Recovery of hydroxycinnamic acids from renewable resources by adsorption on zeolites

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HIGHLIGHTS

- Adsorption of hydroxycinnamic acids is quantified onto FAU- and *BEA-type structures.
- Zeolites have higher adsorption capacities than those of polymer resin XAD16.
- Zeolites can be regenerated and reused in the extraction.
- Zeolites can be used to concentrate plant extracts.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT
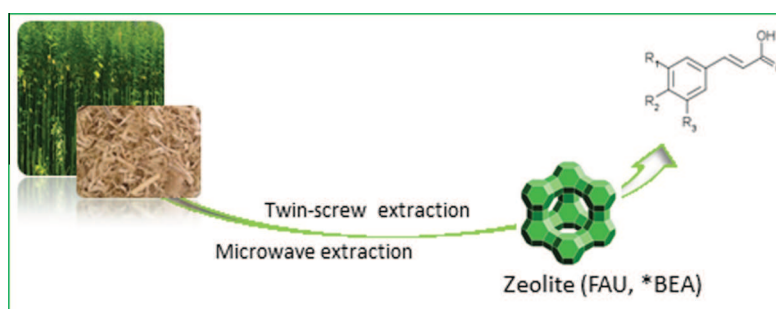
The aim of the study was to examine the adsorption capacity of hydroxycinnamic compounds (ferulic acid, p-coumaric acid, cinnamic acid) on zeolite adsorbents (FAU- and *BEA-type structures) versus Amberlite resin XAD16. The pH and contact time effects on adsorption were evaluated. The adsorption capacity was dependent on pH and higher at pH less than pKa_1. The kinetic adsorption is faster onto FAU and *BEA zeolites than onto XAD16 resin. Maximum adsorption capacities were calculated for the target compounds for pH = 3.5 by using the Langmuir isotherm model. They reached higher values for zeolites than for XAD16 and are respectively of 139, 122 and 109 mg g^{-1} for ferulic, p-coumaric and cinnamic acids. Values around 30 mg g^{-1} were observed for XAD16. Desorption ratios were close to 100% for *BEA zeolite and XAD16 resin in the presence of ethanol 96%. The use of regenerated zeolites led to a loss of adsorption capacities of 10% for *BEA zeolite. The latter is a particularly interesting adsorbent to isolate the hydroxycinnamic compounds from vegetal extracts.

1. Introduction

The concept of biorefinery is more and more present and we attend a strong political and technical focus on the energy valuation of the biomass under its various forms. The industrial transformation processes of the major vegetable productions generate significant amounts of by-products, which can often find use as sources of molecules with high added value for biobased

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chemicals. Secondary plant metabolites like hydroxycinnamic compounds have received a lot of attention in recent years. This class of naturally occurring compounds has a particular interest for industry because of their high antioxidative, antimicrobial, anti-inflammatory and antiviral activities linked to their free radical-scavenging properties [1–4].

Solvent extraction is a conventional established technique for the recovery of hydroxycinnamics, but its selectivity is poor and the recoveries are often low. Further purification and concentration are required, involving additional costs and generation of wastes. The environmental problems caused by solvents have favored the development of simpler, selective, efficient and environmentally friendly technologies.

The technologies dedicated to the recovery and purification of bioactive compounds from natural effluents and biowastes are under implementation. The recovery of hydroxycinnamic compounds was mostly proposed by membrane processes and liquid–liquid extraction, semi-preparative HPLC, adsorption, solid phase extraction (SPE) with diverse resins (Amberlite XAD7, XAD16,…) [5–12]. Adsorption enables the separation of selected compounds from dilute solutions. Compared to alternative technologies, adsorption is attractive for its relative ease of design, operation and scale up, high capacity, ease of regeneration and low cost. It is the preferred method for phenolic compounds recovery. But a disadvantage of adsorbents is that they have either adsorption or high desorption performance but not both simultaneously. Zeolites, used to remove traces of hydroxycinnamic compounds from wastewater [13,14] could represent a feasible alternative compared with the traditional adsorbents, since it relies on simple, effective and cheap procedures [15].

In this context, the aim of this work is to characterize the adsorption and desorption of three hydroxycinnamic compounds (p-coumaric acid, ferulic acid, cinnamic acid) frequently present in plant extracts [16–18] onto zeolites of different characteristics in comparison with a styrenedivinylbenzene-based resin: Amberlite XAD16 which is already employed in recovery of phenolic compounds from agricultural wastes [19–21].

