

Article

Hydrotalcites as a Promising Adsorbent for Hemicellulose Hydrolysate Detoxification in Xylitol Production

Débora D. V. da Silva ¹, Kelly J. Dussán ^{2,3,*}, Isabela A. L. Costa ⁴, Marcus B. S. Forte ⁵ and Maria G. A. Felipe ^{4,*}

¹ Department of Biochemistry and Organic Chemistry, Institute of Chemical, São Paulo State University (Unesp), Araraquara 14800-900, São Paulo, Brazil; debora.virginio@unesp.br

² Department of Chemical Engineering, Institute of Chemical, São Paulo State University (Unesp), Araraquara 14800-900, São Paulo, Brazil

³ Bioenergy Research Institute (IPBEN), Institute of Chemical, São Paulo State University (Unesp), Araraquara 14800-900, São Paulo, Brazil

⁴ Department of Biotechnology, School of Engineering of Lorena (EEL), University of São Paulo, Lorena 12600-000, São Paulo, Brazil; isabela.alc@hotmail.com

⁵ Food Engineering and Technology Department (DETA), Faculty of Food Engineering (FEA), University of Campinas (UNICAMP), Campinas 13083-862, São Paulo, Brazil; forte@unicamp.br

* Correspondence: kelly.medina@unesp.br (K.J.D.); mgafelipe@usp.br (M.G.A.F.)

Abstract: The worldwide demand for sustainable bioprocesses is undeniable, as well as for research aimed at the biotechnological exploitation of lignocellulosic materials, especially their hemicellulosic fractions rich in xylose. Various bioproducts can be obtained from these fractions, although some bottlenecks still exist, such as the presence in hemicellulosic hydrolysates of compounds that are toxic for microorganisms, which requires a previous step of detoxification to reduce them to non-inhibitory levels. The present investigation proposes the use of hydrotalcites as a new detoxifying agent for the hemicellulosic hydrolysate of sugarcane straw to produce xylitol by *Candida tropicalis*, aiming at a greater removal of phenolics and less loss of sugars. The design of these experiments was used for factorial effect analysis in a simultaneous way; the influences of pH and temperature were evaluated, considering the detoxification process at different times for both uncalcined and calcined hydrotalcite adsorbents. While for the calcined hydrotalcite, the temperature was the significant factor, for the uncalcined, there was also an influence of pH and little effect on the factors of yield and productivity. The effectiveness of hydrotalcites as demonstrated in this research, mainly regarding the ability to reduce the content of phenolic compounds in hydrolysates with a low loss of sugar content, followed by fermentability to produce xylitol, is a strong requirement for the proposition of these new adsorbents in investigations of the development of sustainable technologies for obtaining bioproducts in a biorefinery context.



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1. Introduction

The advantages and benefits of using xylitol as a food additive or as an ingredient in the cosmetic and pharmaceutical industries are well-known [1,2]. This polyol is an artificial sweetener with anticariogenic and oral prebiotic properties [3–5] and has been used in the treatment of diabetes and the prevention of otitis, osteoporosis and respiratory infections [6–9]. Recently, xylitol has been evaluated for its use as a biomarker for early cancer detection and also for its potential anticancer and anti-inflammatory activities [10,11]. These properties have supported the use of xylitol in the management of severe cases of COVID-19, helping to reduce the duration of treatment for COVID-19 patients [12].

The commercial production of xylitol is performed by chemical reactions with the reduction of xylose from lignocellulosic materials at high temperatures and pressures, making the final product with a high cost [13]. However, there are many studies on the biotechnological production of this polyol using the biological conversion of xylose to xylitol by microorganisms, mainly yeasts [11,14,15]. Several species of the genus *Candida* have been described as xylose-fermenting yeasts [16,17], and *Candida guilliermondii* stands out for its good performance in xylose-to-xylitol bioconversion from lignocellulosic hydrolysates [18–22]. This biotechnological route could be considered a sustainable green process with lower costs, especially when combined with biofuel production in biorefineries, since the hemicellulosic hydrolysate (C5 fraction) could be used for xylitol production and the C6 fraction obtained in the pretreatment directed to ethanol-2G production.

For successful xylose-to-xylitol bioconversion, three main steps are required: (1) the hydrolysis of lignocellulosic biomass (this work deals specifically with sugarcane straw as a biomass and dilute sulfuric acid hydrolysis) to obtain a xylose-rich hemicellulosic hydrolysate; (2) the detoxification of the hemicellulosic hydrolysate (the main focus of this work) to reduce the concentrations of the toxic compounds released during acid hydrolysis and (3) fermentation.

During acid hydrolysis, various compounds are released and/or formed, such as acetic acid from acetyl group hydrolysis; phenolic compounds from partial lignin degradation and furfural and 5-hydroxymethylfurfural from pentose and hexose degradation, respectively. Such compounds, depending on their concentrations, can be inhibitors of microbial metabolism, resulting in decreased xylitol formation [23–26]. Phenolic compounds (including 4-hydroxybenzoic acid, ferulic acid and guaiacol) are among the main inhibitors found in the hemicellulosic hydrolysate. The presence of these inhibitors in concentrations ranging from 0.1 to 1.0 g/L can cause oxidative stress and the loss of the integrity of biological membranes, affecting xylose consumption, cell growth and xylitol production [27,28].

Therefore, it is necessary to reduce the concentrations of these toxic compounds in the hydrolysate to non-inhibitory levels, which can be achieved in the detoxification process. Luo et al. [29] and Guo et al. [30], in their review articles, present how inhibitors are generated during the pretreatment step and the main methods of the removal of these compounds from the hydrolysate. One of the main detoxification strategies used is pH adjustment using CaO and H₃PO₄, combined with adsorption in activated carbon, which provides the partial removal of toxic compounds or their conversion into inactive compounds [22,31,32]. Other materials, such as ion exchange resins, have also been reported as an efficient strategy that could be used to improve the detoxification process [19,33,34]. An example of material with good adsorption properties for this application is hydrotalcites [35].

