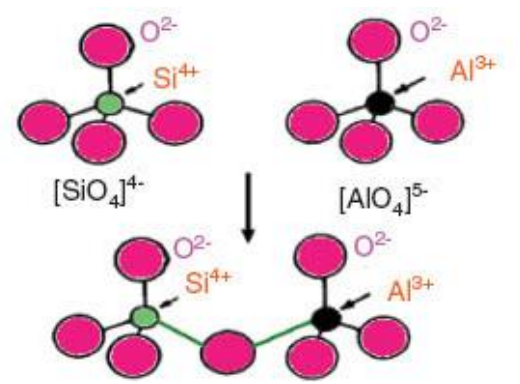
Valorization of agricultural by-products with zeolites

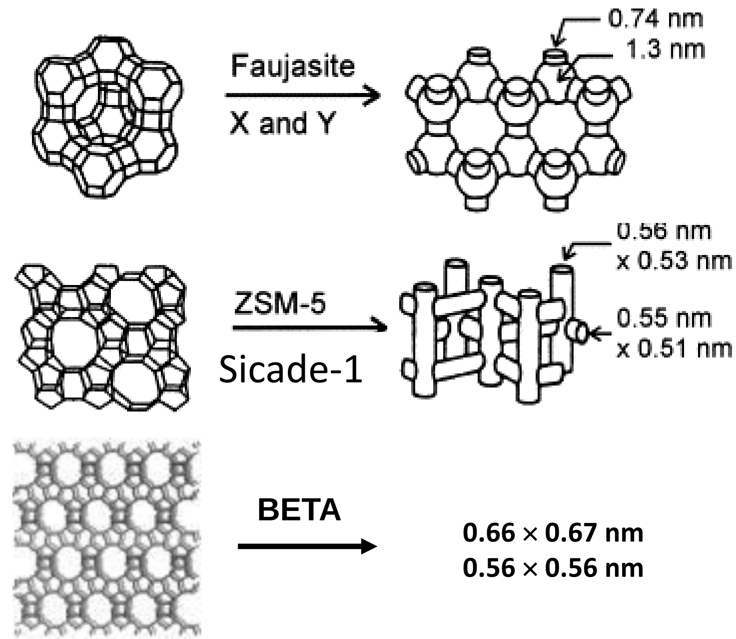
A. Simon-Masseron, C. Raynaud, V. Simon

Zeolites

(alumino)silicates



T = Si, Al



T - O - T

Structural type

FAU

MFI

***BEA**

Properties :

- Adsorption (molecular sieves, size and shape selectivities)
- Intrinsic acidity (Brönsted, Lewis)
- Ions exchange

Valorization of agricultural by-products with zeolite

Raw material as T source
(*Ex.* : rice husk/straw for Si)

Rice Straw

→ Zeolite synthesis

Precursor of molecules
(*Ex.* : pyrolysis of red pepper stems to obtain aliphatic and aromatic hydrocarbons)

→ Zeolite = acid catalyst

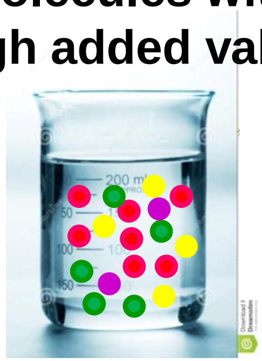
Biomass as **sources of molecules with high added value**

- - - → Zeolite = adsorbent

Recovery of molecules with high added value from vegetables

Extraction →

MIXTURE
Molecules with high added value



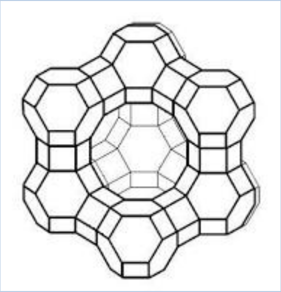
Separation →

via adsorbents
= resins

Separate molecules

→ Problem: lack of adsorbents with high adsorption and desorption performance

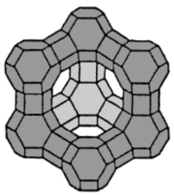
→ **Our work : zeolites as adsorbents**



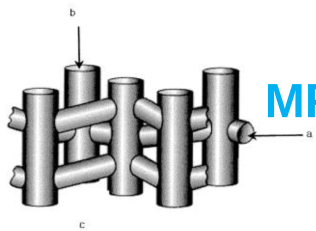
- Micropores (channels, cavities) with molecular dimensions, calibrated porosity ($\phi < 2$ nm)
- High surface area
- High thermal stability
- Ease of regeneration

Materials and methods

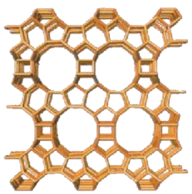
Zeolites



FAU



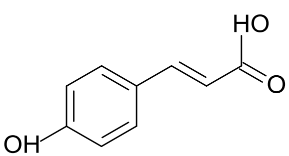
MFI



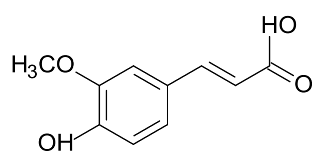
*BEA

Adsorbent	*Molar ratio Si/Al*	*BET surface (m^2/g)*	*Pore size (nm)*
USY30	14.5	749	0.74
Sicade-1	∞	400	0.51 × 0.55 0.53 × 0.56
BETA	88	659	0.66 × 0.67 0.56 × 0.56
XAD16	-	≥ 800	n.d.