Batch adsorption and desorption experiments were first conducted with synthetic solutions of the target components. The property of the adsorbents was then evaluated in extracts obtained from renewable resources. Extracts from hemp wood, an important industrial hemp by-product, were selected for the present study to validate the possibility of using these materials for industrial scale valorization of hydroxycinnamic compounds.

2. Materials and methods

2.1. Chemicals

Gallic acid, p-coumaric acid, ferulic acid, cinnamic acid, acetonitrile and ethanol (HPLC grade), orthophosphoric acid and sodium hydroxide (99% purity) were purchased from Sigma Aldrich (L'Isle d'Abeau, France). Folin reagent and sodium carbonate are from VWR (Fontenay-sous-Bois, France). HCl is from Fisher Chemical (Illkirch, France). Ultrapure water was prepared using a Milli-Q filter system (Millipore, Bedford, MA, USA).

The main physical characteristics of the target compounds are listed in Table 1.

2.2. Preparation and characterization of adsorbent

FAU and *BEA-type zeolites are selected for their pore size (Table 2) and they are used in their H+ form. USY30 and USY50 (FAU-type structure) are purchased from Süd-Chemie AG (München, Germany) and BETA (*BEA-type structure) from

Table 1
Main characteristics of the target compounds.

Compounds	Formula	M (g mol^{-1})	pKa	Molecular size (nm)*
p-Coumaric acid	$C_9H_8O_3$	164.16	4.64, 9.45	0.500×1.024
Ferulic acid	$C_{10}H_{10}O_4$	194.19	4.58, 8.75	0.500×1.000
Cinnamic acid	$C_9H_8O_2$	148.16	4.44	0.499×0.945

* Calculated with Hyperchem software.

Table 2
Characteristics of the adsorbents.

Adsorbent	Pore size (nm)	Molar ratio Si/Al	BET surface (m^2 g^{-1})
USY30	0.74[a]	14.5	749[c]
USY50	0.74[a]	25	675[c]
BETA	0.66×0.67[a]	88	659[c]
	0.56×0.56[a]		
Zeolite A[b]	0.64[b]	70[b]	543[b]
XAD16	–		⩾800

[a] Atlas of zeolite framework types [22].
[b] Thiel et al. [15]. Not studied in this work, but cited in Section 3.
[c] Determined in this work.

Clariant (München, Germany). The Amberlite XAD16 resin is purchased from Sigma-Aldrich (L'Isle d'Abeau, France) as macroporous polystyrene crosslinked polymers. Their characteristics are reported in Table 2.

Nitrogen sorption isotherms are carried out with a Micromeritics ASAP 2040 apparatus at liquid nitrogen temperature (77 K). Equivalent specific surface areas are calculated using the BET equation. Prior to the measurement, the zeolite samples are outgassed under vacuum at 300 °C overnight.

Before use, zeolites were dried at 140 °C during 36 h. Amberlite XAD16 resin was soaked in methanol for 10 min and then washed with ultra pure water under agitation during 1 h. It was then dried in an oven during 24 h at 100 °C.

2.3. Plant material

Hemp wood is a hemp by-product generated during the industrial processing of the fiber. Its lignin content (∼20%) is very close to that of wood [23]. So is this material a potential source of aromatic compounds. Hemp wood was provided by Agrofibre (Cazères-sur-Garonne, France). It was crushed in 0.5 mm particles before the implementation of the extraction process. For characterization of the dry matter, the crucibles are subjected beforehand to a temperature of 103 °C for a few hours in an oven, then placed in a desiccator.

Once cooled, their mass is measured. 2 g of extract were then placed in the crucible, which was placed in an oven at 103 °C for 12 h minimum. Monitoring the mass is carried out until a stabilization of the value. The percentage of dry matter is then determined by the following relationship:

$$\% \text{ dry weight} = \frac{\text{final weight}}{\text{initial weight}} * 100 \tag{1}$$

2.4. Extraction processes

Extracts obtained by microwave extraction and twin-screw extraction were studied.

The microwave extractions were performed in an oven MARS 5 from CEM instruments according to operating conditions developed by Bassil [24]. The samples consist of a quantity of hemp wood and extraction solvent in a liquid/solid ratio 1:16. The extraction solvent used is 96% ethanol. 14 g of dry hemp wood

were extracted with 224 g of solvent. The extraction temperature ranged from 25 to 80 °C in 7 min and was kept for 3 min (Microwave power: 1000 W. Pressure and temperature values were of 12 bar and 80 °C. The extracts are then centrifuged for 15 min at 20 °C (9000 rpm), and the liquid phase was recovered. The ethanol was removed under vacuum at 43 °C, and the extract was taken up in ultra-pure water. This step is necessary because the contact with the zeolites should be in an aqueous solution, not ethanolic one, because ethanol interferes in the interactions between the hydroxycinnamic compounds and the adsorbent [15].