Hydrotalcites are an important class of layered double hydroxides with ion exchange and adsorption properties [36–38]. Hydrotalcite-like compounds can be described structurally as the stacking of positively charged layers formed by the partial substitution of a trivalent metal by a divalent one, and anions and water molecules are contained in the interlayer [39,40]. Although hydrotalcites occur as natural minerals, they are relatively easy and inexpensive to synthesize [41]. Hydrotalcites exhibit suitable chemical and structural stability under the mildly acidic to neutral pH conditions commonly found in hemicellulosic hydrolysates [37,42–44]. The layered structure of a hydrotalcite facilitates reversible adsorption mechanisms, allowing regeneration and reuse over multiple adsorption–desorption cycles [44,45]. Studies have shown that hydrotalcites can maintain significant detoxification efficiencies, particularly for the removal of organic inhibitors (e.g., phenols, furfural, hydroxymethylfurfural), for up to approximately five consecutive cycles, with only a modest reduction in performance after each reuse. Regeneration typically involves washing

with mild alkaline or organic solvent solutions to effectively desorb captured inhibitors. However, prolonged use or exposure to highly acidic conditions can eventually lead to structural degradation, affecting the adsorption capacities [35,37,38,42,45]. Therefore, periodic regeneration or replacement of hydrotalcites should be considered in the overall process design of sustainable detoxification applications. In this sense, the use of hydrotalcites as adsorbents rises as a potential opportunity for the detoxification of hemicellulosic hydrolysates [38,39].

There are, in specific works of the literature, few studies that directly compare the use of hydrotalcites and activated carbon in the detoxification of hemicellulosic hydrolysates from sugarcane bagasse. Candido et al. [35] reported no statistical difference between hydrotalcites and activated charcoal in detoxifying sugarcane bagasse hemicellulosic hydrolysate. However, it is possible to find studies that have documented that hydrotalcites present advantages in the detoxification of hemicellulosic hydrolysates, such as selective adsorption (advantageous when targeting specific contaminants without removing desirable compounds) and regeneration (it could be reused multiple times after the regeneration process, maintaining efficiency over extended periods) [43,46].

In this study, the detoxification of sugarcane straw hemicellulosic hydrolysate was evaluated using pH adjustment combined with hydrotalcites as an adsorbent to enhance xylitol production by *Candida tropicalis*.

2. Materials and Methods

2.1. Preparation of Sugarcane Straw Hemicellulosic Hydrolysate (SSHH)

Sugarcane straw was sourced from Usina Pederneiras (Tietê, São Paulo, Brazil) and sun-dried until it reached approximately a 10% moisture content. Dilute acid hydrolysis was performed using 1.0% (*w/v*) sulfuric acid at a solid-to-liquid ratio of 1:10 in a 40 L stainless steel reactor, maintained at 121 °C for 20 min [47]. After hydrolysis, the hydrolysate was filtered, and vacuum concentration at 70 °C achieved a fourfold increase in the xylose concentration. This concentration step was necessary to enhance the substrate availability for efficient microbial fermentation, improving the economic feasibility. The sugar composition and inhibitor concentrations were characterized before and after the concentration step.

2.2. Detoxification of the Sugarcane Straw Hemicellulosic Hydrolysate

In order to reduce the concentrations of the toxic compounds present in sugarcane straw hemicellulose hydrolysate (SSHH), the effect of pH adjustment in combination with an adsorbent was evaluated. Two different hydrotalcites ([Mg-Al-CO₃], PURAL[®]MG 30, 30% MgO composition) [37] were tested: one without pretreatment (HT30, uncalcined) and one calcined at 500 °C for 3 h (HT30c, calcined). In all conditions studied, the pH of the hydrolysate was initially adjusted to 7.0 using commercial CaO, a step previously optimized by Marton et al. [31].

Experimental Design: 2² Full Factorial Approach

The experiments were performed according to a 2² full factorial design (FFD) for each adsorbent (HT30 and HT30c). The independent variables (factors) considered were x_1 (pH) and x_2 (temperature, °C), evaluated at different residence times (15, 30 and 45 min). The objective was to balance the responses to ensure high phenol removal (%) while minimizing the sugar loss (%). During this phase, the pH was adjusted with H₃PO₄, and adsorbent addition (1% *w/v*) was performed in 125 mL Erlenmeyer flasks containing 50 mL of hydrolysate under stirring at 100 rpm [31]. Pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used for kinetic model fitting.

A combination of CaO (calcium oxide) and H₃PO₄ (phosphoric acid) was used to optimize the adsorption process. Initially, CaO, a strong alkaline agent, was used for pH adjustment, reacting with water to form Ca(OH)₂, which neutralizes acidic components in hydrolysates and facilitates the precipitation of impurities such as organic acids and metal ions, improving the process efficiency. However, for precise pH control, H₃PO₄ was introduced in the subsequent steps, as it prevents the introduction of unwanted ions and acts as a buffer to stabilize the pH during adsorption experiments [31].

The factors were analyzed for their effects on the responses, and the coded models with statistically significant terms were evaluated using analysis of variance (ANOVA) at a 95% confidence level ($p < 0.05$). Response surface plots of the validated models were then generated [48]. Statistical tests were performed using the online Protimiza Experimental Design software (<https://experimental-design.protimiza.com.br/>, accessed on 24 October 2022).

2.3. Microorganism and Inoculum Preparation

The experiments were performed with *Candida tropicalis*, previously designated as *Candida guilliermondii* FTI 20037 [49], maintained on malt extract agar slants at 4 °C.

The inoculum was cultured in a medium containing xylose (30.0 g/L), rice bran extract (20.0 g/L), (NH₄)₂SO₄ (2.0 g/L), and CaCl₂·2H₂O (0.1 g/L) in 125 mL Erlenmeyer flasks containing 50 mL of medium each. The cultures were incubated on a rotary shaker (200 rpm, New Brunswick Scientific Inc., Edison, NJ, USA) at 30 °C for 24 h [50].

