Coupling ultrasound treatment and adsorption on activated carbon for the removal of micropollutants from water

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Context

- Micropollutant : « Product released by human, mineral or organic, may be toxic at tiny concentration (from ng/L to µg/L) »

- Activated carbon adsorption and ultrafiltration used for tertiary treatment of Waste Water Treatment Plant (WWTP): [Margot et al., Sci Total Environ, 461-462, 2013]

- In waste water, the presence of Organic Matter may hinder and slow the adsorption process, long kinetics are related to the fabric or granulated activated carbons textures

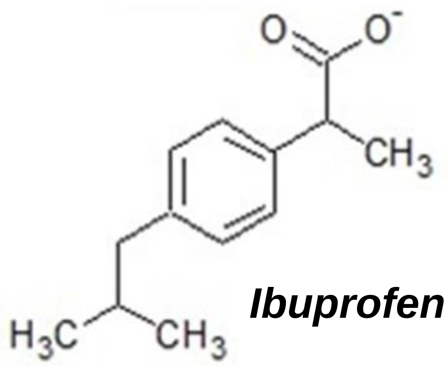
- Ultrasound irradiation known to :
  - generate more hydroxyl radicals at higher frequency (300 kHz)
  - involve more mechanical effects (cavitation) enhancing the mass transfer at lower frequency (20 kHz, 40 kHz)

[O. Hamdaoui et al…, C. Pétrier, Ultrason. Sonochem. 10 (2003) 109–114]

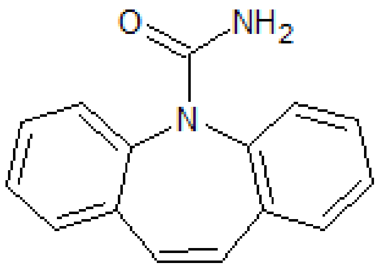
Objectives

- Accelerate the adsorption kinetics of a micropollutant through ultrasound irradiation coupled to adsorption
- Understand the effect of ultrasound irradiation mechanical effects on the adsorption phenomena
- Simulate the adsorption kinetics in macroporous carbon by diffusion models

Models of micropollutants



Ibuprofen



Carbamazepine

Buffered solution (KH_2PO_4/Na_2HPO_4) 0.04 M
(pH = 7.5, close to the one of waste water)

Adsorption kinetics studies

Initial conditions :

- pH=7,5 phosphate buffer (KH_2PO_4/Na_2HPO_4) 0.04 M
  T=25°C
- Ibuprofen C_0= 4 ppm ; V= 250 mL, 500 mL
  Disk of fabric or braids or fibers (12 mg)
- Carbamazepine C_0= 20 ppm ; V= 1L
  Disk of fabric or granulated or powdered AC (20 mg)

Ultrasound Reactor (Cup-horn)

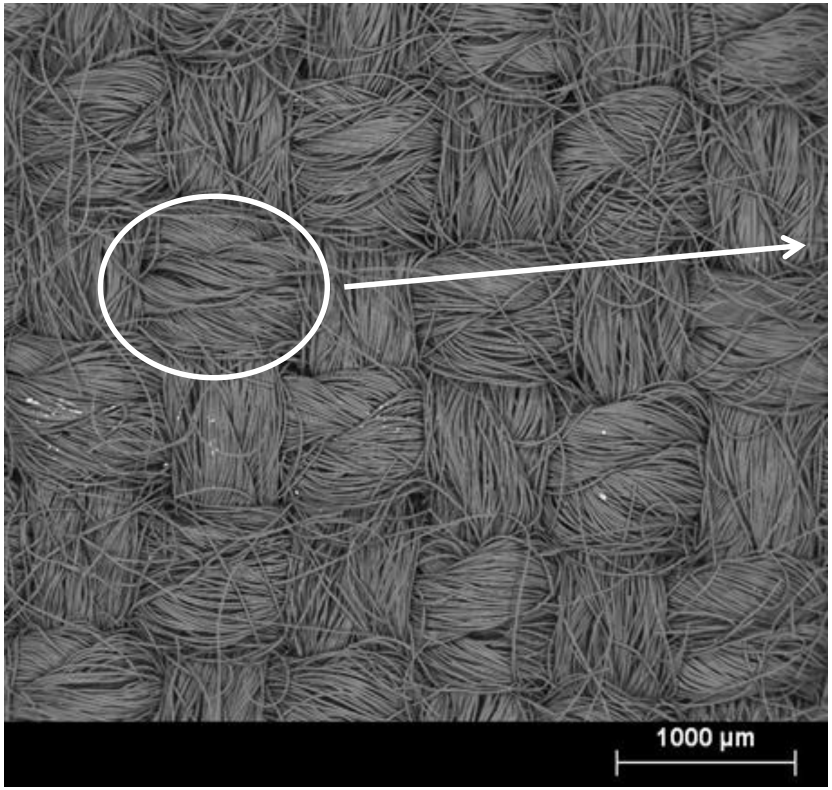
Different agitation modes :

- Orbital agitation 250 round/min
- Reactor with ultrasonic probe, 20 kHz (50% Amplitude, ~86 W/L)
- Ultrasonic bath, 40 kHz (~10 W/L) + adsorbent or not

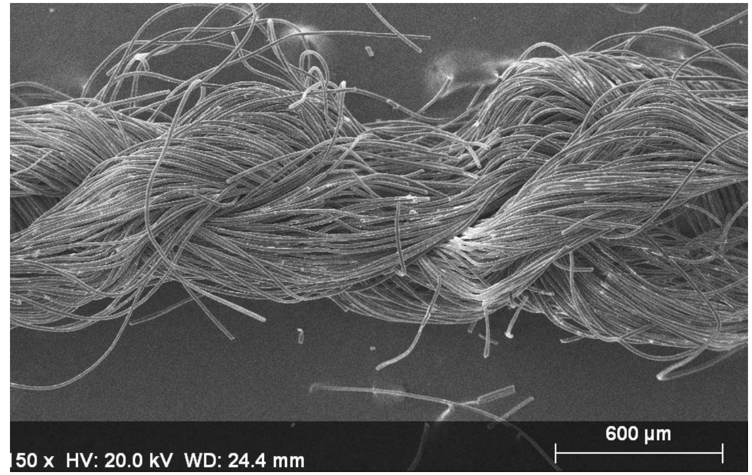
Waste water medium:

- Dissolved Organic Matter (Humic Acid)

Activated carbon fabric

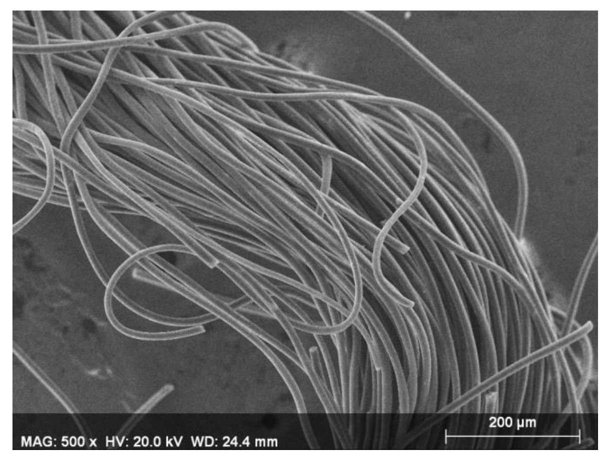


KIP1200 Fabric (Dacarb, France)



Yarn
Ø=295 µm

<u>Braid</u> (Ø=750 µm) formed of 3 yarns

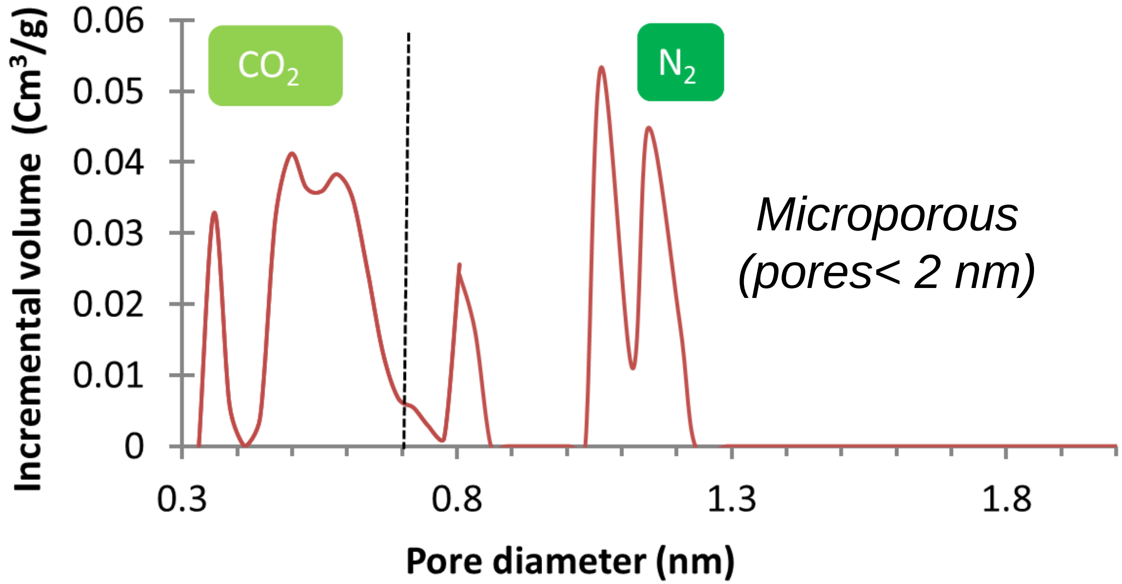


The yarns are formed of carbon fibres Ø=12 µm

Activated carbon fabric

Pore size distribution by gas adsorption

S_{BET} = 1560 m²/g
Vµp = 0.54 cm³/g



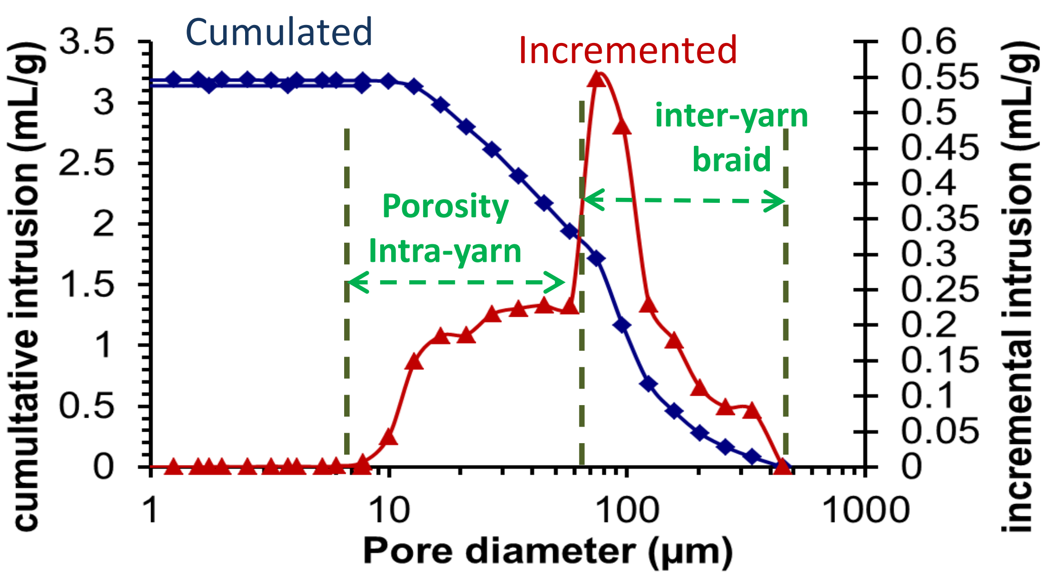
Pore size distribution of fabric by mercury porosimetry

- **Intra-yarn porosity**
[0.8-60] µm
V = 1,24 cm³/g

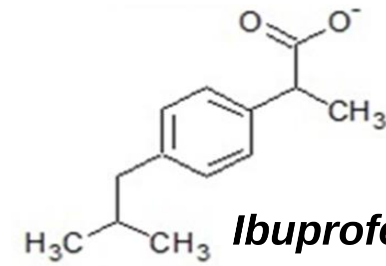
- **Braid porosity (inter-yarn & inter-braid) [60- 450] µm**
V = 1,94 cm³/g