Extractions were also conducted with a co-rotating and co-penetrating Clextral BC 45 (Firminy, France) twin-screw extruder according to operating conditions developed by Bassil [23]. Hemp wood and water were fed into the twin-screw extractor (Clextral 40, France): solvent/solid ratio 3.5. A filter consisting of six hemispherical units with perforations of 1 mm in diameter, was used to separate the liquid and the solid phases. The phase liquid was recovered, centrifuged to eliminate residual fine particles.

The concentration in total phenolics (mg g^{-1}) of the extracts is determined by the Folin–Ciocalteu titration.

2.5. Batch adsorption

About 50 mg of adsorbent and 10 mL of aqueous solution of hydroxycinnamic acids with the same initial concentrations C_0 from 10 to 500 mg L^{-1} were placed in 50 mL glass flask under agitation at room temperature (24 ± 2 °C). This domain of concentrations includes the real concentrations of the plant extracts and allows to realize adsorption isotherms. Parallel blank experiments were carried out by adding 10 mL of the aqueous solution in identical glass flask without adsorbent. Two replicates were set up for each experiment.

Initially, the experiments are carried out with aqueous model solutions made up with known concentrations of p-coumaric acid, ferulic acid and cinnamic acid C_0 (mg L^{-1}). Tests were carried out by changing the pH of the solutions by the addition of HCl or NaOH. Tests were then conducted on plant extracts. At different time, the concentration C_t (mg L^{-1}) of solution was determined by HPLC with UV detection. Samples (200 μL) are made over a period of 24 h.

The adsorption capacity (Q) was calculated according to the following equation:

$$Q = \frac{V(C_0 - C_t)}{w} \tag{2}$$

where Q (mg g^{-1}) is the adsorption capacity; V (L) is the volume of the solution; w (g) is the adsorbent dry weight.

After reaching the adsorption equilibrium, the equilibrium concentration (C_e) was determined. The equilibrium adsorption capacity (Q_e) was calculated according to the following equation:

$$Q_e = \frac{V(C_0 - C_e)}{w} \tag{3}$$

Adsorption ratios (A, %) were calculated as follows:

$$A = \frac{C_0 - C_e}{C_0} * 100 \tag{4}$$

2.6. Determination of phenolic content

2.6.1. HPLC analysis

Qualitative and quantitative analysis of hydroxycinnamic compounds were achieved via HPLC-DAD reverse phase system (DIONEX Ultimate 3000 HPLC) operating at 280 and 320 nm wavelengths and equipped with a Omnispher C18 (3 μm) 3 × 100 mm column (Varian, France). Column temperature was kept at 30 °C at a flow rate of 0.7 mL min^{-1}. Injection volume was 10 μL. The employed eluents were pure water acidified by orthophosphoric acid (pH = 2) (A) and pure acetonitrile (B). The gradient was: 0–5 min 95% A, 5–10 min 90% A, 10–17 min 72% A, 17–22 min 0% A, 22–24 min 0% A, 24–28 min 95% A. Calibration curves were prepared at 6 levels (0, 10, 50, 100, 200, 500 mg L^{-1}) and each calibration level was injected in triplicate. The linearity range extends in the whole calibration curve with regression coefficients from 0.9990 (p-coumaric acid) to 0.9995 (ferulic acid). To study the repeatability of the analysis, a standard solution containing low hydroxycinnamic concentrations (10 mg L^{-1}) was injected 10 times. The standard deviation, determined for each compound appeared to be lower than 5%.

Limit of detection (LOD) and limit of quantification (LOQ) were estimated as equal to 3 times the background (S/N = 3) and the LOQ as 10 times the background (S/N = 10) [25]. The quantification limits are for ferulic acid, p-coumaric acid and cinnamic acid respectively 1.7, 1.4 and 0.4 mg L^{-1}.

The concentration of each component was calculated using a calibration curve from the corresponding synthetic solution.

2.6.2. Determination of polyphenol content

The concentrations of total polyphenol content were determined using the Folin–Ciocalteu (FC) method. 1 mL sample, 7.5 mL distilled water, 1 mL sodium carbonate (20%), and 0.5 mL FC reagent were mixed at 70 °C for 10 min. Absorbances were then measured at 760 nm (UV-1800 spectrophotometer, Shimadzu) against a blank sample at 23 °C. Determination of the total phenolic compound content was performed in triplicate and calculated using a calibration curve with gallic acid as a standard. The results were expressed in gallic acid equivalent (mg GAE g^{-1}).