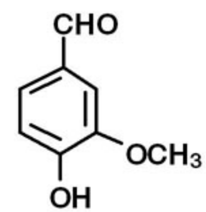
Molecules with high added value



p-coumaric acid 1.0 × 0.5 nm



ferulic acid 1.0 × 0.5 nm



vanillin 0.71 × 0.69 nm

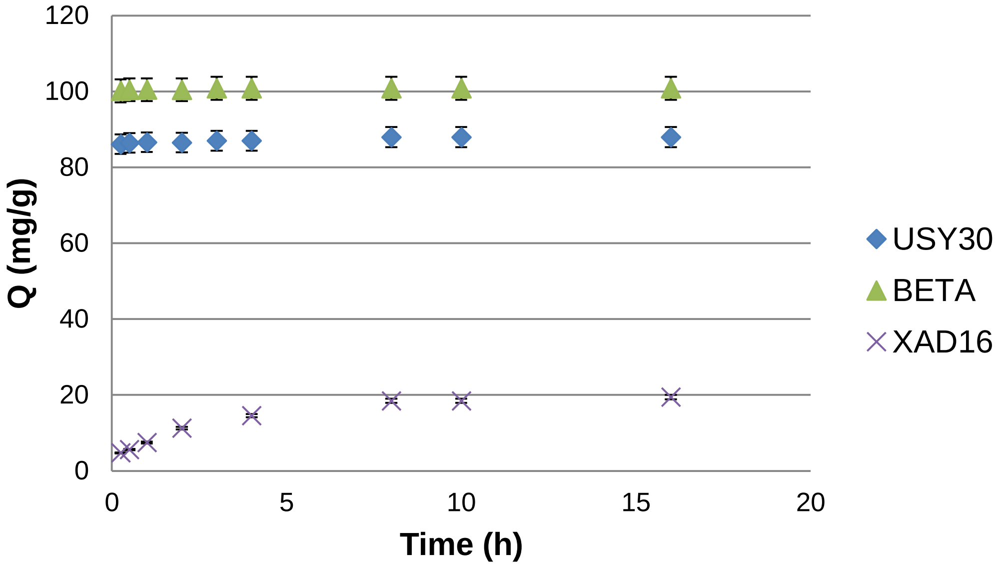
Adsorption

Aqueous synthetic solutions at 21-24°C±2.

10-200 mg adsorbent (dried at 140°C, 6h) + 10 mL solution (C_i = 10 to 500 $mg.L^{-1}$)

Kinetic adsorption curves

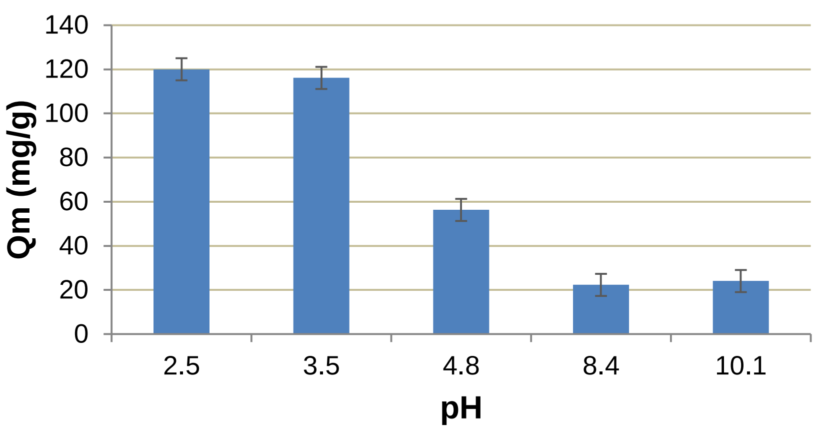
Ex. :
Ferulic acid
C_i = 200 mg.L^{-1}
m = 50 mg
pH = 3.5



