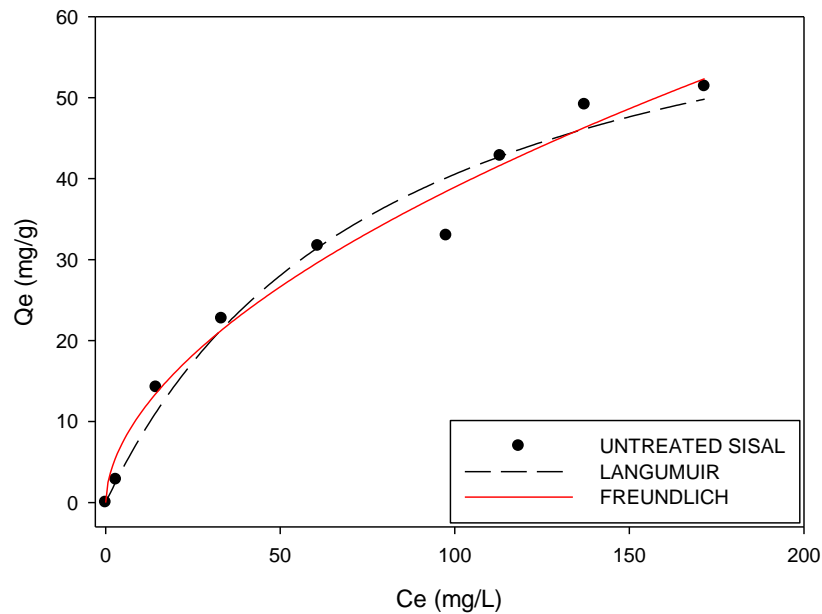


Figure 6: Analysis of the Ni(II) adsorption isotherm by chemically untreated sisal fiber.

Figure 7 illustrates the **Langmuir** and Freundlich isotherm for a chemically treated sisal sample. The first model ($R^2 = 0.9643$) of **Langmuir** is considered a better correlation with the experimental and calculated data. The other parameters of this model were calculated at $K = 0.0864$ and $q_{max} = 64.58$.

How would be the log Q_e vs log C_e curve would look like?

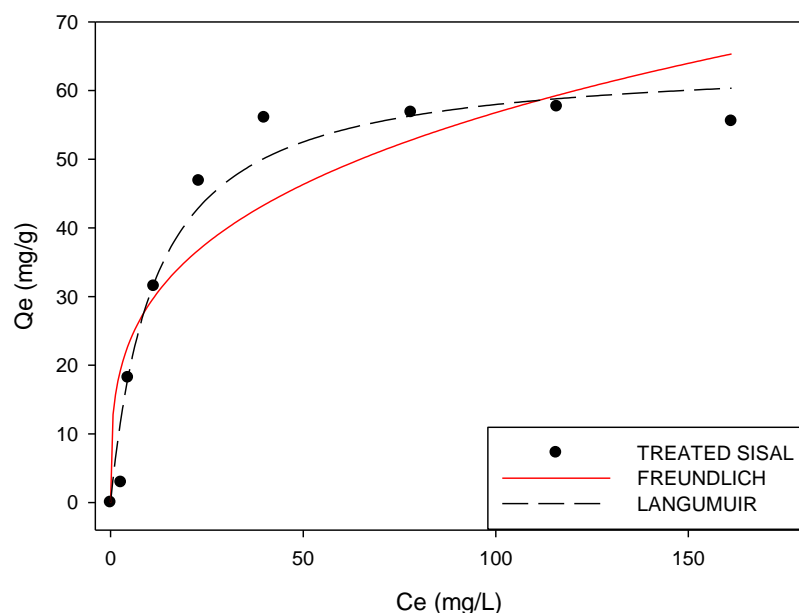


Figure 7: Analysis of the Ni(II) adsorption isotherm by chemically treated sisal fiber.