- **Fibre Density 0,76 cm³/g**

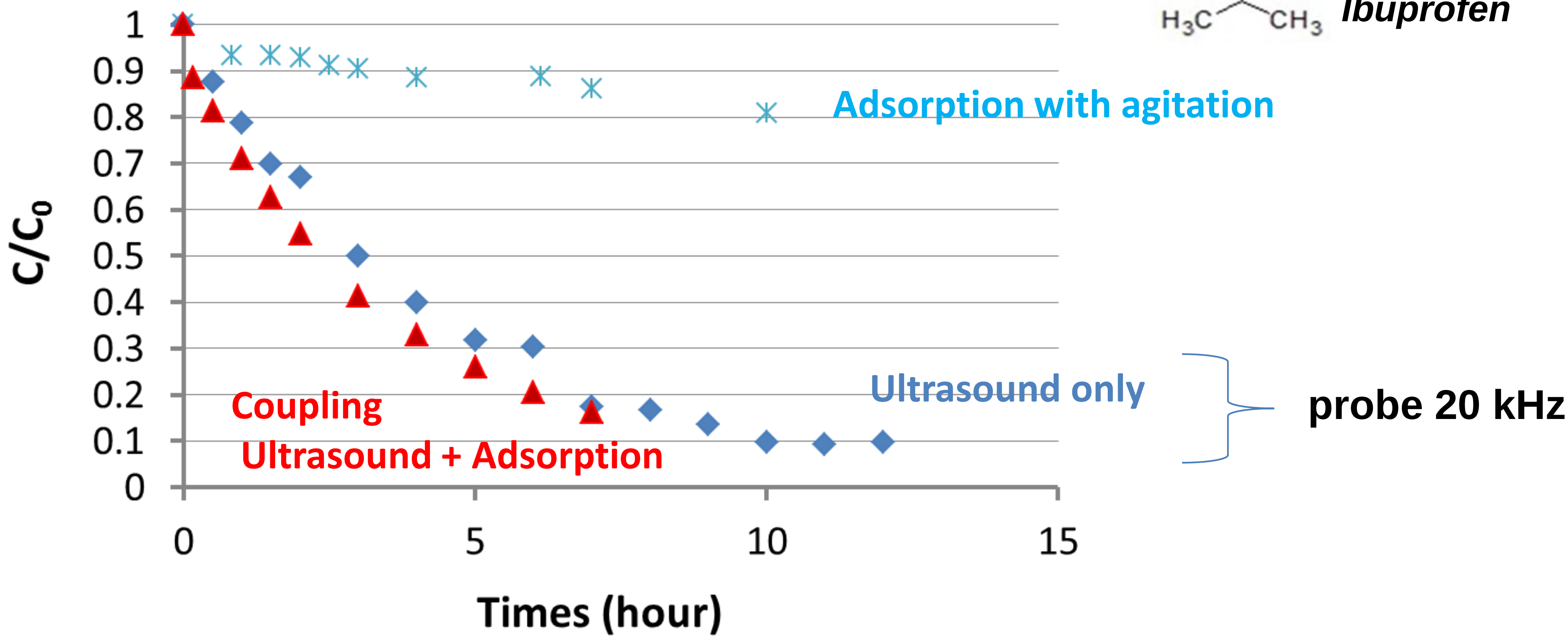
- **Apparent Density 0,22 cm³/g**



Effect of ultrasound (probe 20 kHz, power 86 W/L) on fabric adsorption



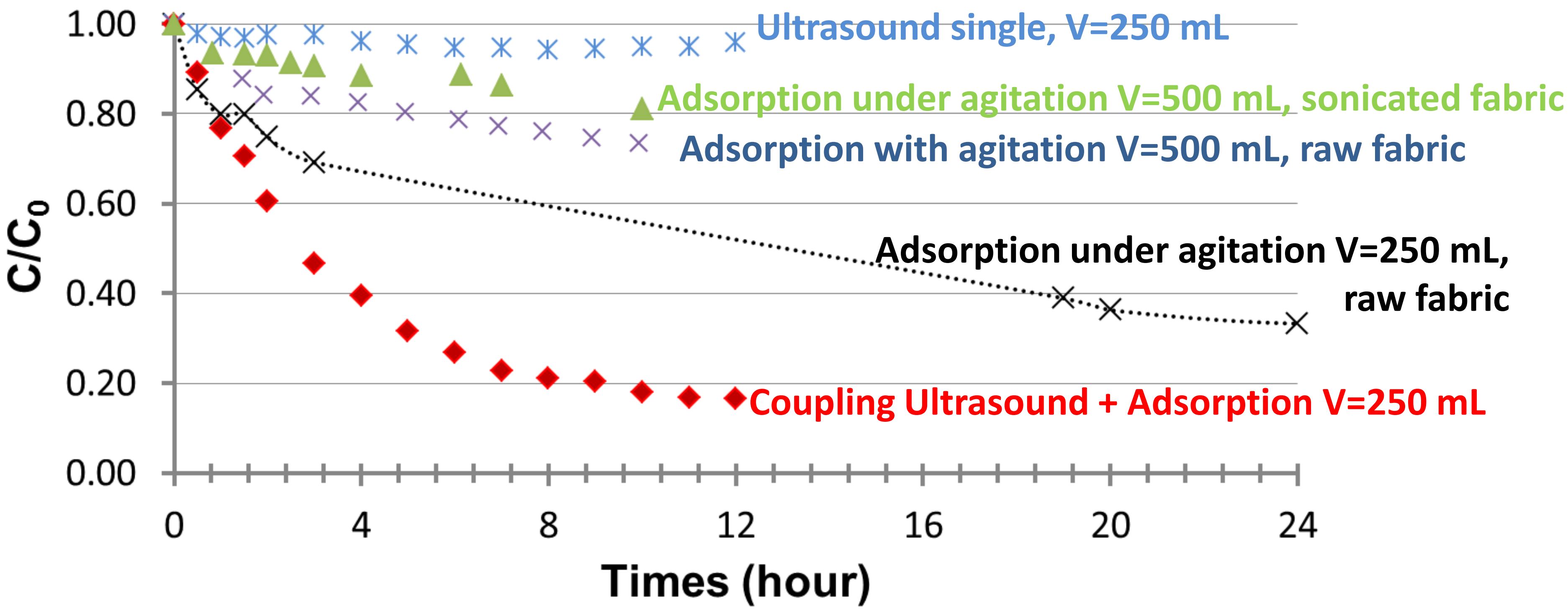
Ibuprofen



pH = 7.34 ; T = 24±2°C ; C_0 = 4 ppm ; Disk of fabric m_{Fabric} = 12 mg ; $V_{Solution}$ = 500 mL