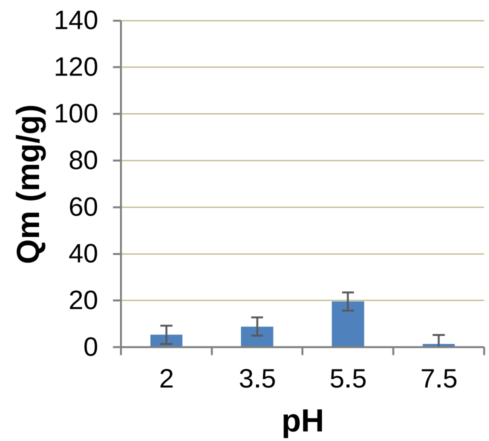
Contact time : zeolite → 2h, XAD16 → 10h

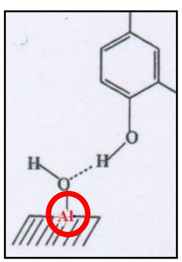
Influence of pH value

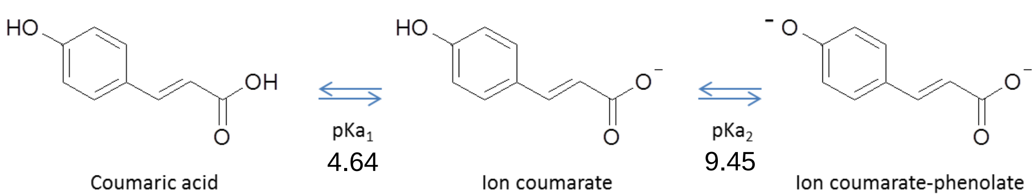
p-coumaric acid - BETA (zeolite Si/Al)



ferulic acid - Sicade-1 (Si)





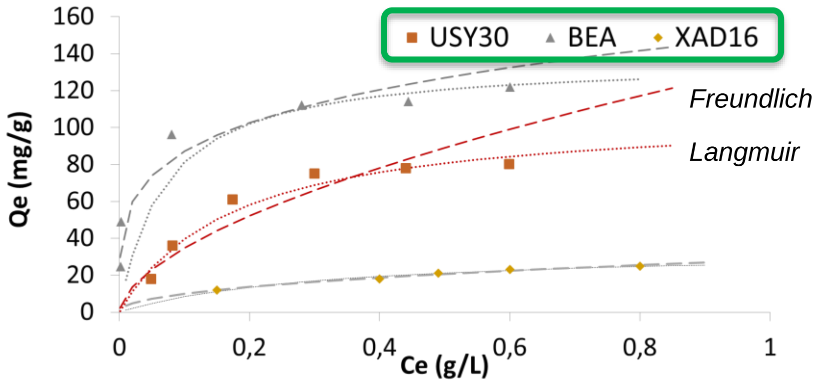


→ **pH = 3.5**

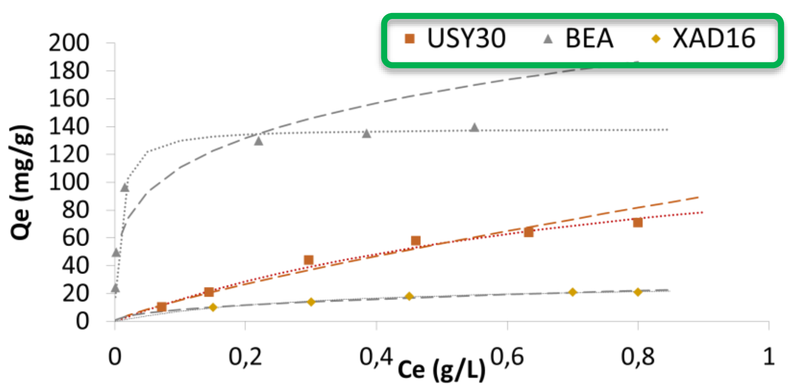
→ **pH = 5.5**

Isotherms

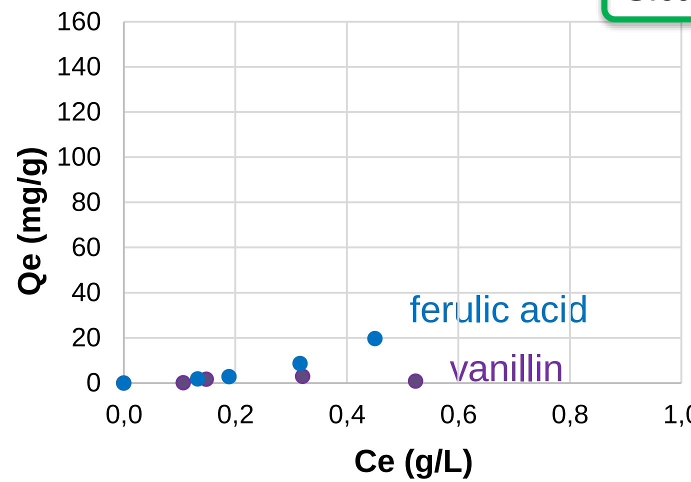
p-coumaric acid *pH = 3.5*



ferulic acid *pH = 3.5*



Sicade-1



pH = 5.5

- **Langmuir model** : better description for the adsorption
- **Amberlite XAD16** : less effective than zeolites (factor 3.5-4)
- **Maximum adsorption capacities** :