Nickel in wastewater is a toxic element and can lead to carcinogenicity, and the efficiency of using biomass (sisal fiber) was demonstrated in the present study with removal rates above 80%. This, with low-cost chemical treatment, abundant and cheap biomass and easy handling, as a potential use in the treatment of effluents containing nickel (II) ions. **More discussion is needed.**

Further, how is this fiber compare with reported biomass materials?

4. CONCLUSIONS

The data presented in the study made it possible to confirm through SEM, XRD and FTIR that the chemical treatment of sisal fiber was efficient, demonstrating greater crystallinity, absence of dirt and the presence of the carbonyl group. These aspects contributed to greater efficiency in the removal of Nickel (II) in aqueous solution by the chemically treated fiber, presenting a higher percentage in the XRF test and better performance in the kinetic tests and influence of pH.

Therefore, sisal fiber presents itself as an efficient, low-cost and highly available biomass for application in the removal of Nickel in aqueous solution.

REFERENCES

- Alhawas M. et al. Removal of nickel from aqueous solution by low-cost clay adsorbents. proceedings of the International Academy of Ecology and Environmental Sciences, 2013, 3(2): 160-169
- Bo Z. et al. Adsorption of copper ions from aqueous solution by citric acid modified soybean straw; *Journal of Hazardous Materials* Volume 153, Issues 1-2, 1 May 2008, Pages 300-308.
- Chen JP. et al. Surface modification of a granular activated carbon by citric acid for enhancement of copper adsorption; *Carbon* Volume 41, Issue 10, 2003, Pages 1979-1986.
- Eser A. et al. A. Removal of nickel(II) ions by histidine modified chitosan beads. *Chemical Engineering Journal* Volume 210, 1 November 2012, Pages 590-596.
- Ezekiela N. et al. Effect of temperature and durations of heating on coir fibers. *Industrial Crops and Products* Volume 33, Issue 3, May 2011, Pages 638-643.
- Hoang MT et al. Esterification of sugarcane bagasse by citric acid for Pb²⁺ adsorption: effect of different chemical pretreatment methods. *Environ Sci Pollut Res* 28, 2021. 11869-11881.
- Krishnan KA et al. Nickel(II) adsorption onto biomass based activated carbon obtained from sugarcane bagasse pith. *Bioresource Technology* Volume 102, Issue 22, November 2011, Pages 10239-10247
- Leite ACM et al. Prospecção Tecnológica e Mapeamento do Sisal e Seus Subprodutos (1889-2022). *Cadernos De Prospecção*, 16(5), 2023, 1700-1714.
- Leonard Y. et al. Ansell Chemical modification of hemp, sisal, jute, and kapok fibers by alkalization. *Journal of Applied Polymer Science* Volume 84, Issue 12, 2002. pages 2222-2234, 20.
- Levy-Ramos R et al. Modification of corncob with citric acid to enhance its capacity for adsorbing cadmium(II) from water solution. *Chemical Engineering Journal* Volume 180, 15 January 2012, Pages 113-120.
- Lopes FM et al. Estudo dos efeitos da acetilação em fibras de sisal; *Revista Brasileira de Engenharia Agrícola e Ambiental*, v.14, n.7, 2010 p.783-788.
- Ma W. et al. Adsorption and bio-sorption of nickel ions and reuse for 2-chlorophenol catalytic ozonation oxidation degradation from water. *Journal of Hazardous Materials* Volume 266, 15 February 2014, Pages 19-25