Cells were then harvested by centrifugation (2000× *g*, 20 min, Jouan Centrifuge Mod. 1812, Saint-Herblain, France), washed twice and resuspended in sterile distilled water. The initial cell concentration was adjusted to approximately 1.0 g/L for all experiments.

2.4. Medium and Fermentation Conditions

After the selection of the optimal detoxification conditions for each adsorbent (based on the removal of toxic compounds), the effects of these treatments on xylitol production by *Candida tropicalis* were evaluated. The hydrolysates were supplemented with rice bran extract (20.0 g/L), (NH₄)₂SO₄ (2.0 g/L) and CaCl₂·2H₂O (0.1 g/L), with the initial pH adjusted to 5.5. The media (50 mL) were transferred to 125 mL Erlenmeyer flasks and incubated at 30 °C and 200 rpm for 72 h [49]. The experiments were performed in duplicate, with samples collected at the beginning and end of the incubation period.

Control experiments using non-detoxified hydrolysates were not included in the current study, as previous work by this research group [51] has demonstrated that *C. guilliermondii* FTI 20037 shows severely impaired metabolic activity under such conditions. In that study, the sugar assimilation was limited to 6% and the xylitol production reached only 1.2 g/L after 144 h due to the high concentrations of inhibitory compounds, particularly phenolics and acetic acid.

2.5. Analytical Methods

The concentrations of sugars (xylose, glucose, arabinose), xylitol, acetic acid, ethanol, 5-hydroxymethylfurfural (5-HMF) and furfural were determined by HPLC Agilent chromatography (Agilent 1200, Kyoto, Japan) and a Bio-Rad Aminex HPX-87H (300 × 7.8 mm, Hercules, CA, USA) column to check the xylose, glucose, arabinose, xylitol, ethanol and acetic acid. The operating conditions were a temperature of 45 °C and 0.005M sulfuric acid used as an eluent at a flow rate of 0.6 mL/min and a 20 mL sample volume, according to the method described by Dussán et al. [52]. The concentration of the total phenolic compounds was estimated by ultraviolet spectroscopy (DU 640B spectrophotometer, Beckman Coulter, Brea, CA, USA) at 280 nm [53].

Cell growth was monitored by measuring the absorbance at 600 nm, and the cell concentrations were calculated based on the correlation between the optical density (OD₆₀₀) and the cell dry weight using a calibration curve.

Color analysis of the hydrolysate samples was conducted by diluting them at a ratio of 1:50 in distilled water, followed by pH adjustment to 10 using 6N NaOH, filtering through a SWINNEX filter (13 mm, Millipore, Bedford, MA, USA), and measuring the absorbance at 420 nm using a spectrophotometer (DU 640B spectrophotometer, Beckman Coulter, Brea, CA, USA). The International Commission for Uniform Methods of Sugar Analysis (ICUMSA) method, adapted for sugarcane biomass hydrolysate [54], was also used.

In addition, the pH was adjusted to 5.0 ± 0.2 with 6N NaOH and filtered through a SWINNEX filter (13 mm, Millipore, Bedford, MA, USA), and the absorbance was measured at 420 nm. The degrees Brix (% soluble solids) of the hydrolysate samples were also determined to calculate this parameter.

3. Results and Discussion

3.1. Characterization of the Sugarcane Straw Hemicellulosic Hydrolysate

As shown in Table 1, the hydrolysis process effectively solubilized the sugars present in the hemicellulosic fraction of the sugarcane straw. The glucose-to-xylose ratio in the initial hydrolysate (~1:6) remained stable after the concentration step and was comparable with the ratio (1:5) considered optimal for enhancing xylitol production by *Candida tropicalis* [55].

Table 1. Characteristics of sugarcane straw hemicellulosic hydrolysate before and after the concentration step.

Characteristics		Sugarcane Straw Hemicellulosic Hydrolysate	
		Original	Concentrated 4×
Sugars (g/L)	Glucose	2.47	12.39
	Xylose	15.63	72.65
	Arabinose	2.83	11.99
Toxic compounds (g/L)	Acetic acid	2.50	2.95
	Furfural	0.147	0.165
	5-HMF	0.302	1.12
	Total phenols	2.61	6.82
Color	Absorbance (420 nm)	0.240	0.873
	ICUMSA Method	0.099	0.362
°Brix		4.0	15.6
pH		0.79	0.29

Regarding the toxic compounds, it was observed that, except for the phenolics, all other compounds were present at concentrations below the toxicity threshold for *Candida tropicalis*, even after the concentration step [23–25].

In particular, a comparison of the furfural and 5-HMF concentrations in the original hydrolysate with those reported for the acid hydrolysis of sugarcane straw by Hernández-Pérez et al. [47] and Ingle et al. [56] was performed. The furfural and 5-HMF levels obtained here are 55–70% and 47–62% lower, respectively.

Despite these favorable results, Table 1 shows that after the concentration step, the total phenolic content exceeded the threshold considered non-inhibitory for yeast growth [23,57]. This finding emphasizes the importance of this study, which aims to evaluate hydrotalcites as adsorbents in the detoxification process.

3.2. Influence of pH and Temperature at Different Residence Times

The sugar loss (SL, %) and phenol removal (PR, %) during detoxification with the two adsorbents—HT30 and HT30c—are summarized in Table 2. Overall, HT30 showed significantly lower sugar loss ($6\% < \text{SL} < 24\%$) compared to HT30c ($14\% < \text{SL} < 33\%$), while the phenol removal was slightly lower for HT30 ($58\% < \text{PR} < 70\%$) than for HT30c ($64\% < \text{PR} < 80\%$). However, the improved phenol removal achieved with HT30c did not outweigh the higher sugar loss observed for this material. This trend is likely related to the calcination step, which increases the surface areas and pore volumes of hydrotalcites by enhancing their porous structures [37,58]. No significant differences were observed between the different adsorption times, indicating that equilibrium was reached in less than 15 min. Among the conditions tested, HT30 (Assay 3: hydrolysate at pH 2.0 and detoxification at 60 °C) achieved optimal performance with low sugar loss (~7% on average) and high phenol removal (~65% on average).

