Valorization of agricultural by-products with zeolites

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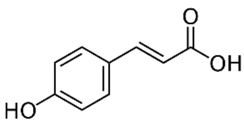
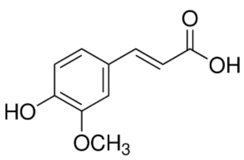
The concept of biorefinery is more and more present in Europe and we attend a strong political and technical focus on the energy recovery of biomass under its various forms. However, not much attention is still given to agroressources as potential reserve for the chemical industry. On the other hand, the industrial transformation processes of the major vegetable productions generate significant amounts of by-products. The replacement of compounds stemming from the petrochemistry by those stemming from agroressources could play a key-role in the preservation of the growth of the chemical industry. Our work is part of the exploitation/valorization of the renewable carbon by the non-food utilization of products and by-products from agriculture, forestry and agro-industries.

A way to valorise by-products/waste is to use them as sources of molecules with high added value for basic chemicals. Then extraction can be realized *via* microwave assisted extraction, twin-screw extraction, ultrasonic extraction … (Candy et al, 2017). This step is often associated to a purification/concentration step mainly by membrane process (nanofiltration …) or by adsorption. In this last case, diverse resins are used. The originality of this work lies in the use of a new kind of adsorbents: zeolites. These materials are crystallized hydrated aluminosilicates with exchangeable cations located inside micropores. These aluminosilicates display a 3D (three-dimensional) opened framework consisting of AlO_4 and SiO_4 tetrahedra linked to each other by sharing oxygen atoms. These assemblies determine channels and cavities of molecular dimensions, with precisely defined sizes. Natural and synthetic zeolite are commonly used as commercial adsorbents and/or catalysts. They are also adsorbents for the design of air depollution process or gas sensing applications (M. Ben Abda et al (2015), L. Bullot et al (2017)). Their use as sorbents is emphasized by their high adsorption capacity. This capacity depends on the structure type, the pore opening, and the chemistry of the surface, as well as other factors such as temperature and humidity. Due to their calibrated porosity, high capacity, thermal stability, ease of regeneration and low cost, zeolite could enable selective adsorption/desorption of molecules with added value.

In this context, we focus our study on one family of compounds which are phenolic compounds frequently present in plant extracts (Figure 1). Some of them have high antioxidant, antimicrobial, anti-inflammatory and antiviral activities linked to their free radical-scavenging properties for example. Other, as vanillin is used as a flavoring agent in foods, beverages, and pharmaceuticals. We present results of adsorption/desorption of these molecules on zeolite of different characteristics (FAU-, MFI-, *BEA-type structures) (Figure 2) according to a methodology described by Simon et al (2015). USY30 (FAU zeolite with Si/Al = 15), BETA (*BEA zeolite with Si/Al = 88) and Sicade-1 (purely siliceous MFI zeolite) are used for this work. Their effectiveness is compared with the styrenedivinylbenzene-based resin (Amberlite XAD16) behaviour, adsorbent which is already employed in recovery of phenolic compounds from agricultural wastes (M.L. Soto et al (2012), A. Scoma et al (2012), L. Bertin et al (2011)).

(a) 

(b) 

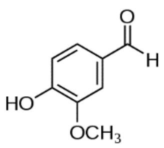
(c) 

Figure 1. (a) *p*-coumaric acid, (b) ferulic acid, (c) vanillin

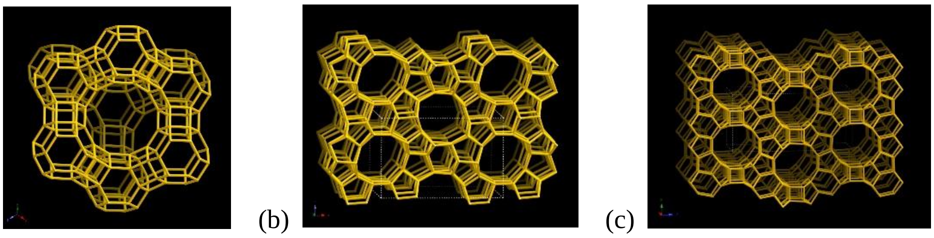


Figure 2. (a) FAU-, (b) MFI-, (c) *BEA-type structures with pore openings diameter close to (a) 7.4 Å, (b) 5.5 Å and (c) 6.6 and 5.6 Å. (IZA, 2017)

Experiments are first conducted with synthetic aqueous solutions and then with plant extracts obtained with techniques mentioned above. Kinetic adsorption curves allow to determine the contact times necessary to reach the adsorption equilibria. Thus the adsorption isotherms of the selected molecules are determined. Langmuir and Freundlich models are employed to fit the experimental data and the maximum adsorption capacities of the adsorbents are estimated. The influence of the pH value on adsorption capacity is determined.