- Marshall WE et al. Enhanced metal adsorption by soybean hulls modified with citric acid; *Bioresource Technology* Volume 69, Issue 3, September 1999, Pages 263–268.
- Martin AR. et al. Caracterização química e estrutural de fibra de sisal da variedade Agave sisalana. *Polímeros* vol.19 no.2009. pp. 20-23
- Martins AR. et al. Caracterização Química e Estrutural de Fibra de Sisal da Variedade Agave sisalana. *Polímeros: Ciência e Tecnologia*, vol. 19, nº 1, 2009. p. 40-46.
- Neto IL; Martins FM. Anatomia dos órgãos vegetativos da Agave sisalana PERRINE. *Revista Caatinga*, Mossoró, v. 25, n. 2, 2012. p. 72-78
- Norsuhailizah S. et al. A Review on Batch and Column Adsorption of Various Adsorbent Towards the Removal of Heavy Metal. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, 67(2), 2024, 66–88.
- Poh CK. et al. Citric acid functionalized carbon materials for fuel cell application; *Journal of Power Sources* Volume 176, Issue 1, 21 January 2008, Pages 70–75.
- Ramana DK et al. Removal of nickel from aqueous solutions by citric acid modified Ceiba pentandra hulls: Equilibrium and kinetic studies. *The Canadian Journal of Chemical Engineering* Volume 90, Issue 1, 2012. pages 111–119,.
- Rodrigues RF et al. Adsorção de metais pesados em serragem de madeira tratada com ácido cítrico; *Eng. sanit. ambient.* Vol. 11 – Nº 1 – jan/mar 2006, 21-26.
- Santos WNL. Biosorption of Pb(II) and Cd(II) ions by *Agave sisalana* (sisal fiber). *Microchemical Journal* Volume 97, Issue 2, March 2011, Pages 269–27
- Sarkia J. et al. Potential of using coconut shell particle fillers in eco-composite materials, *Journal of Alloys and Compounds* 509 (2011) 2381-2385.
- Shrestha RM. et al. Removal of Ni (II) from Aqueous Solution by Adsorption onto Activated Carbon Prepared from Lapsi (*Choerospondias axillaris*) Seed Stone. *Journal of the Institute of Engineering*, Vol. 9, No. 1, 2013 pp. 166–174
- Vakili M. et al. Nickel ion removal from aqueous solutions through the adsorption process: a review *Reviews in Chemical Engineering*, vol. 37, no. 6, 2021, pp. 755-778.
- Wang R. et al. Adsorption of heavy metals and organic contaminants from aqueous stream with chemically enhanced kapok fibers. *Environ Earth Sci* 75, 2016, 338.
- Wartelle LH, Marshall WE. Citric acid modified agricultural by-products as copper ion adsorbents; *Advances in Environmental Research* Volume 4, Issue 1, 1 June 2000, Pages 1–7.
- Yadava S. et al. Studies on the removal of nickel from aqueous solutions using modified riverbed sand *Environ Sci Pollut Res* (2013) 20:558 –564

Zheng Y. et al. Review on nickel-based adsorption materials for Congo red, Journal of Hazardous Materials, 2021. Volume 403.

Review questions and comments: -Wang

- 1) WHAT IS THE NIO CONTENT BEFORE NI ADSORPTION? ANY XRD DATA FOR THIS?
- 2) SEM, UNTREATED FIBER AND TREATED FIBER HAS DIFFERENT LEGTH SCALE, IT IS HARD TO JUSTFY THE TREATED FIBER HAS SUCH CLEAN IMAGE.
- 3) FIGURE 3 LABELS: TRATED TO TREATED, A SPECTRA WITH NI ADSORBED?
- 4) *FIGURE 4: CONCLUSION OF TIME ADSORPTION PROFILE? MINIMUM TIME NEEDED FOR THE ADSORPTION?*
- 5) IMAGE 1, WHY USE THIS LABEL? ALSO IF HIGH NI INTIAL CONC IS USED, WOULD HIGHER MASS GIVE HIGHER PERCENT OF REMOVAL?
- 6) MORE DISCUSSION FOR FIGURE 6 AND 7, COMPARISON ON THE TREATMENT IS NEEDED.
- 7) Further discussion on how this fiber is compare with reported biomass materials?
- 8) Adding the Log Q_e vs log C_e curve for the adsorption isotherms.
- 9) How was the Ni concentration was determined after the adsorption experiments.