Degradation of Ibuprofen by the OH° radicals from the water sonolysis obtained by the ultrasonic probe (20 kHz)

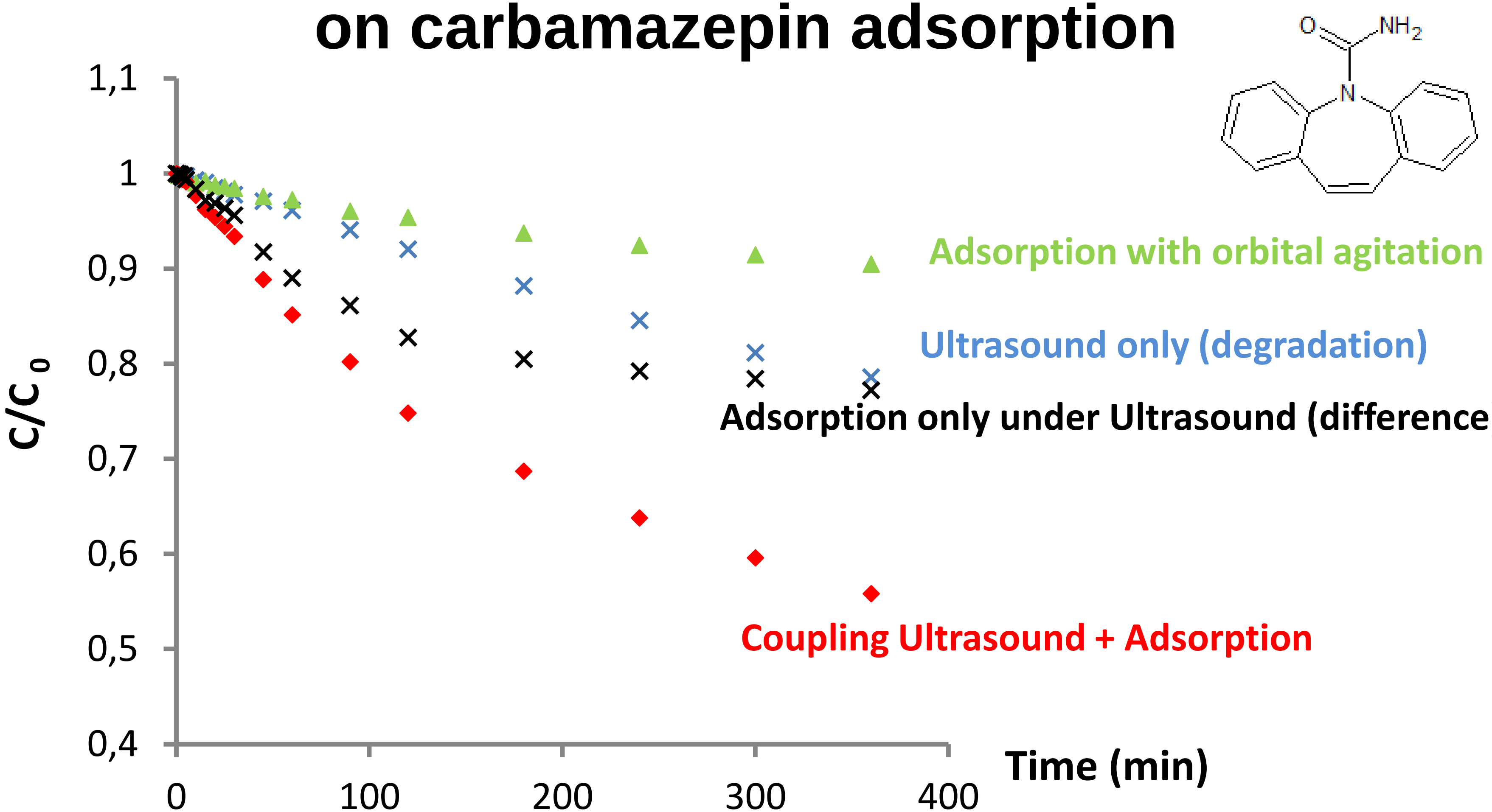
Effect of ultrasound (bath 40 kHz, power 10 W/L) on ibuprofen adsorption



pH = 7.34 ; T = 24±2°C ; C_0 = 4 ppm ; m_{Fabric} = 12 mg

- Absence of ibuprofen degradation in the ultrasonic bath
- Acceleration of the adsorption kinetics in the presence of ultrasound