2.7. Desorption

Recovery of adsorbed compounds was studied in desorption experiments carried out with the exhausted adsorbents employed in adsorption experiments (Table 2). After adsorption, the remaining mixture was spin-dried (10,500 g, 10 min at 20 °C). The solid was removed, then dried in an oven at 60 °C during 24 h and introduced into 2 mL of a non-toxic desorbing solvent: ethanol 70% or ethanol 96%. The solution was shaken in a thermomixer at 60 °C for 3 h at 1300 rpm. Each experiment was realized in triplicate. Desorption ratios (D, %) were calculated for each compound by the following equation:

$$D = \frac{C_d * V_d}{(C_0 - C_e) * V} \tag{5}$$

where C_d (mg L^{-1}) is the final concentration of the compound in the solvent and V_d (L) the employed solvent volume.

2.8. Regeneration process

After desorption, zeolites and resin were regenerated as described in Section 2.2. They are then used according to the protocol described in Section 2.5.

3. Results and discussion

3.1. Kinetic adsorption curve

Examples of kinetic adsorption curves are shown in Fig. 1. Changes in the ferulic acid adsorption capacity (Fig. 1a) are comparable for the three zeolites and reached higher adsorption rates than resin. For this adsorbent, adsorption kinetics are much
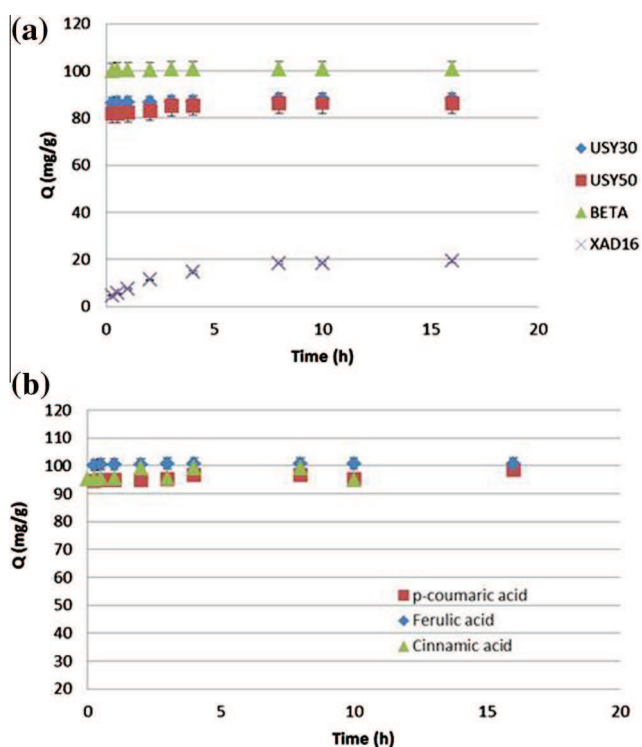
Fig. 1. Kinetic adsorption curves of (a) ferulic acid-USY/BETA/XAD16 and (b) hydroxycinnamic acids-BETA (C_i = 200 mg L^{-1}, m = 50 mg, 24 ± 2 °C, pH = 3.5).

slower: the equilibrium is reached after a contact time of about 8 h *versus* 0.5 h for zeolites. The adsorption capacity at the equilibrium for ferulic acid onto BETA (100 mg g^{-1}) is higher than for other adsorbents, such as USY50 and USY30 (86 mg g^{-1}) and XAD16 (19 mg g^{-1}).

The adsorption reached equilibrium at 0.5 h for BETA zeolite, and the adsorption capacity reached the same order of magnitude for the three compounds (Fig. 1b) (for *p*-coumaric acid and cinnamic acid: 96 mg g^{-1}, and for ferulic acid: 100 mg g^{-1}). In the first 2 h, the adsorption ratio reached more than 94% for the hydroxycinnamic acids with BETA zeolite (Fig. 2). Adsorption rates for ferulic and cinnamic acids were between 77% and 87% with USY zeolites while was only 40–50% for coumaric acid. Much lower values were recorded for XAD16 resin for which only cinnamic acid is adsorbed in significant amounts ($A \sim 70\%$).

