USE OF ION-EXCHANGE RESINS FOR REMOVING TOXIC COMPOUNDS FROM SUGARCANE BAGASSE HEMICELLULOSIC HYDROLYSATE

Giuliano Dragone [1*], Solange I. Mussatto [1], Martha L.V. Morales [1], Larissa Canilha [1], Walter Carvalho [1], Eliana V. Canettieri [2], Ana I.N. Solenzal [3]

[*]Rua Comendador Custódio Vieira, 259, ap. 04, Centro – 12600-030 – Lorena, SP, Brasil.

[1]Departamento de Biotecnologia – Faculdade de Engenharia Química de Lorena (FAENQUIL)
Rodovia Itajubá-Lorena Km 74,5 – 12600-970 – Lorena, SP, Brasil.

[2]Departamento de Energia – Faculdade de Engenharia de Guaratinguetá - FEG – UNESP
Av. Dr. Ariberto Pereira Cunha, 333 – Pedregulho – 12516-410 – Guaratinguetá, SP, Brasil.

[3] Instituto Cubano de Investigaciones de los Derivados de la Caña de Azúcar (ICIDCA)
Vía Blanca 804 y Carretera Central. Apartado Postal 4026. Ciudad Habana, Cuba.

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Abstract

Hemicellulosic hydrolysates obtained from agricultural residues as sugarcane bagasse, present in their composition a variety of sugars (xylose, glucose, arabinose), and toxic compounds (phenolics, aromatics, furan aldehydes, aliphatic acids and metal ions). These hydrolysates can be employed in fermentative processes; however, toxic compounds inhibit the microorganisms' metabolism, the fermentation being hindered as a consequence. To remove these inhibitors, considerable efforts have been focused on hydrolysate detoxification procedures prior to fermentation, and the use of ion-exchange resins have been reported as one of the most efficient methods. The present work evaluated the removal of toxic compounds present in sugarcane bagasse hemicellulosic hydrolysate, employing a sequence of four ion-exchange resins: A-103 S, A-860, Amberlite Cation and Amberlite Anion. The removal of compounds was evaluated for each resin, and the use of this sequence promoted a removal of (%): furfural (82.1), hydroxymethylfurfural (66.5), phenolic compounds derived from lignin degradation (61.9), chromium (100), zinc (46.1), iron (28.5), sodium (14.7), nickel (3.5) and acetic acid (0).

1. Introduction

Sugarcane bagasse is a lignocellulosic material that consists of approximately 25% hemicellulose (Pandey et al., 2000). When hydrolysed with dilute acids under mild conditions, this residue generates a mixture of sugars, xylose being the major component. For this reason, sugarcane bagasse hemicellulosic hydrolysate can be used as fermentation medium in fermentative processes (Alves et al., 1998; Rodriguez et al., 2001; Carvalho et al., 2003; Santos et al., 2003).
One of the major problems associated with fermentative processes from hemicellulosic

hydrolysates is the presence of several toxic compounds that are formed or released from the raw material during the acid hydrolysis. The major toxic compounds include hydroxymethylfurfural and furfural (sugars degradation products), acetic acid (substance released from the hemicellulosic structure), several aromatic and phenolic compounds (lignin degradation products), and metallic ions. These compounds affect the microorganisms' metabolism, the fermentative process being hindered as a consequence (Larsson et al., 1999; Mussatto, 2002).

To decrease the toxicity caused by the inhibitory compounds, considerable efforts have been focused on hydrolysate detoxification procedures prior to fermentation, including neutralisation (Roberto et al., 1991; Martinez et al., 2001), over-liming (Martinez et al., 2000), evaporation (Converti et al., 2000; Rodrigues et al., 2001), ion exchange resins (Larsson et al., 1999; Rodríguez et al., 2000; Nilvebrant et al., 2001) and charcoal adsorption (Alves et al., 1998; Mussatto & Roberto, 2001). Among these methods, ion-exchange resins have been reported as the most efficient (Larsson et al., 1999; Nilvebrant et al., 2001).

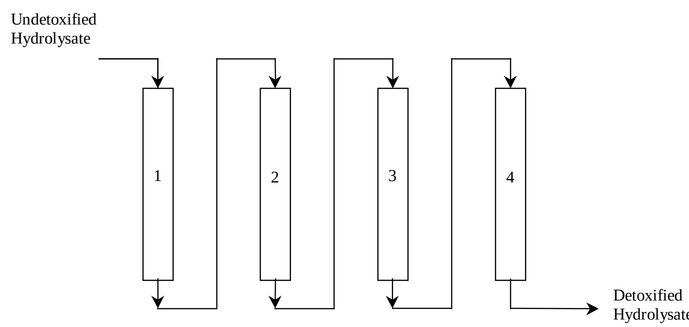
The present study evaluated the use of ion-exchange resins on as a tool for removing toxic compounds from a 5-fold concentrated sugarcane bagasse hemicellulosic hydrolysate.