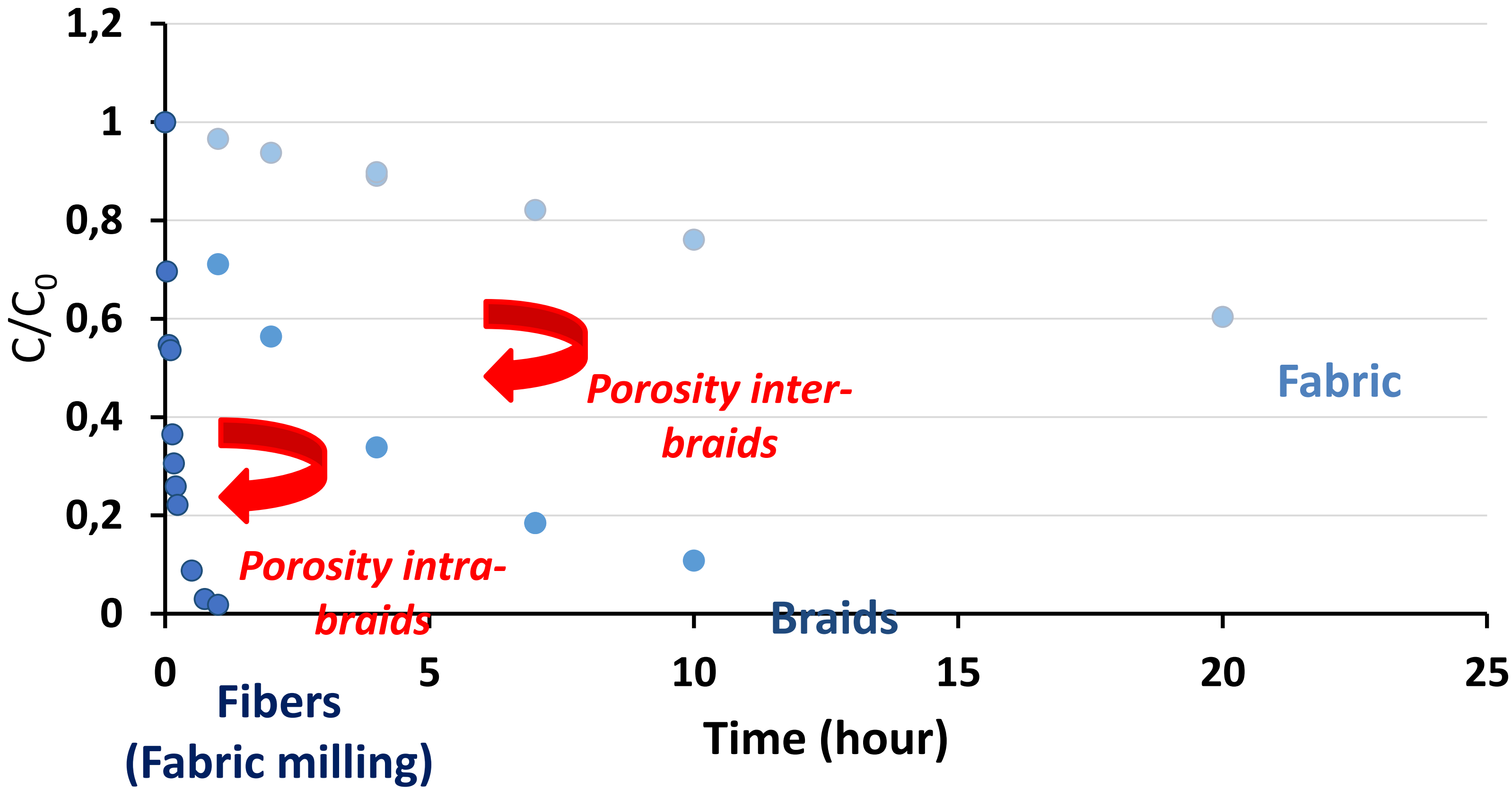
Effect of ultrasound (bath 38 kHz , power 12 W/L) on carbamazepin adsorption



pH = 7.4 ; T = 25±2°C ; C_0 = 20 ppm ; m_{Fabric} = 20 mg

- Degradation of carbamazepin in the ultrasonic bath (12 W/L acoustic power)
- Acceleration of the adsorption kinetics in the presence of ultrasound (40 kHz)

Ibuprofen adsorption under agitation various texture



[IBP] = 4 ppm, T = 25°C, m_{Tissu} = 12 mg, V=250mL, pH = 7,4

Different macroporosities limit the adsorption kinetics

The mass transfer is limited by :

- the intra-yarn diffusion for adsorption on fabric or braids
- the intra-fiber diffusion for adsorption on fibers

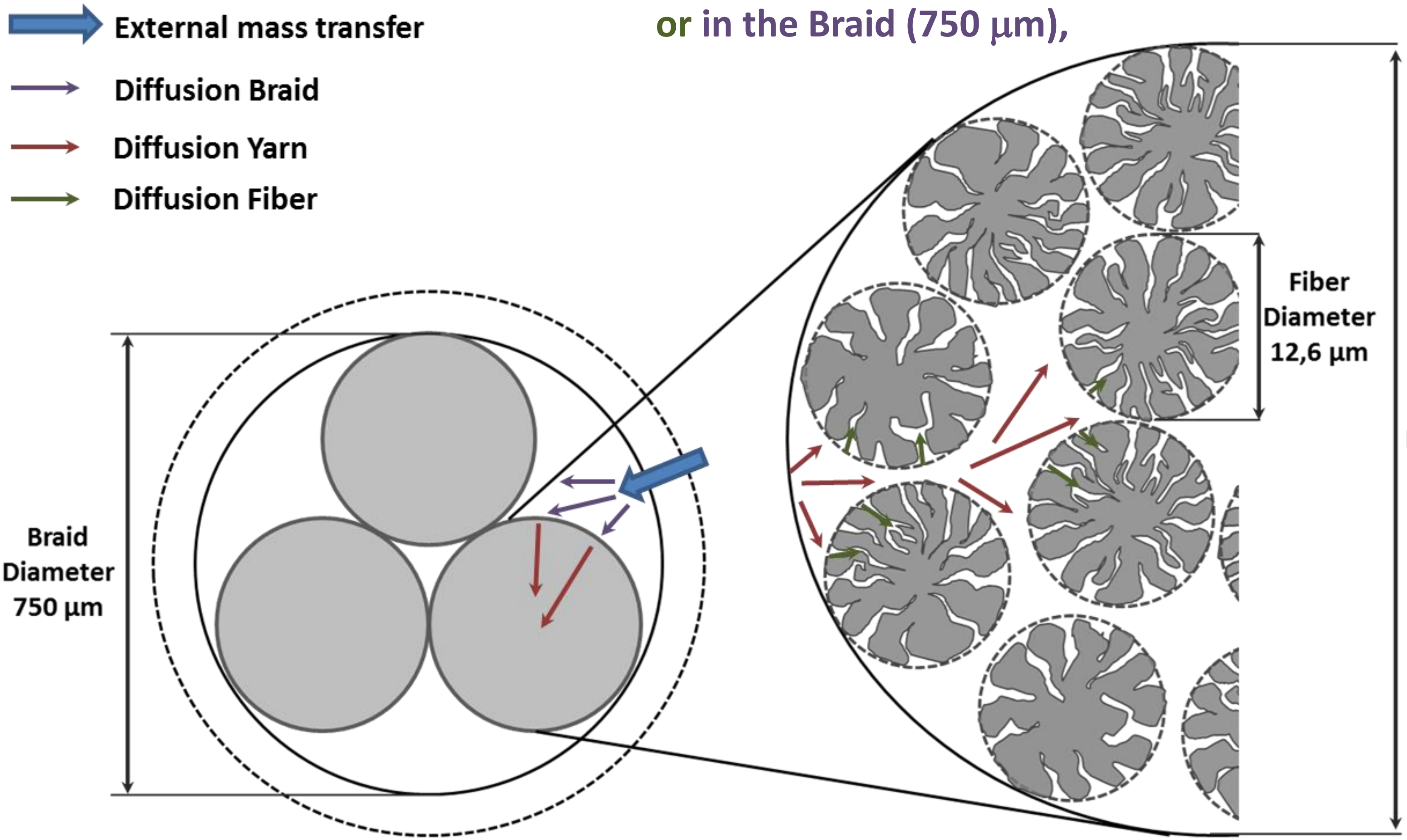
The kinetics acceleration by ultrasound treatment is not observed on powder