Contact times of 2 and 10 h were chosen for the selected range of concentrations to establish adsorption isotherms of zeolites and XAD16 resin respectively because an increased initial
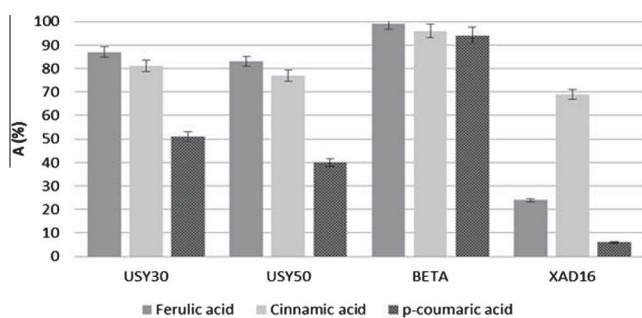
concentration induces a longer required time from the beginning to the equilibrium as a larger equilibrium adsorption capacity.

3.2. Adsorption isotherm

Adsorption isotherm reflects the relationship between the amount of a solute adsorbed at constant temperature and its concentration in the equilibrium solution. It provides essential physicochemical data for assessing the applicability of the adsorption. Langmuir and Freundlich isotherm models are widely used to investigate the adsorption process [6,15,21,26]. The Langmuir isotherm was developed on the assumption that the adsorption process will only take place at specific homogenous sites within the adsorbent surface with uniform distribution of energy level. Once the adsorbate is attached on the site, no further adsorption can take place at that site; which concluded that the adsorption process is monolayer in nature. Contrary to Langmuir, Freundlich isotherm was based on the assumption that the adsorption occurs on heterogeneous sites with non-uniform distribution of energy level. The Freundlich describes reversible adsorption and is not restricted to the formation of monolayer [27,28]. The linear form of Langmuir and Freundlich equations are represented respectively by the following equations:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \tag{6}$$

$$\ln Q_e = \ln k + \frac{1}{n} \ln C_e \tag{7}$$

where Q_e is the amount of compound adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (mg L^{-1}), Q_m (mg g^{-1}) the saturated adsorption capacity, b the Langmuir constant, k and n the Freundlich constants.

Both models were employed to fit the experimental data. The maximum adsorption capacities of the studied adsorbent systems are presented in Table 3. On the bases of r^2 values, the Langmuir model described better the adsorption of each compound on all the tested adsorbents. Comparing the results, it is clear that the Amberlite adsorbent is less effective than the zeolites. The values are systematically 3.5–5 times lower than the highest adsorption rate. For example, the maximum adsorption capacity of ferulic acid is 139 mg g^{-1} for BETA and 29 for XAD16. USY30 and USY50 reach similar capacities with values around 133 mg g^{-1}. For coumaric acid and cinnamic acid, smaller values were obtained. They have been estimated for coumaric acid at respectively 68, 109 and 122 mg g^{-1} for USY50, USY30 and BETA.

BETA zeolite gives the best adsorption performances for ferulic and coumaric acids (Fig. 3) since the slope of their isotherm was significantly higher than those of the other adsorbents. On the other hand, they reach equilibrium at lower concentration values than other adsorbents ($\sim$0.2–0.3 g L^{-1} for BETA and >0.8 g L^{-1} for USY30 and USY50). In comparison, BETA zeolite has higher capacities at low concentrations than the others and a higher affinity for phenolic acids. Thiel et al [15] also studied the adsorption capacity of hydroxycinnamic acids for BETA zeolite (with a close Si/Al ratio (Table 2)) and concluded that BETA zeolite was effective for this purpose and that adsorption values were higher for ferulic than for *p*-coumaric acid. Their results differ from ±30% from the ones presented in this study. Let us note that the adsorption temperature is not quantitatively specified. It is then confirmed that zeolites adsorbents are particularly suitable for the recovery of targeted molecules, specifically the BETA zeolite. Its implementation requires a smaller amount of adsorbent compared to other adsorbents.

Fig. 2. Adsorption ratios for USY/BETA/XAD16 adsorbents (adsorption time: 2 hr, C_i = 200 mg L^{-1}, m = 50 mg, 24 ± 2 °C, pH = 3.5).
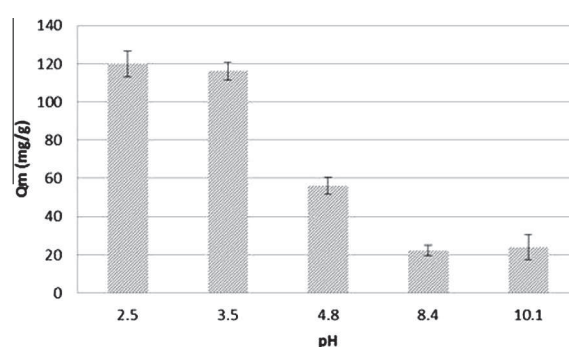
Table 3
Estimated Langmuir and Freundlich equation parameters related to the adsorption of each hydroxycinnamic compound on the tested adsorbents.