2. Materials and Methods

2.1. Preparation and treatment of the sugarcane bagasse hemicellulose hydrolysate

Sugarcane bagasse was hydrolysed with sulphuric acid in a 250-l reactor as previously described by Carvalho et al. (2002). The hydrolysate was then concentrated fivefold at 70ºC under vacuum. To reduce the amounts of the main fermentation inhibitors, the concentrated hydrolysate was detoxified with ion-exchange resins at room temperature as shown in Figure 1. A bed volume of 200 ml and an average flow rate of 4 ml min^{-1} were used for detoxifying the hydrolysate in all the ion-exchange resins. After saturation, as determined by the breakthrough curves, all the resins were washed with 600 ml of distilled water using an average flow rate of 1.5 ml min^{-1} and then regenerated according to the manufacturer recommendations.

Figure 1. Schematic representation of the hydrolysate detoxification with ion-exchange resins: (1) anion-exchanger type A-103S in OH^- form (Purolite International, USA); (2) anion-exchanger type A-860S in Cl^- form (Purolite International, USA); (3) cation-exchanger type Amberlite in H^+ form (Applexion Inc., USA); (4) anion-exchanger type Amberlite in OH^- form (Applexion Inc., USA).



2.2 Analytical methods

Glucose, xylose, arabinose, acetic acid, furfural and hydroxymethylfurfural concentrations were determined by high performance liquid chromatography as already described by Carvalho et al. (2002).

Acid-soluble lignin (ASL) was estimated by ultraviolet spectroscopy at 280 nm. The pH of a hydrolysate sample was raised to 12.0 with NaOH 6.0 N and the resulting solution was diluted with distilled water in order to obtain an absorbance reading not exceeding 0.5. The ASL concentration was then calculated according to the following equations:

$$ASL = [4.187 \times 10^{-2} (A_{LIG280} - A_{PD280}) - 3.279 \times 10^{-4}] \quad (1)$$

$$A_{PD280} = [(C_F\ \varepsilon_F) + (C_{HMF}\ \varepsilon_{HMF})] \quad (2)$$

where *ASL* is the acid soluble lignin concentration (g/l), A_{LIG280} is the absorbance reading at 280 nm after dilution's correction, C_F and C_{HMF} are the concentrations (g/l) of furfural and HMF determined by HPLC, and ε_F and ε_{HMF} are the extinction coefficients (l/g cm) of furfural (146.85) and HMF (114.00) previously determined by ultraviolet spectroscopy at 280 nm.

Metallic ions (Cr, Fe, Ni, Na, Zn) were determined by flame atomic absorption spectrometry, as described by Izario Filho et al. (2001).

3. Results and Discussion

Sugarcane bagasse was submitted to acid hydrolysis under conditions that promoted a selective separation of its hemicellulosic fraction, and also formed and liberated several toxic compounds. Subsequently, the hydrolysate was concentrated to increase the xylose content and the sugars concentrations obtained were (g l^{-1}): xylose (106.5), glucose (6.8) and arabinose (11.7). The content of toxic compounds present in concentrated hydrolysate is given in Table 1.

Table 1. Concentration of toxic compounds in the sugarcane bagasse hydrolysate before and after treatment with different ion exchange resins.

Compound	Undetoxified	A-103 S	A-860 S	Amberlite cation	Amberlite anion
Furfural (g l^{-1})	0.056	0.014	0.01	0.01	0.01
HMF (g l^{-1})	0.176	0.081	0.076	0.061	0.059
ASL (g l^{-1})	13.9	6.5	6.3	6.1	5.3
Acetic Acid (g l^{-1})	4.7	4.7	4.7	4.7	4.7
Cr (mg l^{-1})	76.83	10.82	0	0	0
Ni (mg l^{-1})	119.16	119.16	115	115	115
Fe (mg l^{-1})	2650	2541.17	1894.44	1894.44	1894.44
Na (mg l^{-1})	20805.55	20117.64	17750	17750	17750
Zn (mg l^{-1})	927.77	405.88	622.22	618.18	500

The presence of toxic compounds in the hydrolysate is detrimental to the microorganism and the fermentation of undetoxified hydrolysates is characterised by a slow kinetic with limited yield and productivity (Cruz et al., 2000). For this reason, the hydrolysate was submitted to a detoxification process employing a combination of four different ion-exchange resins, since each kind of resin is able to remove a specific type of compound. Besides, ion-exchange resins differ of other detoxification methods due to the capacity of remove organic and inorganic compounds (Rodríguez et al., 2000).

Figure 2 shows the percentage of toxic compounds removal obtained to each resin employed. It can be observed that the first resin (A-103 S) proportioned high removal rates for furfural, hydroxymethylfurfural, soluble lignin and chromium, while the second resin employed (A-860) removed mainly furfural, chromium and iron. The resins 3 and 4 (Amberlite cation and Amberlite anion, respectively) were efficient to remove hydroxymethylfurfural and soluble lignin, the last removing also zinc. In a general form, anion-exchange resins were very efficient to remove furfural, hydroxymethylfurfural and soluble lignin. Nilvebrant et al., (2001) also observed that the treatment of the wood hydrolysate with anion-exchange resins was more efficient to remove phenols and furans, that the treatment with cation-exchange resins.