Volumic diffusion model in the pores : braids or yarns or fibers

3 models with limited transfer : exclusively in the Fiber (12.5 µm)

or in the yarn (295 µm)

or in the Braid (750 µm),



Volumic pore diffusion model : braids or yarns or fibers

- External mass transfer at external surface of the carbon cloth :

$$V\frac{dC_a}{dt} = -mSk_l\left(C_a - C_{Ar}\Big|_{r=R}\right)$$

k_l external transfer coefficient
Ca concentration in liquid phase
$C_{Ar}|_{r=R}$ concentration in the pore at r value

- **Mass balance into a braid (yarn or fibre) :**

$$\varepsilon_P\frac{\partial C_{Ar}}{\partial t} + \rho_P\frac{\partial q}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left[r\left(D_{ep}\frac{\partial C_{Ar}}{\partial r}\right)\right]$$

q : adsorbed amount
ρ_P: apparent volumic mass
ε_P: porosity ratio
D_{ep}: diffusion coefficient

– **Boundary conditions (Braids) :**

$$\left.\frac{\partial C_{Ar}}{\partial r}\right|_{r=0} = 0 \qquad D_{ep}\left.\frac{\partial C_{Ar}}{\partial r}\right|_{r=R} = k_l\left(C_a - C_{Ar}\Big|_{r=R}\right)$$

– **Boundary conditions (Yarns or fibers) :**

$$\left.\frac{\partial C_{Ar}}{\partial r}\right|_{r=0} = 0 \qquad C_{Ar=R} = C_\varepsilon$$

Mass balance to calculate C_ε

$$\frac{m\varepsilon}{\rho_{app}}\frac{\partial C_\varepsilon}{\partial t} = S_{ext}k_l(C_a - C_\varepsilon) - S_{ref}D_{ep}\left.\frac{\partial C_{Ar}}{\partial r}\right|_{r=R}$$

– **Initial conditions** :

$$t = 0\,;\ C_A = C_{A0} \qquad t = 0\,;\ q_r = 0\ \forall\, r \qquad t = 0\,;\ C_{Ar} = 0\ \forall\, r$$

[Leyva Ramos et al., Carbon, 2280-89, 2007]

Simulation of the ibuprofen adsorption kinetics

- **Equilibrium law** Langmuir-Freundlich

$$q = \frac{q_{max}(kC)^n}{1+(kC)^n}$$

- **Coefficient of external transfer**

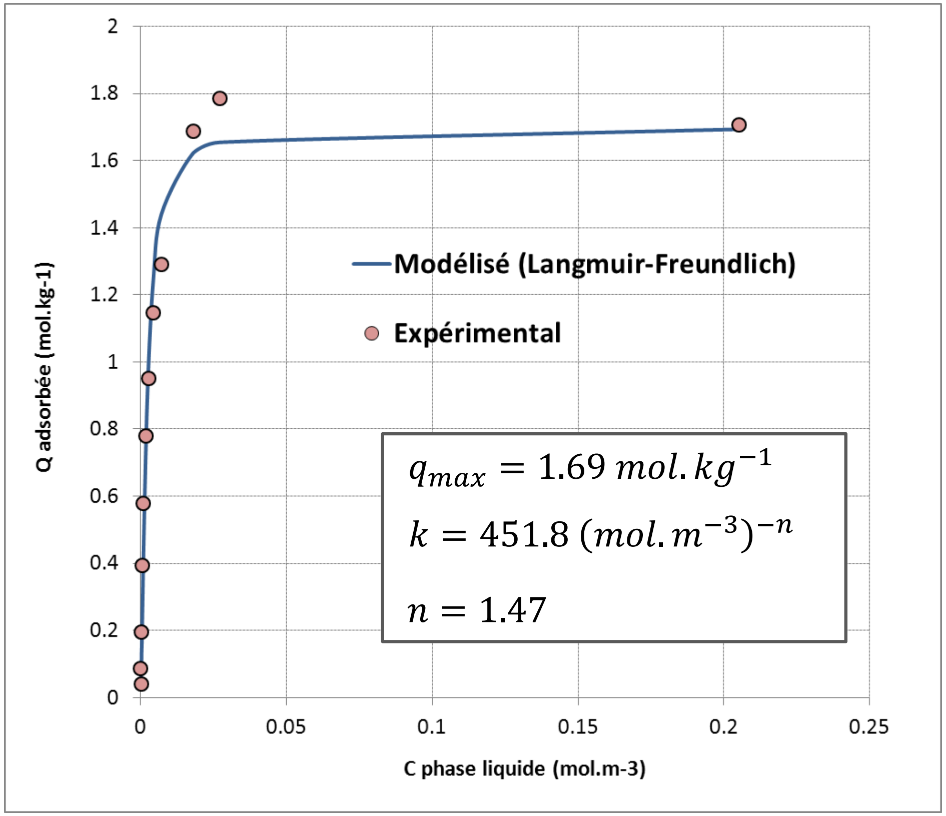
$$\left[\frac{d(C_A/C_{A0})}{dt}\right]_{t=0} = -\frac{mSk_l}{V}$$

- **Coefficient of diffusion**
  - **Molecular (Wilke-Chang correlation)**

$$D_m = 7{,}4.10^{-8}\frac{(\varphi M_b)^{1/2}T}{\eta_B {V_A}^{0{,}6}}$$

  - **Effective**

$$D_{eff} = \frac{\varepsilon_P}{\tau} D_m K_R K_P$$



τ: tortuosity

$$\begin{cases} K_p = (1-\lambda)^2 \\ K_R = (1 - 2.104\lambda + 2.09\lambda^3 - 0.95\lambda^5) \end{cases}$$

$$\lambda = \frac{d_m}{d_f} < 0{,}4$$

d_m: molecule diameter (adsorbate)
d_f: pore diameter

Model of volumic diffusion

Hypothesis :