Table 2. Matrix of the 2² full factorial design (FFD) for the detoxification of hemicellulosic hydrolysates using hydrotalcites (HT30 and HT30c). The code values are in brackets.

HT30			15 min		30 min		45 min	
Assay	pH (x ₁)	T (°C) (x ₂)	SL (%)	PR (%)	SL (%)	PR (%)	SL (%)	PR (%)
1	2 (−1)	30 (−1)	9.80	65.27	11.11	66.01	9.98	68.43
2	5 (+1)	30 (−1)	15.37	63.68	16.10	67.75	23.78	67.43
3	2 (−1)	60 (+1)	6.60	63.69	6.32	67.27	7.56	64.94
4	5 (+1)	60 (+1)	11.20	69.75	12.35	66.93	17.46	69.73
* 5	3.5 (0)	45 (0)	9.72	57.77	10.07	62.61	14.29	63.21
* 6	3.5 (0)	45 (0)	16.66	63.65	10.76	64.14	16.45	64.52
* 7	3.5 (0)	45 (0)	16.60	68.64	10.52	67.30	26.49	58.82

HT30c			15 min		30 min		45 min	
Assay	pH (x ₁)	T (°C) (x ₂)	SL (%)	PR (%)	SL (%)	PR (%)	SL (%)	PR (%)
1	2 (−1)	30 (−1)	20.74	65.83	19.90	75.69	20.59	66.39
2	5 (+1)	30 (−1)	20.47	72.09	22.42	79.10	19.03	77.96
3	2 (−1)	60 (+1)	15.53	68.66	15.06	65.36	14.80	67.10
4	5 (+1)	60 (+1)	19.29	79.98	14.20	73.45	17.53	74.73
* 5	3.5 (0)	45 (0)	15.82	64.45	15.87	65.41	16.65	72.19
* 6	3.5 (0)	45 (0)	32.61	72.37	17.50	75.12	30.05	80.08
* 7	3.5 (0)	45 (0)	16.71	66.31	17.00	66.67	16.15	65.77

* central points.

In the hydrotalcite treatments, decreases in the concentrations of certain sugars, especially glucose and xylose, were observed under certain conditions. While this reduction was initially attributed to the adsorption or degradation process, the potential catalytic activity of hydrotalcites in promoting isomerization reactions must also be considered. Hydrotalcite-like compounds have been shown to catalyze the isomerization of aldoses to ketoses, such as glucose to fructose, due to their basic sites and layered double-hydroxide (LDH) structures, especially under relatively mild thermal conditions (90–140 °C) and extended reaction times (60–300 min) [59–62].

Although the conditions used in this study (30–60 °C, pH 2.0–5.0 and 15–45 min; Table 2) are considered moderate, we cannot exclude the possibility of isomerization, as fructose and other potential isomerization products were not quantified. Therefore, some of the observed sugar loss may be due to isomerization reactions and not solely to degradation or adsorption mechanisms.

All experiments were analyzed using a design of experiment (DOE) approach. For this step, a detoxification time of 30 min was chosen for both materials, as it provided the best balance between minimal sugar loss and maximum phenol removal.

Extending the detoxification time beyond 30 min could have resulted in increased sugar degradation, negatively impacting the process efficiency by reducing the availability of the fermentable sugars. In addition, prolonged detoxification resulted in adsorbent saturation, where the material reached its capacity to remove phenols, making additional processing time ineffective or even counterproductive.

Figure 1 shows the Pareto charts for the detoxification process using HT30 and HT30c. For HT30, the pH and temperature were the most significant variables, whereas for HT30c, only the temperature had a significant effect.

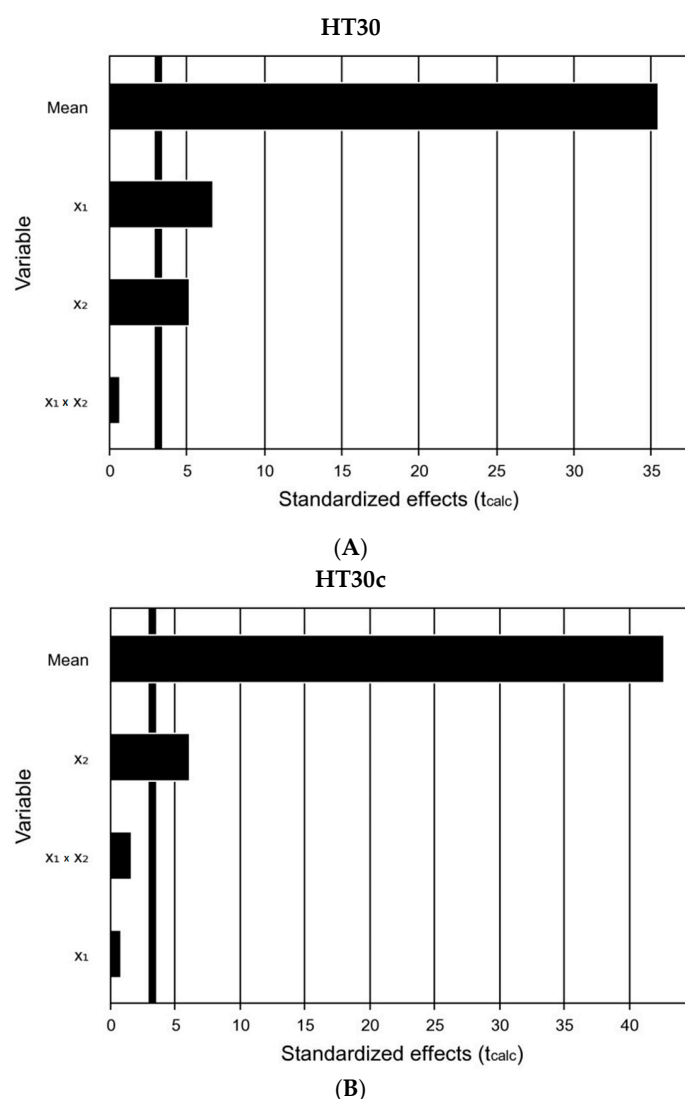


Figure 1. Pareto plots of standardized effects for the response sugar loss (%) using a detoxification time of 30 min and (A) HT30 and (B) HT30c as functions of the variables x_1 (pH) and x_2 (temperature, °C).