For example, Figure 3a reports an adsorption isotherm of vanillin for Sicade-1, and Figure 3b shows adsorption/desorption ratios related to *p*-coumaric and ferulic acid for some adsorbents. Maximum adsorption capacity of ferulic acid onto BETA is estimated to 140 mg/g at 21°C. It appears that BETA zeolite is a better adsorbent than XAD16 resin and other zeolites with adsorption and desorption ratios close to 95%. The use of regenerated zeolites leads to a weak loss of adsorption capacities. BETA zeolite is a particularly interesting adsorbent to isolate the phenolic compounds from vegetal extracts.

The use of zeolite is an undeniable asset for biomass valorization.

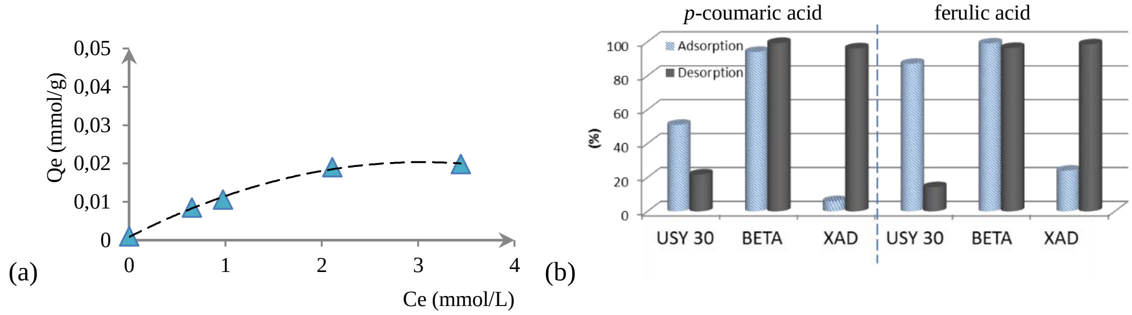


Figure 3. a) Adsorption isotherm of vanillin for Sicade-1 (T= 21°C, adsorption time: 3h, pH = 5), b) Adsorption/desorption ratios related to *p*-coumaric and ferulic acid for some adsorbents (desorption with ethanol 96%). XAD for Amberlite XAD16.

M. Ben Abda, O. Schäf, L. Bullot, A. Simon-Masseron, C. Coste, S. Reynaud, S. Defour, Y. Zerega, E. Fiani, The use of zeolites as selective adsorbents for dioxins in waste incineration plant emissions, *Organohalogen compounds* 77 (**2015**) 109-112.

L. Bertin, F. Ferri, A. Scoma, L. Marchetti, F. Fava, Recovery of high added value natural polyphenols from actual olive mill wastewater through solid phase extraction, *Chemical Engineering Journal* 171 (**2011**) 1287-1293.

L. Bullot, M. Ben Abda, A. Simon-Masseron, T. J. Daou, G. Chaplais, H. Nouali, O. Schäf, Y. Zerega, E. Fiani, J. Patarin, Dioxin and 1,2-dichlorobenzene adsorption in aluminosilicate zeolite Beta, *Adsorption* 23 (**2017**) 101-112.

L. Candy, S. Bassil, L. Rigal, V. Simon, C. Raynaud, Thermo-mechano-chemical extraction of hydroxycinnamic acids from industrial hemp by-products using a twin-screw extruder, *Industrial Crops and Products* 109 (**2017**) 335-345.

IZA (International Zeolite Association, database of zeolite structures) (12/**2017**) http://europe.iza-structure.org/IZA-SC/ftc_table.php

A. Scoma, C. Pintucci, L. Bertin, P. Carlozzi, F. Fava, Increasing the large scale feasibility of a solid phase extraction procedure for the recovery of natural antioxidants from olive mill wastewaters, *Chemical Engineering Journal* 198-199 (**2012**) 103-109.

V. Simon, A. Thuret, L. Candy, L. Bassil, S. Duthen, C. Raynaud, A. Masseron, Recovery of hydroxycinnamic acids from renewable resources by adsorption on zeolites, *Chemical Engineering Journal* 280 (**2015**) 748–754.

M.L. Soto, E. Conde, N Gonzalez-Lopez, M.J. Conde, A. Moure, J. Sineiro, E. Falqué, H. Dominguez, M.J. Nunez, Recovery and concentration of antioxidants from winery wastes, *Molecules* 17 (**2012**) 3008-3024.