- Equilibrium type : Langmuir-Freundlich

- Instantaneous adsorption at equilibrium

-1 radial dimension

1/ Limiting phenomena : diffusion in **the braid**

2/ Limiting phenomena : diffusion in **the yarn**

3/ Limiting phenomena : diffusion in the **fibre**

+ Homogeneous concentration in the yarn porosity

Object	Øpore	λ	D_{eff}	t_{diff}
	m	-	$m^2.s^{-1}$	s
Fiber (micropore)	1.4×10^{-9}	3.3×10^{-1}	1.6×10^{-11}	10
Yarn (porosity inter-fibre)	0.8×10^{-6} 60×10^{-6}	5.9×10^{-4} 9.9×10^{-6}	1.0×10^{-10} 1.6×10^{-10}	547
Braid	60×10^{-6}	7.9×10^{-6}	1.8×10^{-10}	3046

Calculated Coeff. Dm = 4.26×10^{-10} $m^2.s^{-1}$

Tortuosity (fibre and yarn) : 2

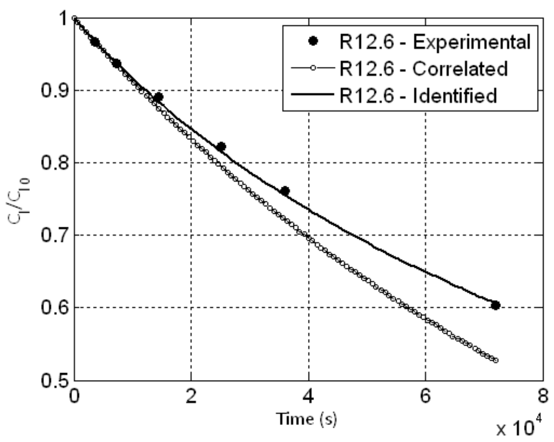
Calculation of the typical diffusion time :

L : lenght (diameter of the object)

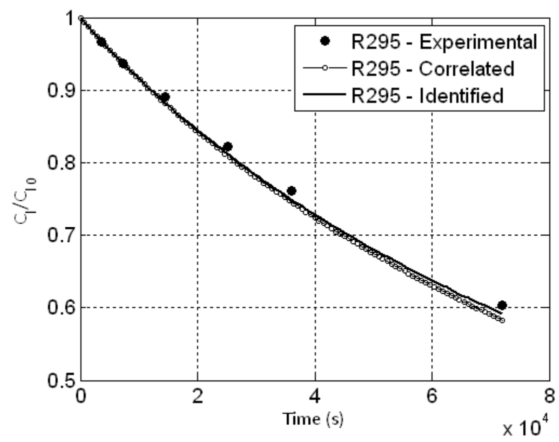
$$t_{diff} = \frac{L^2}{D_{eff}}$$

Fabric kinetics : fibre or yarn or braid diffusion?

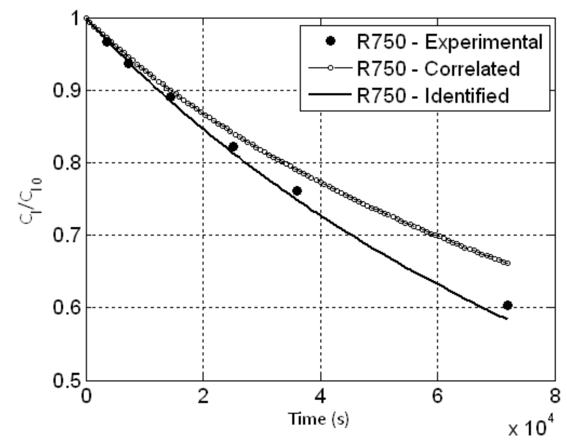
Diffusion in **the fibre**



Diffusion in **the yarn**



Diffusion in **the braid**



C_0=4 ppm /12.5mg CA/250 mL reactor

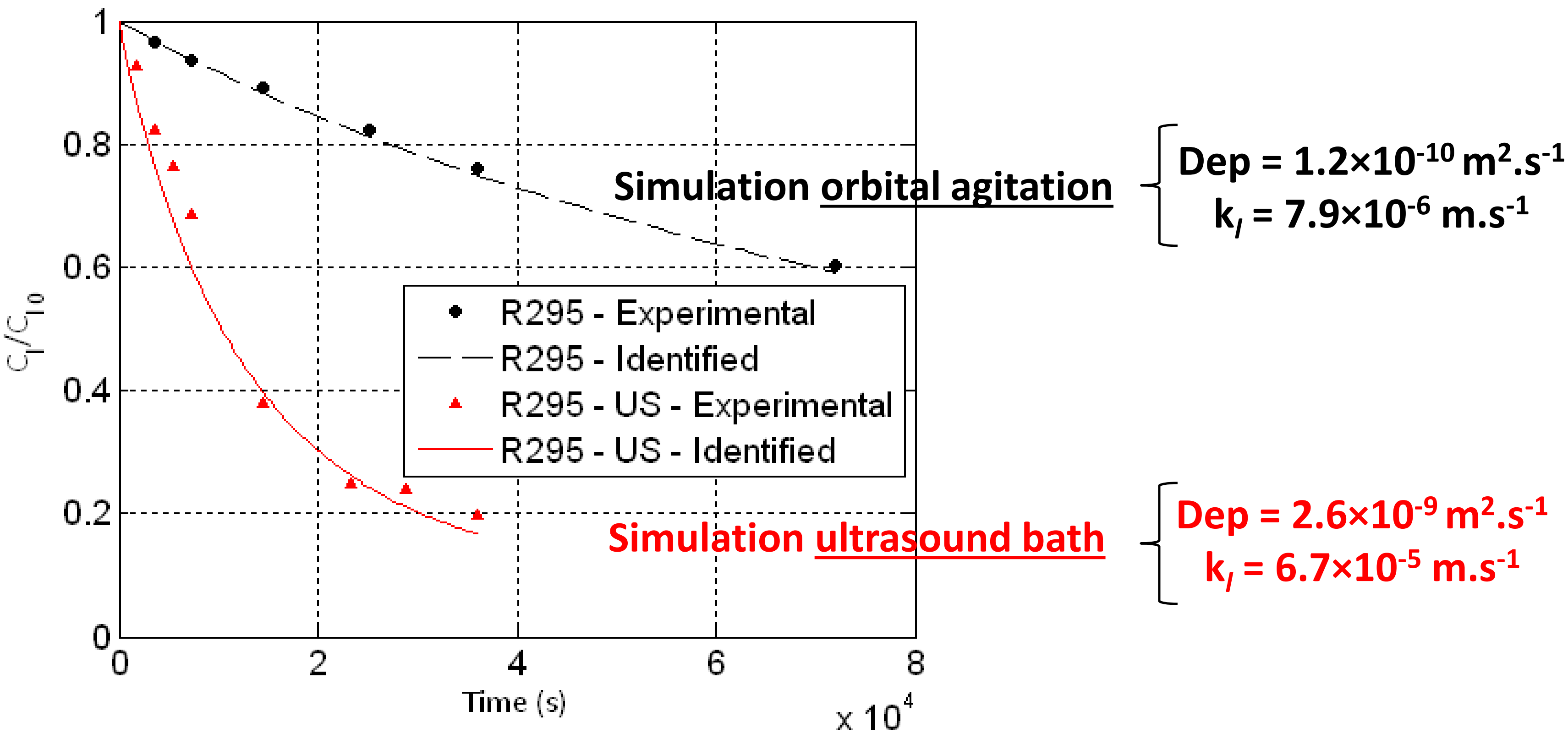
Ø ref.	k_l Coeff. ext. transfer	Biot matter	D_{ep} fitted	D_{eff} Calculated
µm	$m.s^{-1}$	-	$m^2.s^{-1}$	$m^2.s^{-1}$
12.6	7.9×10^{-6}	165	3.0×10^{-14}	1.6×10^{-11}
295	7.9×10^{-6}	9.7	1.2×10^{-10}	1.6×10^{-10}
750	7.9×10^{-6}	3.8	7.8×10^{-10}	1.8×10^{-10}