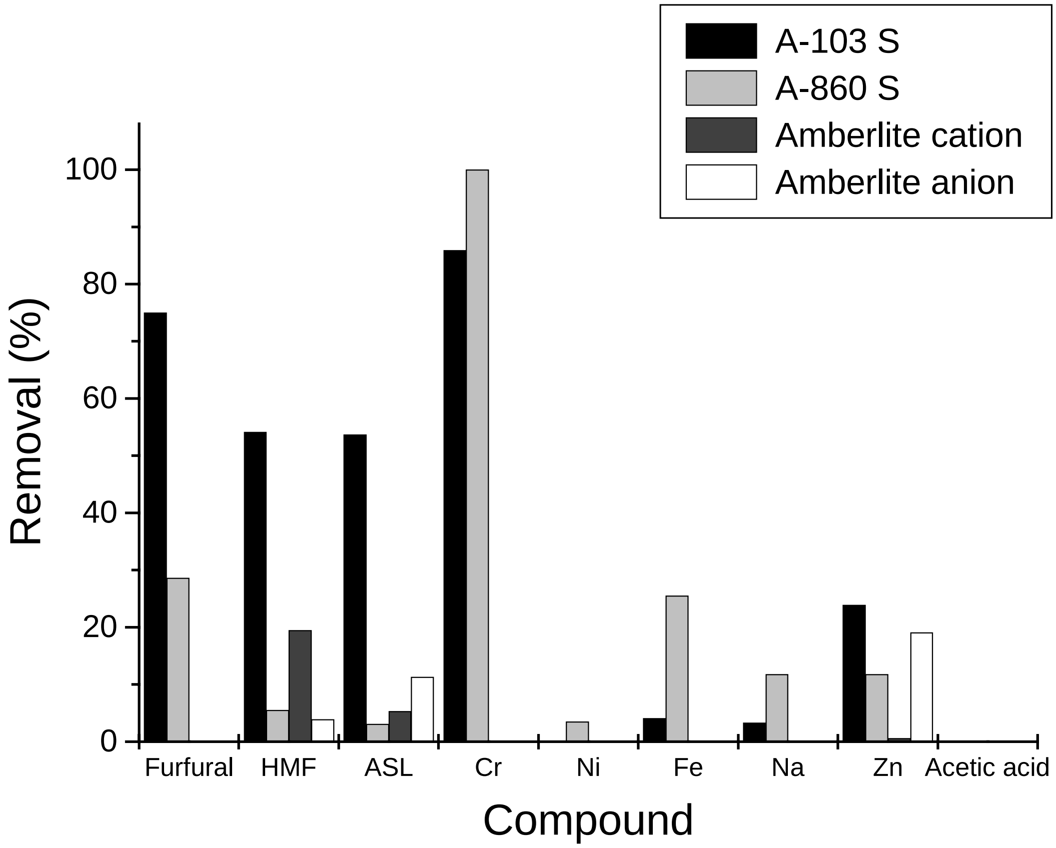


Figure 2. Removal of toxic compounds for each ion exchange resin.

The results obtained in the present work showed that the effect of each resin was complementary to the other; all compounds being removed totally or partially at the end of the process (except acetic acid, which was not removed in none resin). The concentration of all toxic compounds at the end of each resin as well as at the end of the treatment is shown in Table 1. Is also important report that there was not sugars removal by this treatment. Rodríguez et al., (2000) treated the sugarcane bagasse hemicellulose hydrolysate with a system constituted by four resins (A-860, A-103 S, A-400 and C-100) and found similar results to the present work. These authors also attained the best removals of phenols and furfural by use of the resin A-103 S, and acetic acid was almost totally removed by the resin A-400 (96,8%), which was not employed in the present work.

In relation to the undetoxified hydrolysate, the system of treatment with the four resins promoted a total removal to each compound of (%): furfural (82.1), hydroxymethylfurfural (66.5), soluble lignin (61.9), chromium (100), zinc (46.1), iron (28.5), sodium (14.7) and nickel (3.5), acetic acid (0). These results were similar to those attained by Larsson et al., (1999) in the detoxification of wood hemicellulose hydrolysate with anion-exchange resins (removals (%): furfural (73), hydroxymethylfurfural (70) and phenolic compounds (soluble lignin) (91)) and by Rodríguez et al., (2000) in the treatment of sugarcane bagasse hemicellulose hydrolysate with ion-exchange resins (removals (%): furfural (89.2) and phenols (99.9)).

4. Conclusions

The combination of four ion-exchange resins (A-103 S, A-850, Amberlite cation and Amberlite anion) for treatment of the sugarcane bagasse hemicellulosic hydrolysate was able to promote removal rates of (%): furfural (82.1), hydroxymethylfurfural (66.5), soluble lignin (61.9), chromium (100), zinc (46.1), iron (28.5), sodium (14.7) and nickel (3.5). Sugars were not removed by this treatment. Each kind of resin acted specifically on removal of certain types of compounds. Anion-exchange resins were very efficient to remove furfural, hydroxymethylfurfural and soluble lignin.

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