The effect of pH on adsorption processes using lamellar double hydroxides requires careful consideration due to the pH-regenerative capacity of these adsorbents. Studies have shown that this material can restore the pH of a solution, and the use of pH control buffers can alter its adsorption capacity for certain ions [37,58,63,64]. In addition, the effects of other process parameters (e.g., adsorbate concentration, adsorbent dosage) can further influence the adsorption performance.

Furthermore, the effect of pH may be less pronounced within narrow pH ranges [37,65], which may explain why the pH had a lesser influence compared to the temperature in the present study.

The one-way analyses of variance (ANOVA) for both HT30 and HT30c (Table 3) indicate that the regression is statistically significant, with the models accounting for 96.0% and 88.6% of all experimental conditions, respectively. In addition, Fisher's F-test confirms the validity of both coded models, as the calculated F-values (F_{calc}) exceed the listed values (F_{list}) [48].

Table 3. One-way analysis of variance for the full factorial design of the detoxification process of hemicellulosic hydrolysates using the adsorbents HT30 and HT30c for 30 min.

Variation Source	Sum of Squares	Degrees of Freedom	Mean Square	$F_{\text{calc}} F_{\text{list}}$	R^2 (%)
HT30					
Regression	48.86	3	16.29	24.08 9.28	95.5
Residues	2.03	3	0.68		
Total	50.89	6			
HT30c					
Regression	42.64	1	42.64	30.32 6.61	85.8
Residues	7.03	5	1.41		
Total	49.67	6			

For HT30 and HT30c, the models for the response sugar loss (SL, %) were

$$Y (\text{SL}\%, 30 \text{ min}) = 11.03 + 2.76 x_1 - 2.14 x_2 \quad (1)$$

$$Y (\text{SL}\%, 30 \text{ min}) = 17.42 - 3.26 x_2 \quad (2)$$

where x_1 is the pH and x_2 is the temperature ($^{\circ}\text{C}$).

Figure 2 shows the fitted surface plots for the sugar loss (%) responses for the HT30 and HT30c adsorbents. The primary objective was to optimize this response by minimizing the sugar loss.

For HT30, the lowest sugar loss was achieved when the temperature was at its maximum (60°C) and the pH was at its minimum (2.0). In contrast, for HT30c, a minimal sugar loss was observed when the temperature was at 60°C , regardless of the pH.

In the balance of adsorption–desorption equilibrium mechanisms, higher temperatures favor sugar desorption. The diffusion of organic molecules in porous adsorbents can be either endothermic or exothermic [66], depending on the adsorption mechanisms and mass transport resistances (both external and internal to the adsorbent particle).

Optimal detoxification conditions were identified for HT30 and HT30c at 30 min of incubation. For HT30, the best results were obtained at 60°C and pH 2.0, resulting in 6.32% sugar loss and 67.27% phenol removal, with the final concentrations of xylose (68.60 g/L), glucose (10.86 g/L), arabinose (11.44 g/L), acetic acid (3.4 g/L) and phenols (2.232 g/L). For HT30c, the optimal conditions were 60°C and pH 5.0, resulting in 14.2% sugar loss and 73.45% phenol removal, with the final concentrations of xylose (62.71 g/L), glucose (10.38 g/L), arabinose (10.16 g/L), acetic acid (2.82 g/L) and phenols (1.810 g/L).

The use of HT30c (calcined at 500°C for 3 h) as an adsorbent in a biorefinery context can be considered part of sustainable technology, but its overall sustainability depends on several factors. The calcination process requires a significant amount of energy, which must be considered in environmental impact assessments. However, by using renewable

energy sources or industrial waste heat for calcination, the environmental footprint of HT30c production can be significantly reduced.