	Langmuir					Freundlich			
	USY30	USY50	BETA	XAD16		USY30	USY50	BETA	XAD16
Coumaric acid									
Q_m (mg g^{-1})	108.7	68.0	122.0	34.2	k	133.49	76.93	149.25	28.21
b (L g^{-1})	5.8	11.3	82	3.2	$1/n$	0.584	0.382	0.235	0.452
r^2	0.953	0.998	0.998	0.983	r^2	0.882	0.921	0.866	0.991
Ferulic acid									
Q_m (mg g^{-1})	137.0	131.6	138.9	29.4	k	97.73	79.38	182.02	24.46
b (L g^{-1})	1.33	1.2	144.0	3.3	$1/n$	0.803	0.763	0.236	0.461
r^2	0.900	0.938	0.999	0.993	r^2	0.973	0.984	0.870	0.983
Cinnamic acid									
Q_m (mg g^{-1})		65.8	108.7	31.2	k		67.4	105.7	27.8
b (L g^{-1})	ND	8.44	153.33	3.57	$1/n$	ND	0.388	0.115	0.6171
r^2		0.903	0.999	0.983	r^2		0.903	0.953	0.955
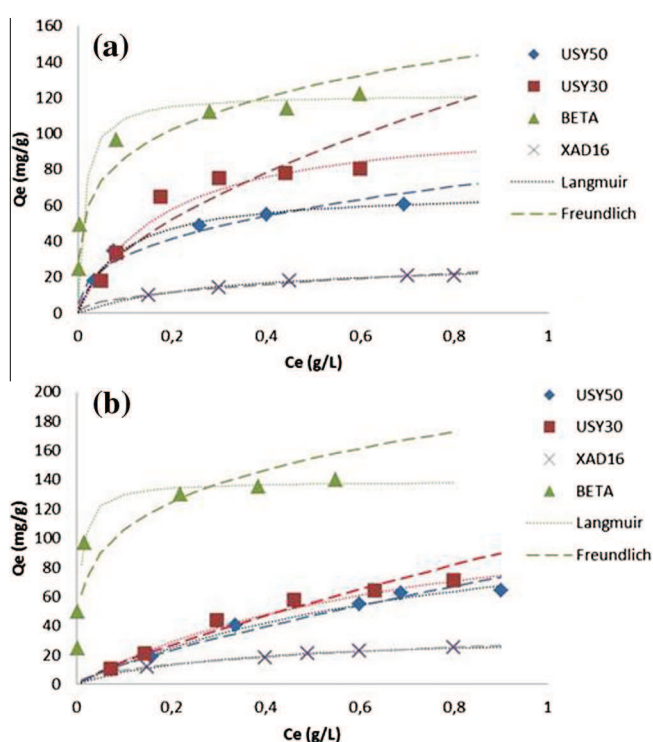
Fig. 3. Adsorption isotherms of *p*-coumaric acid (a) and ferulic acid (b) for USY50/USY30/BETA/XAD16 (temperature: 24 ± 2 °C, adsorption time: 2 h except for XAD16 10 h, pH = 3.5).

Fig. 4. Influence of pH on maximum adsorption capacity of *p*-coumaric acid on BETA.

3.3. The influence of pH value on adsorption capacity

A decrease of the maximal adsorption capacity of *p*-coumaric acid was observed for BETA zeolite according to the pH increase (Fig. 4). A factor 6 is approximately observed between pH 3 and pH 8–10. The pH of the solution influences the surface charge of the adsorbents as well as the degree of ionization of the adsorbate (Fig. 5). At pH < pKa$_1$, the phenolic compound is predominantly in the neutral molecular form, while the zeolite surface charge is positive for acid pH as reported by Kuzniatsova et al. [30]. It results from the protonation or dissociation of the hydroxyl groups (SiOH and AlOH). Thus complexes are probably formed involving silanol and aluminol sites of zeolite and hydroxyl and carboxyl groups of the phenolic compound [31,32]. At pKa$_2$ > pH > pKa$_1$, the compound is mainly in the form of negatively charged carboxylate ions and at pH > pKa$_2$ the form of negatively charged phenolate ion is added. As the functional groups of the zeolite surface are deprotonated and negatively charged, electrostatic repulsive forces lead to a decrease of the adsorption capacity.