  ferulic acid

  139 mg.g^{-1} BETA *29 mg.g^{-1}* XAD16

  p-coumaric acid

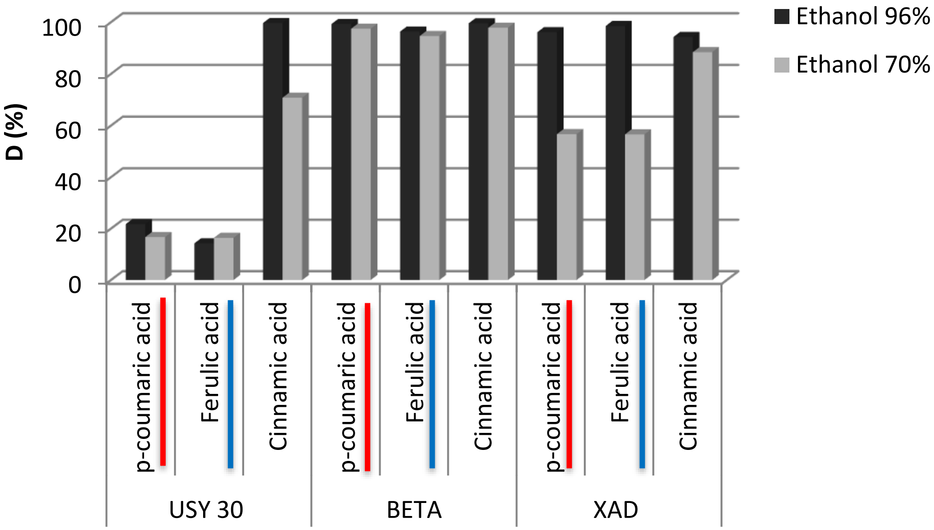
  122 mg.g^{-1} BETA *34 mg.g^{-1}* XAD16

Desorption - regeneration

DESORPTION

Solid dried at 60°C-24h, + 2mL desorbing solvent/50mg zeolite)

Mixture : 60°C-3h-1300 rpm



⇨ Ethanol 96% > ethanol 70%

⇨ USY30 → D = 10-20 %

⇨ BETA → D ~ 100 %

REGENERATION

Decrease of adsorption capacity for the second use (%)

	***p*-coumaric acid**	**ferulic acid**
USY30	13	14
BETA*	21	23
BETA**	7	9
XAD16	0	11

Zeolite dried at * 140°C and ** 200°C before the second adsorption

⇨ Loss of zeolite efficiency

Application to vegetable extracts

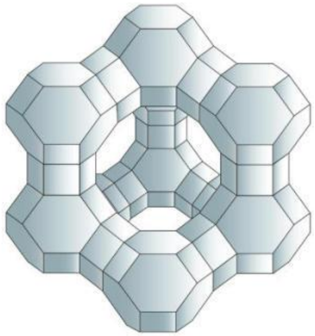
Hemp wood

Adsorption rates (%) (contact time 2h)

		p-coumaric acid	ferulic acid
Hemp wood extract (microwave) *p*-coumaric : ~ 20 mg.L^{-1} ferulic acid: < LOQ	USY30	68 ± 6	n.d.
	BETA	**94 ± 6**	n.d.
	XAD16	8 ± 3	n.d.
Hemp wood extract (twin screw) *p*-coumaric : ~ 30 mg.L^{-1} ferulic acid: < LOQ	USY30	63 ± 5	n.d.
	BETA	**92 ± 4**	n.d.
	XAD16	n.d.	n.d.
Synthetic solution at 200 mg.L^{-1}	USY30	51 ± 3	n.d.
	BETA	**94 ± 5**	n.d.
	XAD16	6 ± 1	n.d.

- ⇨ Presence of other phenolic compounds : does not seem to affect the adsorption of *p*-coumaric acid
- ⇨ Adsorption rates (hemp extracts) equivalent to those obtained from synthetic solution.

Conclusion



USY30 (FAU) and BETA (*BEA) zeolites / XAD16 :
➪ better adsorption capacities for *p*-coumaric and ferulic acids
➪ faster adsorption

- Adsorption capacity = f(pH) pH < pKa_1
- Maximum adsorption capacities : BETA 139 $mg.g^{-1}$ ferulic acid
  122 $mg.g^{-1}$ *p*-coumaric acid

- Desorption (BETA) : close to 100% with ethanol 96%

↳ New application of zeolites as adsorbents for high added value molecules (ferulic and *p*-coumaric acids) detected in the plant extracts