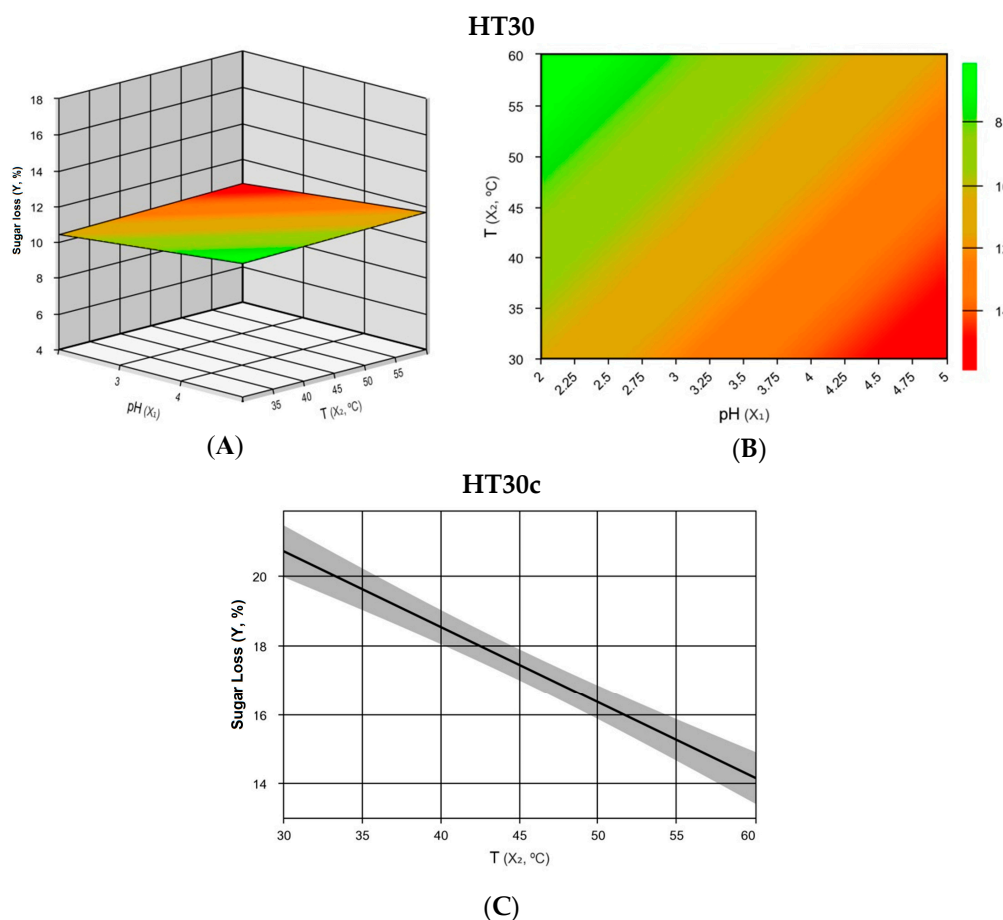


Figure 2. Fitted response surfaces for sugar loss (%) during detoxification at 30 min. (A) 3D surface plot and (B) 2D contour plot correspond to the HT30 condition. (C) Linear regression of sugar loss (%) as a function of temperature under the HT30c condition.

In addition, HT30c offers key advantages such as a selective adsorption capacity, reusability and regeneration potential, which can offset its energy costs over multiple adsorption cycles and increase its viability in sustainable biorefinery applications. Compared to activated carbon, HT30c requires a lower calcination temperature but lacks the potential for energy recovery inherent in the pyrolysis process of activated carbon production. Therefore, the choice between these adsorbents should be based on a comprehensive life cycle assessment (LCA) that considers the trade-offs between energy consumption, adsorption efficiency and regeneration potential. If the HT30c synthesis process can be optimized to utilize waste-derived precursors and sustainable energy sources, it could become a viable and environmentally friendly alternative for pollutant removal in biorefinery applications.

3.3. Kinetic Models for Sugarcane Straw Hemicellulosic Hydrolysate Detoxification

The detoxification process has been evaluated using kinetic models to determine the mechanisms governing the removal or degradation of toxic compounds. The kinetic models that are widely used include pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The efficiency of these processes is influenced by temperature and pH, which affect the reaction rates, adsorption behavior and degradation pathways. Tables 4 and 5 present the fitting results of different kinetic models under varying temperature and pH conditions, providing insight into the dominant detoxification mechanisms.

Table 4. Kinetic model fits for the detoxification process of hemicellulosic hydrolysates using the adsorbent HT30.

Model	Pseudo-First-Order	Pseudo-Second-Order	Intraparticle Diffusion
	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$q_t = k_{id} t^{0.5} + C$
Assay 1 pH: 2.0 Temperature: 30 °C	$k_1 = 0.0763$ /min $q_e = 236.75$ mg/g $R^2 = \text{negative}$	$k_2 = 56865.12$ g/mg·min $q_e = 221.12$ mg/g $R^2 = 0.992$	$k_{id} = -7.38$ mg/g·min ^{0.5} $C = 267.39$ mg/g $R^2 = 0.867$
Assay 2 pH: 5.0 Temperature: 30 °C	$k_1 = 0.0574$ /min $q_e = 247.57$ mg/g $R^2 = \text{negative}$	$k_2 = 56366.61$ g/mg·min $q_e = 223.04$ mg/g $R^2 = 0.995$	$k_{id} = -9.41$ mg/g·min ^{0.5} $C = 280.19$ mg/g $R^2 = 0.753$
Assay 3 pH: 2.0 Temperature: 60 °C	$k_1 = 0.0756$ /min $q_e = 247.51$ mg/g $R^2 = 0.993$	$k_2 = 849.60$ g/mg·min $q_e = 234.80$ mg/g $R^2 = 0.992$	$k_{id} = -3.61$ mg/g·min ^{0.5} $C = 255.86$ mg/g $R^2 = 0.172$
Assay 4 pH: 5.0 Temperature: 60 °C	$k_1 = 0.0683$ /min $q_e = 225.45$ mg/g $R^2 = \text{negative}$	$k_2 = -0.0058$ g/mg·min $q_e = 206.36$ mg/g $R^2 = 0.990$	$k_{id} = -0.62$ mg/g·min ^{0.5} $C = 209.33$ mg/g $R^2 = 0.006$
Assays 5, 6 and 7 pH: 3.5 Temperature: 45 °C	$k_1 = 0.1172$ /min $q_e = 257.79$ mg/g $R^2 = \text{negative}$	$k_2 = -103845.38$ g/mg·min $q_e = 252.11$ mg/g $R^2 = 0.993$	$k_{id} = 2.39$ mg/g·min ^{0.5} $C = 209.33$ mg/g $R^2 = 0.159$

Table 5. Kinetic model fits for the detoxification process of hemicellulosic hydrolysates using the adsorbent HT30c.