A decrease of the maximum adsorption capacity as a function of pH was also observed for ferulic and cinnamic acids with the three zeolites under study. The turning point is around 4.5 and relevant with the pKa$_1$ value. The effect of pH upon adsorption of phenolic compounds has already been related to the degree of ionization of the phenolic sorbate by various authors [33,34]. Davila-Guzman et al. [29] also demonstrated that the adsorption capacity of ferulic acid decreased with a pH increase for XAD16. Working at an acidic pH lower than pKa$_1$ will promote the recovering of the maximum of molecules in an aqueous medium.

3.4. Desorption experiments

The desorption rates of ferulic and *p*-coumaric acids are between 10% and 20% whatever the ethanol concentration of the extraction solvent for faujasites (Fig. 6). However, they vary between 71% and 100% for cinnamic acid. It is interesting to note that desorption with ethanol 96% allows to selectively desorb cinnamic acid trapped by the USY zeolites. The implication of OH$_{phenolic}$ for adsorption of coumaric and ferulic acid creates another adsorption possibility that does not exist in cinnamic acid and strengthens the interactions with the zeolite.

The desorption rates are much higher for the BETA zeolite (close to 100%) and of the same order of magnitude as those obtained by Thiel et al. [15] for ferulic acid. Desorption is easier in the case of BETA zeolite. This could be explained by the Si/Al ratio of zeolite and/or by the zeolite structure. Those of FAU-type structure (USY) have a porosity in the form of cavity while the pores of the BETA zeolite (*BEA-type structure) are in the form of channels
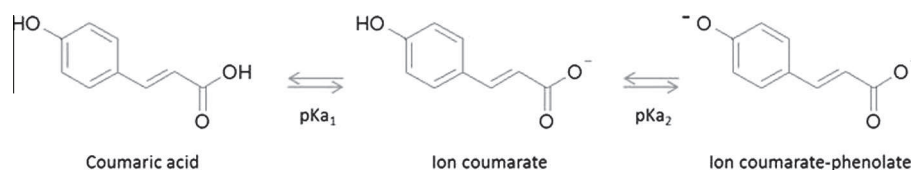
Fig. 5. Chemical equilibrium of *p*-coumaric acid (pKa$_1$ = 4.64, pKa$_2$ = 9.45).
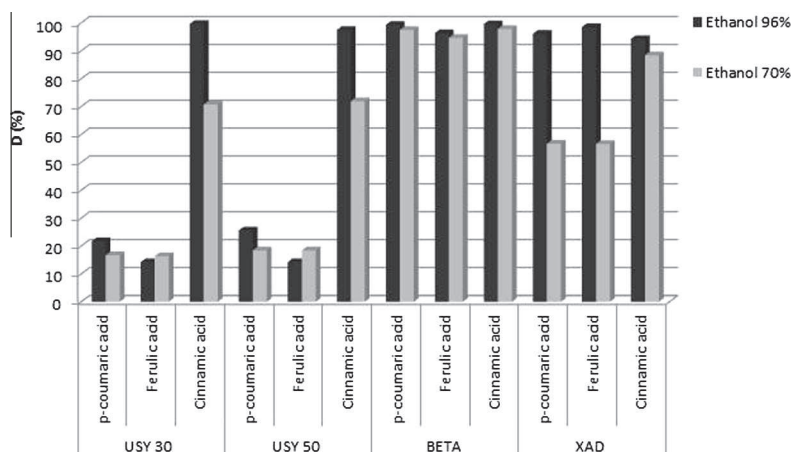

Fig. 6. Overall desorption ratios related to the three hydroxycinnamic compounds for the four studied adsorbents with ethanol 70% and ethanol 96%.

[22]. Concerning the XAD16 resin, the use of ethanol 96% leads to results close to those obtained for the BETA zeolite.

Cinnamic acid is then the compound for which the desorption yields are the highest. This molecule is the less polar among the 3 studied. Furthermore, ethanol 96% provides the highest rate desorption rate. The protocol provides 10-fold concentrated extracts by using of the BETA zeolite.

