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Extraction of Carboxylic Acids from Anaerobic Fermentation Processes by the Anion Exchange Resin Amberlite IRA-400(Cl)

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Abstract

This work describes a methodology for the valorization of non-food biomass for the production of biosourced molecules via the production of biohydrogen and metabolites of fermentations such as volatile fatty acids. The commercial anion exchange resin Amberlite IRA-400(Cl) was chosen for the extraction of carboxylic acids. Different operating conditions were set up namely the amount of resin to be used, activation methods, pH and their effects on the extraction capacity of the solvent.

I. Introduction

Carboxylic acids are molecules with high added value and unique in their kind. Their physico-chemical properties give them a high reactivity. The carboxylic acid function is highly polar thanks to the carbonyl group and the hydroxyl group that compose it. This allows the creation of hydrogen bridges for example with a polar solvent such as water, alcohols with short carbon chain... etc. Because of this property, small carboxylic acids (up to butyric acid) are completely soluble in water. The acid molecules are able to form stable dimers by hydrogen bonding, which explains why their boiling temperature is higher than that of the corresponding alcohols.

They are weak acids (pKa between 3 and 5), they have a relatively strong acidity for organic compounds. In solution in water, the acid dissociates partially into carboxylate ion.

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Almost all carboxylic acids are obtained by chemical synthesis, mainly by oxidation of aldehydes, thus a double oxidation of primary alcohols. Nevertheless, extractive fermentation is an essential way of producing these acids [1]. Indeed, the anaerobic fermentation process applied to the formation of carboxylic acids is one of the bacterial conversion processes [2-4].

Ion exchange resins are insoluble macromolecules with ionizable groups, which have the property of reversibly exchanging some of their ions, in contact with other ions from a solution. There are cationic resins (positively charged) and anionic resins (negatively charged). Ion exchange resins have been used to recover lactic acid from fermentation processes. These authors used anion exchange resins (Amberlite IRA-420, Amberlite IRA-92) to recover lactic acid for biomedical applications. This resin only binds lactic acid without interacting with amino acids [5-8].

In this work the commercial Amberlite IRA-400(Cl) anion exchange resin was chosen for the extraction of carboxylic acids from our fermentation mediums.

II. Materials and Methods

The Amberlite IRA-400(Cl) anion exchange resin was introduced into an open chromatographic column and packed with distilled water. For the activation of the resin a 1N sodium hydroxide (NaOH) solution was used (ratio 1g/1 NaOH(mL) / T0 aqueous phase (mL)). After having finished dripping the volume of NaOH, the aqueous phase (T0) containing the acids is introduced. Its acid concentration has already been measured by GPC (about 50 g/L). Once the complete passage of the aqueous phase (TF) a GPC analysis was performed to know the concentration of carboxylic acids extracted by the resin. The recovery of our acids in the resin is done for a passage of a 2.5 N hydrochloric acid solution (ratio 1/1 HCl (mL) / T0 aqueous phase (mL)). After measuring the concentrations of recovered acids (AR: after resin), we proceeded to extractions with pentane (ratio 1/1 Pentane (mL) / AR (mL)) followed by an evaporation of the solvent (PO) with a rota-vapor to determine the exact mass of acid obtained.

For the optimization of this method, we performed several methods with different operating conditions (see Table 1).

Table 1. Operating conditions.

Methods	**Resin in g / aqueous phase in mL**
Method 1	20/100
Method 2	10/50 with double passage on the resin
Method 3	10/50 without activation with NaOH and double recovery with pentane
Method 4	40/100 without acid solution and direct recovery with pentane
Method 5	40/100 with double recovery with acid solution

III. Results and Discussions

A series of chromatography with the resin was performed with ratios 20/100, 10/50 and 40/100 (Resin / aqueous phase)).

Table 2. Results of chromatography with the resin.

Quantity in g	**Method 1**	**Method 2**	**Method 3**	**Method 4**	**Method 5**
T0	100,1	50,6	51,1	102,2	101,5
TF1	96,8	49,1	49,2	103,8	99,3
TF2		48,8			
R1	100.2	81,6			98,2
R2	60.0				97,9
PO1	99.3	45.1	23,6	57,8	116,2
PO2			22,5	36,9	110
Acid mass	**0.6**	**0.2**	**0.3**	**0.7**	**0.9**

First, we used 20 g of resin and 100 mL (100.1 g) of an aqueous solution containing 51 g/L of carboxylic acids. The extraction rate of the resin in this case is 58% and our hydrochloric acid solution allowed us to recover 75% of these acids retained by the resin. This corresponds to an overall recovery yield of 43%. The solution containing our acids (AR, pH = 0.34) was again extracted with pentane and 24% of the recovered acids were extracted with this solvent. This corresponds to 18% recovery with pentane.