Model	Pseudo-First-Order	Pseudo-Second-Order	Intraparticle Diffusion
	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$q_t = k_{id} t^{0.5} + C$
Assay 1 pH: 2.0 Temperature: 30 °C	$k_1 = 0.0776$ /min $q_e = 232.91$ mg/g $R^2 = 0.632$	$k_2 = -17213.52$ g/mg·min $q_e = 206.74$ mg/g $R^2 = 0.826$	$k_{id} = -3.34$ mg/g·min ^{0.5} $C = 227.14$ mg/g $R^2 = 0.016$
Assay 2 pH: 5.0 Temperature: 30 °C	$k_1 = 0.0449$ /min $q_e = 190.29$ mg/g $R^2 = \text{negative}$	$k_2 = 17853.08$ g/mg·min $q_e = 150.14$ mg/g $R^2 = 0.977$	$k_{id} = -14.90$ mg/g·min ^{0.5} $C = 240.76$ mg/g $R^2 = 0.681$
Assay 3 pH: 2.0 Temperature: 60 °C	$k_1 = 0.0767$ /min $q_e = 236.15$ mg/g $R^2 = \text{negative}$	$k_2 = -123535.14$ g/mg·min $q_e = 226.71$ mg/g $R^2 = 0.994$	$k_{id} = 4.26$ mg/g·min ^{0.5} $C = 201.87$ mg/g $R^2 = 0.289$
Assay 4 pH: 5.0 Temperature: 60 °C	$k_1 = 0.0783$ /min $q_e = 180.99$ mg/g $R^2 = 0.754$	$k_2 = -70923.64$ g/mg·min $q_e = 171.40$ mg/g $R^2 = 0.950$	$k_{id} = 13.37$ mg/g·min ^{0.5} $C = 91.68$ mg/g $R^2 = 0.649$
Assays 5, 6 and 7 pH: 3.5 Temperature: 45 °C	$k_1 = 0.0643$ /min $q_e = 220.12$ mg/g $R^2 = \text{negative}$	$k_2 = 31521.62$ g/mg·min $q_e = 194.88$ mg/g $R^2 = 0.978$	$k_{id} = -11.65$ mg/g·min ^{0.5} $C = 268.08$ mg/g $R^2 = 0.894$

The detoxification of lignocellulosic hydrolysates is essential to remove inhibitory compounds that can negatively affect microbial fermentation. Several kinetic models are commonly used to analyze and optimize the removal of these toxic compounds.

The pseudo-first-order model assumes that the reaction rate is directly proportional to the concentration of a single reactant. This model is often applied to adsorption processes and certain chemical degradation reactions where the limiting step is often physisorption or mass transfer. It has been used in studies evaluating the adsorption of inhibitors from

hydrolysates, such as furfural and 5-hydroxymethylfurfural (5-HMF), on activated carbon or other adsorbents [67].

The pseudo-second-order model suggests that the reaction rate depends on the square of the reactant concentration, typically indicating a chemisorption mechanism or surface interactions. This model is widely used to describe adsorption processes where strong interactions, such as covalent bonding, ion exchange or electron sharing, occur between the adsorbate and the adsorbent. Studies on the detoxification of lignocellulosic hydrolysates often report that this model provides the best fit, especially when materials such as ion exchange resins, activated carbon or modified clays are used for inhibitor removal [68–70].

The intraparticle diffusion model evaluates whether the detoxification process is primarily controlled by the diffusion of toxic compounds into porous materials. In the context of hydrolysate detoxification, this model is relevant when the adsorption process occurs within the pores of adsorbents such as biochar, zeolites or layered double hydroxides (LDHs). It is particularly useful for determining whether the process is limited by external mass transfer or internal pore diffusion, which can significantly affect adsorption efficiency and overall reaction kinetics [71].

Understanding these kinetic models is critical for designing efficient detoxification strategies for lignocellulosic hydrolysates. By identifying the rate-limiting step in inhibitor removal, researchers can optimize adsorption conditions, select appropriate adsorbents and improve hydrolysate quality for subsequent microbial fermentation.

The pseudo-second-order model provides the best fit ($R^2 \approx 0.99$) for five assays and considers two adsorbents, HT30 and HT30c (Tables 4 and 5), confirming that the detoxification mechanism is chemisorption-driven rather than purely diffusion-controlled [68–70]. The pseudo-first-order model does not describe the data, as indicated by the negative R^2 values. The intraparticle diffusion model does not fit well, with low R^2 values and inconsistent rate constants.

Detoxification follows pseudo-second-order kinetics, suggesting that it is driven by chemisorption or surface interactions rather than a simple first-order reaction or diffusion-limited process. Temperature and pH are likely to affect the adsorption sites, making the second-order model a better fit. Intraparticle diffusion plays a minor role, as indicated by high boundary layer constants (C), suggesting that external adsorption dominates over internal diffusion [71,72].

3.4. Fermentation of Detoxified Sugarcane Straw Hemicellulosic Hydrolysate

The hydrolysates detoxified by the two adsorbents (HT30 and HT30c) under better operating conditions were used as a fermentation medium by *C. tropicalis* for xylitol production (Figure 3).

In observing Figure 3, it is possible to verify that the hydrolysate detoxified with hydrotalcite HT30c provided the highest sugar consumption (about 6% higher), although the xylitol production is 8.7% lower than that of the hydrolysate detoxified with hydrotalcite HT30, resulting in low values of the fermentative parameters, with an efficiency of xylose conversion to xylitol that is 15.4% lower. These data also show that sugars are directed to cell growth (Figure 3C), since the cell biomass is 9% higher with the HT30c hydrolysate compared to the HT30 hydrolysate, indicating a preference of the cells to use the sugars for growth over xylitol production. This behavior may be related to the content of the phenolic compounds in the hydrolysates (2.23 g/L HT30 and 1.8 g/L HT30c).

Although it is generally reported that phenolics reduce cell growth [23,25,50,73], it is possible that, depending on their concentration, compounds called fermentation inhibitors could stimulate the fermentation process. Similar behavior was observed by Suko and Bura [74], and those authors used the term fermentation enhancers to refer to

the toxic compounds that enhanced xylitol production by *C. guilliermondii* in hybrid poplar hydrolysates, especially phenolics (concentrations of lower than 3 g/L).