3.5. Application to hemp wood extracts

Hydroxycinnamic compounds in aqueous extract from hemp wood have been quantified by HPLC-DAD. *p*-Coumaric acid is the most abundant among the targeted acids [23,35]. The total polyphenol content in microwave and twin screw extracts were respectively 65 and 896 mg GAE L^{-1}. The presence of other phenolic compounds and more generally organic/inorganic compounds in the extracts, does not seem to affect the adsorption of *p*-coumaric acid. Moreover, desorption rates obtained by ethanol 96% are equivalent to those presented in Fig. 6. Similar conclusions could be drawn for the spiked hemp extract (Table 4). The experimental results obtained with synthetic solutions can be applied to the hemp wood extracts.

3.6. Regeneration of zeolites

Regeneration of adsorbents was tested for all adsorbents. A loss of efficiency of microporous solid to retain the hydroxycinnamic compounds was recorded in a second use of the adsorbent and whichever studied (Table 5). The most interesting BETA material lost about 20% of adsorption capacity of *p*-coumaric acid which was the most abundant investigated hydroxycinnamic acid in the hemp wood extract. This is certainly due to the remaining ethanol molecules inside the pores despite drying which are responsible for co-adsorption phenomena. On the other hand, it also affects in these conditions the adsorption kinetics which is slower in the second use. For example, for BETA zeolite, the equilibrium is reached only after 1.5 h. Additional tests show that adsorption

Table 4
Comparison of adsorption rates of hydroxycinnamic acids (%) for synthetic solutions and plant extracts (contact time: 2 h).

		A (%) at *t* = 2 h		
		p-Coumaric acid	Ferulic acid	Cinnamic acid
Hemp wood extract (MW) (*p*-coumaric acid: ∼20 mg L^{-1} ferulic acid: <LOQ cinnamic acid: ∼9 mg L^{-1})	USY30	68 ± 6	ND	81 ± 6
	USY50	39 ± 4	ND	76 ± 4
	BETA	94 ± 6	ND	93 ± 7
	XAD16	8 ± 3	ND	61 ± 4
Hemp wood extract (Ext) (*p*-coumaric acid: ∼30 mg L^{-1} ferulic acid: <LOQ cinnamic acid: <LOQ)	USY30	63 ± 5	ND	ND
	BETA	92 ± 4	ND	ND
Synthetic solution at 200 mg L^{-1}	USY30	51 ± 3	87 ± 4	81 ± 4
	USY50	40 ± 2	83 ± 4	77 ± 4
	BETA	94 ± 5	99 ± 5	96 ± 5
	XAD16	6 ± 1	24 ± 1	69 ± 3
Hemp wood extract (MW) spiked at around 200 mg L^{-1}	USY30	59 ± 3	83 ± 4	75 ± 4
	USY50	36 ± 2	79 ± 4	70 ± 4
	BETA	93 ± 5	99 ± 5	96 ± 5
	XAD16	8 ± 1	20 ± 1	70 ± 3

ND: not determined because of concentrations less than limit of quantification (LOQ).
MW: microwave extraction, Ext: twin-screw extrusion.

Table 5
Decrease of adsorption capacity for the second use (%) (contact time: 2 h, synthetic solution (*C$_i$* = 200 mg L^{-1}), *m*$_{adsorbent}$ = 50 mg, 24 ± 2 °C, pH = 3.5).

	p-Coumaric acid	Ferulic acid	Cinnamic acid
USY30	13	14	27
USY50	10	11	27
XAD16	0	11	30
BETA[a]	21	23	13
BETA[b]	7	9	6

[a] According to Section 2.8.
[b] Zeolites dried at 200 °C before the second adsorption.

capacity can be of the same order of magnitude for the second adsorption when BETA zeolite is beforehand dried at 200 °C instead of 140 °C. Regeneration conducted by washing with isopropyl alcohol like proposed by Thiel et al. [15] and dried at 200 °C in this work leads to the same results. Thermal regeneration avoids to use solvent.

4. Conclusion

USY and BETA zeolites (respectively FAU-type structure and *BEA-type structure) have more important adsorption capacities for hydroxycinnamic acids than XAD16 resin as well as faster adsorption kinetics. The adsorption capacity was dependent on pH and higher at pH less than pKa$_1$. Maximum adsorption capacities were calculated for the targeted compounds for pH = 3.5 by using the Langmuir isotherm model. They reached higher values for zeolites than for XAD16 and are respectively of 139, 122 and 109 mg g^{-1} for ferulic, p-coumaric and cinnamic acids for BETA zeolite. For the latter, desorption ratios of the three targeted compounds are close to 100% with ethanol 96%. The possible regeneration of this adsorbent constitutes a great asset for its implementation. It is the first use of these zeolites for plant extracts applications; they offer promising results with the highest adsorption ratios from vegetal extracts.

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