In order to test the retention capacity of our acids by the resin, our TF1 aqueous phase (pH = 7.92) was reintroduced into the resin for a second pass. This time, instead of obtaining a decrease in concentration, there was a slight increase in the concentration of acids (25.9 to 27.8) in the TF2 phase (pH = 5.33). Extraction with pentane gave us 11% of the recovered acids which corresponds to 9% recovery rate.

The introduction of our aqueous phases containing the acids without activation of the column with the NaOH solution leads to a decrease in the percentage of recovery of the acids by the resin, the resin extraction rate goes from 49% to 40% (the pH goes from 4.4 to 4.2). In this case also we decided to pass the pentane directly into the resin to recover the acids. The extraction results with pentane are quite satisfactory with a recovery balance of 25% which corresponds to a 17% recovery rate.

Doubling the quantity of resin does not lead to a considerable increase in the resin extraction rate, it simply goes from 58 to 62%. In this case also, we note the non-reproducibility of the direct recovery with pentane. The recovery balance (15%) and the recovery rate (10%) decrease compared to the results of the 10/50 ratio (25% and 17% respectively). These low yields are explained by the increase in pH (from 4.4 to 5.3) due to the regeneration with NaOH and these results further confirm the important role that pH plays in solvent extractions.

Table 3. Recovery balance and recovery rate.

Methods	Resin extraction balance in %	Extraction rate with pentane %
1	24	18
2	11	9
3	25	17
4	15	10
5	**33**	**29**

Although the increase in the amount of resin does not affect the resin extraction rate, the recovery rate of the acids with the hydrochloric acid solution increases considerably. The recovery rate increased from 48% (20/100) to 56% (40/100), which allowed us to have very good extraction yields with pentane (33% extraction balance and 29% extraction rate).

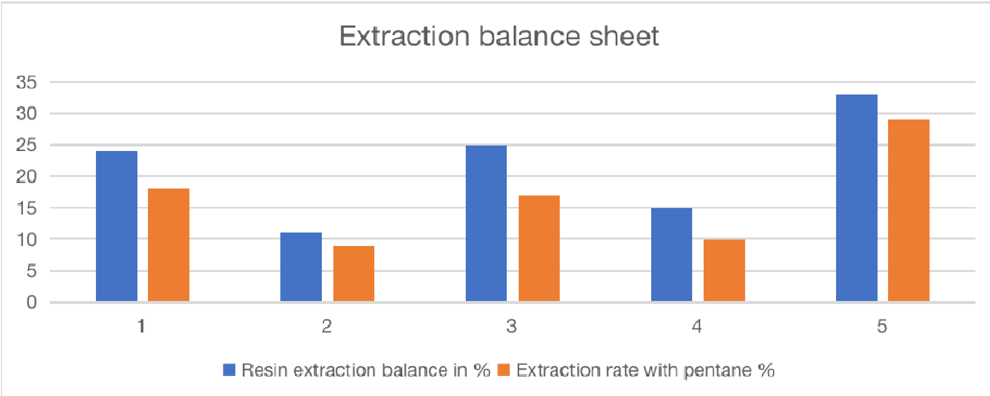

Figure 1. Extraction balance sheet.

The GPC analysis allowed us to evaluate all the carboxylic acids recovered, namely: acetic acid (I), propionic acid (II), isobutyric acid (III), butyric acid (IV), iso-valeric acid (V), valeric acid (VI), iso-capric acid (VII) and capric acid (VIII).

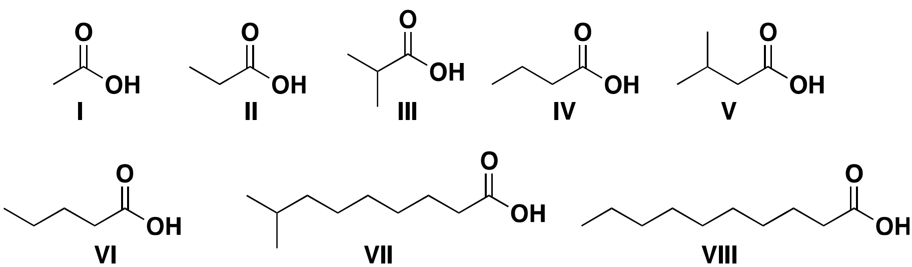

Figure 2. Acids recovered.

The results obtained during the recovery of acids by introducing pentane into the resin show that activation with NaOH solution penalizes the extraction capacity of the solvent because of the increase in pH. It seems interesting to optimize this method with the operating conditions without activation with sodium hydroxide solution (NaOH). Our best extraction result is the 40/100 ratio.

IV. Conclusion

This work describes a research methodology for the recovery of carboxylic acid from anaerobic fermentation processes. With regard to these results of extractions with the Amberlite anion exchange resin, it is to note the important influence of the pH. The use of hydrochloric acid solution remains the best method for carboxylic acid recovery and the 40/100 ratio gives the best yields.

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