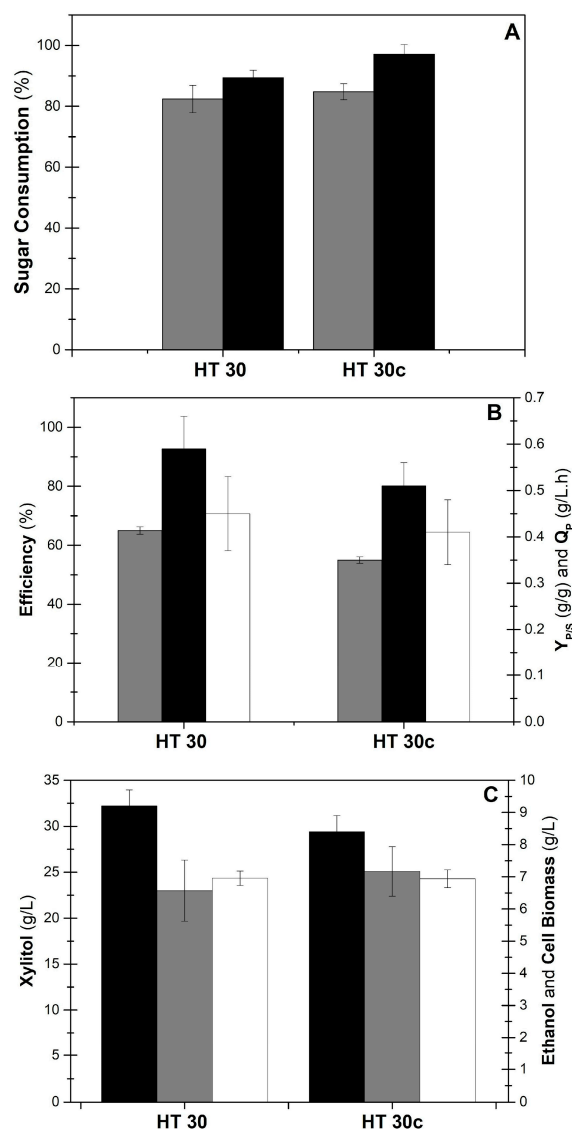


Figure 3. (A) Glucose (gray) and xylose (black) consumption; (B) xylitol yield ($-Y_{P/S}$) (black), productivity ($-Q_P$) (white) and production efficiency (gray); and (C) cell biomass (gray), ethanol (white) and xylitol (black) production by *C. tropicalis* after 72 h fermentation of sugarcane straw hemicellulosic hydrolysate detoxified with HT30 and HT30c.

The results presented in Figure 3A highlight that the xylose consumption was higher than the glucose consumption for both adsorbents, consistent with previous studies showing that *C. tropicalis* preferentially metabolizes xylose under oxygen-limited conditions [75,76]. The slightly higher sugar consumption observed in HT30c suggests a potentially improved detoxification process; however, this did not necessarily translate into higher xylitol production, as seen in Figure 3B. Here, HT30 showed a superior xylitol yield and production efficiency, suggesting that the detoxification with HT30 created a more favorable environment for xylitol accumulation, possibly by reducing the inhibitory compounds that interfere with the xylose reductase (XR) and xylitol dehydrogenase (XDH) enzyme systems [17].

Metabolically, the balance between xylitol and ethanol production depends on oxygen availability and cofactor regeneration. Under microaerophilic conditions, *C. tropicalis*

utilizes xylose via the oxido-reductive pathway, where xylose is converted to xylitol by XR using NAD(P)H as a cofactor. Xylitol is then oxidized to xylulose by XDH, which requires NAD⁺, before entering the pentose phosphate pathway (PPP) and glycolysis. However, when the NAD⁺ regeneration is inefficient—either due to metabolic limitations or the presence of fermentation inhibitors—*C. tropicalis* can redirect some of the carbon flux to ethanol production via pyruvate decarboxylation and alcohol dehydrogenase (ADH) activity, as observed in Figure 3C [75]. The similar ethanol and biomass production in both adsorbents used for detoxification suggests that while the ethanol formation remained stable, the xylitol production was more affected by the detoxification conditions.

These results support a previous study highlighting the importance of detoxification strategies in optimizing xylitol yield [77]. The superior performance of HT30 suggests that this detoxification method may reduce the presence of inhibitory compounds such as furfural and acetic acid, which are known to affect yeast metabolisms by increasing NADH accumulation and shifting the metabolisms toward ethanol production rather than xylitol synthesis. This is consistent with studies showing that reducing fermentation inhibitors leads to higher xylitol accumulation and improved microbial performance [78]. Therefore, while both adsorbents used for detoxification allowed for effective fermentation, HT30 resulted in a more efficient process by redirecting the metabolic flux toward xylitol rather than ethanol, making it a better strategy for bioprocess optimization.

4. Conclusions

Hydrotalcites have demonstrated significant potential as efficient adsorbents for the detoxification of hemicellulosic hydrolysates, effectively facilitating their use in xylitol bioproduction by *Candida tropicalis*. Both uncalcined (HT30) and calcined (HT30c) hydrotalcites were able to significantly reduce phenolic compounds, achieving removal efficiencies of 67.3% and 73.5%, respectively, with HT30 showing superior fermentative performance by favoring xylitol production and reducing sugar loss. Process optimization showed that the temperature had a significant effect on the adsorption performance, especially for the calcined hydrotalcites, while the pH also contributed significantly for the uncalcined variant. Considering their favorable adsorption–desorption kinetics, ease of regeneration and potential for reuse in multiple cycles, hydrotalcites represent a promising alternative for sustainable biorefineries aiming at the valorization of agro-industrial residues. Further investigations should focus on long-term operational stability, economic viability and life cycle assessment to better position hydrotalcites as an industrially feasible and environmentally beneficial detoxification solution.

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Abbreviations

The following abbreviations are used in this manuscript:

5-HMF	5-Hydroxymethylfurfural
ADH	Alcohol dehydrogenase
DOE	Design of experiment
FFD	Full factorial design
HPLC	High-Performance Liquid Chromatography
HT30	[Mg-Al-CO ₃], PURAL [®] MG 30, 30% MgO composition uncalcined
HT30c	[Mg-Al-CO ₃], PURAL [®] MG 30, 30% MgO composition calcined
ICUMSA	International Commission for Uniform Methods of Sugar Analysis
OD ₆₀₀	Optical density measured at 600 nm
PPP	Pentose phosphate pathway
PR	Phenol removal
SL	Sugar loss
SSH	Sugarcane straw hemicellulosic hydrolysate
XR	Xylose reductase
XDH	Xylitol dehydrogenase

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