Best agreement identified Dep – calculated Deff
The model of diffusion in the yarn makes sense

$Biot=k_l \times L/Dep$

[M. Ondarts, et al..., L. Duclaux, Chemical Engineering Journal 343 (2018) 163–172]

Adsorption in fabric modelled by the diffusion in yarn, effect of ultrasound



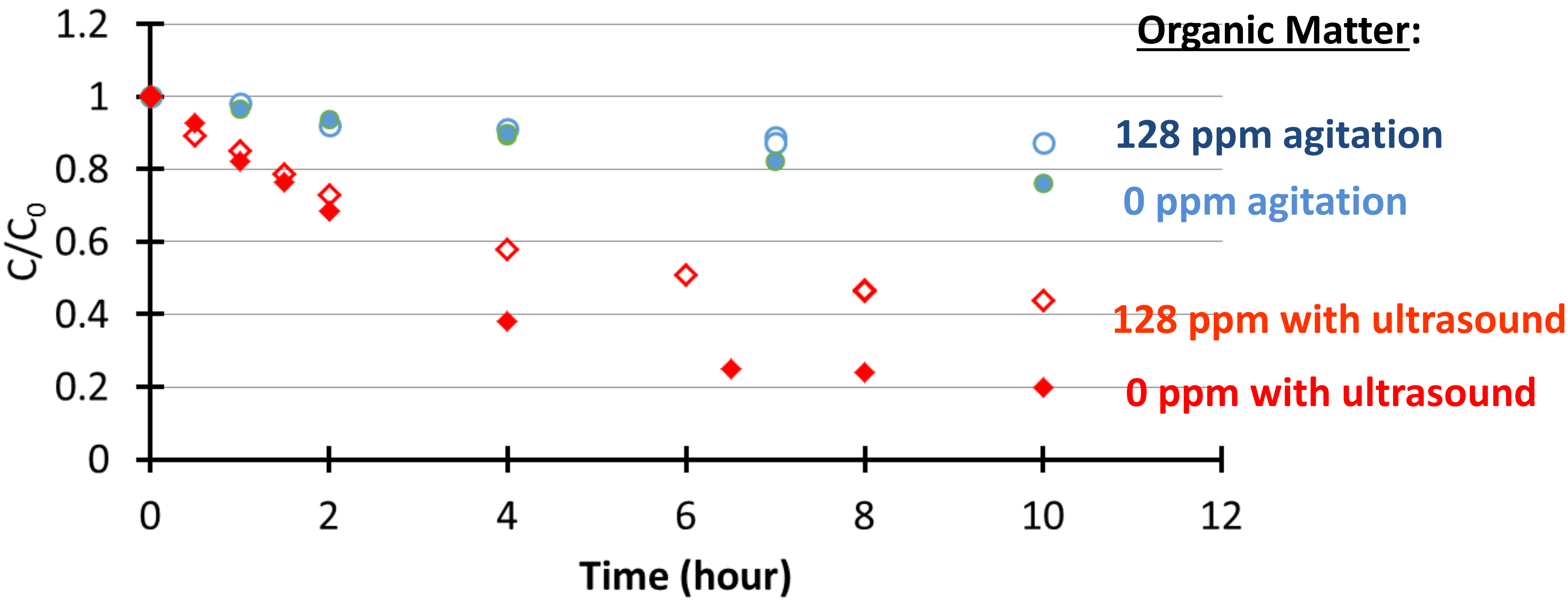
V=250 mL, pH = 7.34 ; T = 24±2°C ; C_0 = 4.4 ppm ; m_{Fabric} = 12 mg

The ultrasounds increase both external transfer and the diffusion within the yarn, **value higher than for the diffusion in a liquid,** effect of cavitation?

Coeff. Dm liquid = 4.26×10^{-10} $m^2.s^{-1}$

[M. Ondarts et al..., L. Duclaux Chemical Engineering Journal 343 (2018) 163–172]

Effect of the ultrasounds (38 kHz bath) on the ibuprofen adsorption kinetics on fabric in presence of organic matter (OM, TOC=40 ppm)



pH = 7.34 ; T = 24±2°C ; C_0 = 4 ppm ; V=250 mL, m_{Fabric} = 12.5 mg

The presence of organic matters slows the adsorption kinetics but the ultrasonic irradiation still accelerates the kinetics compared to agitation in presence or not of organic matter

Conclusion

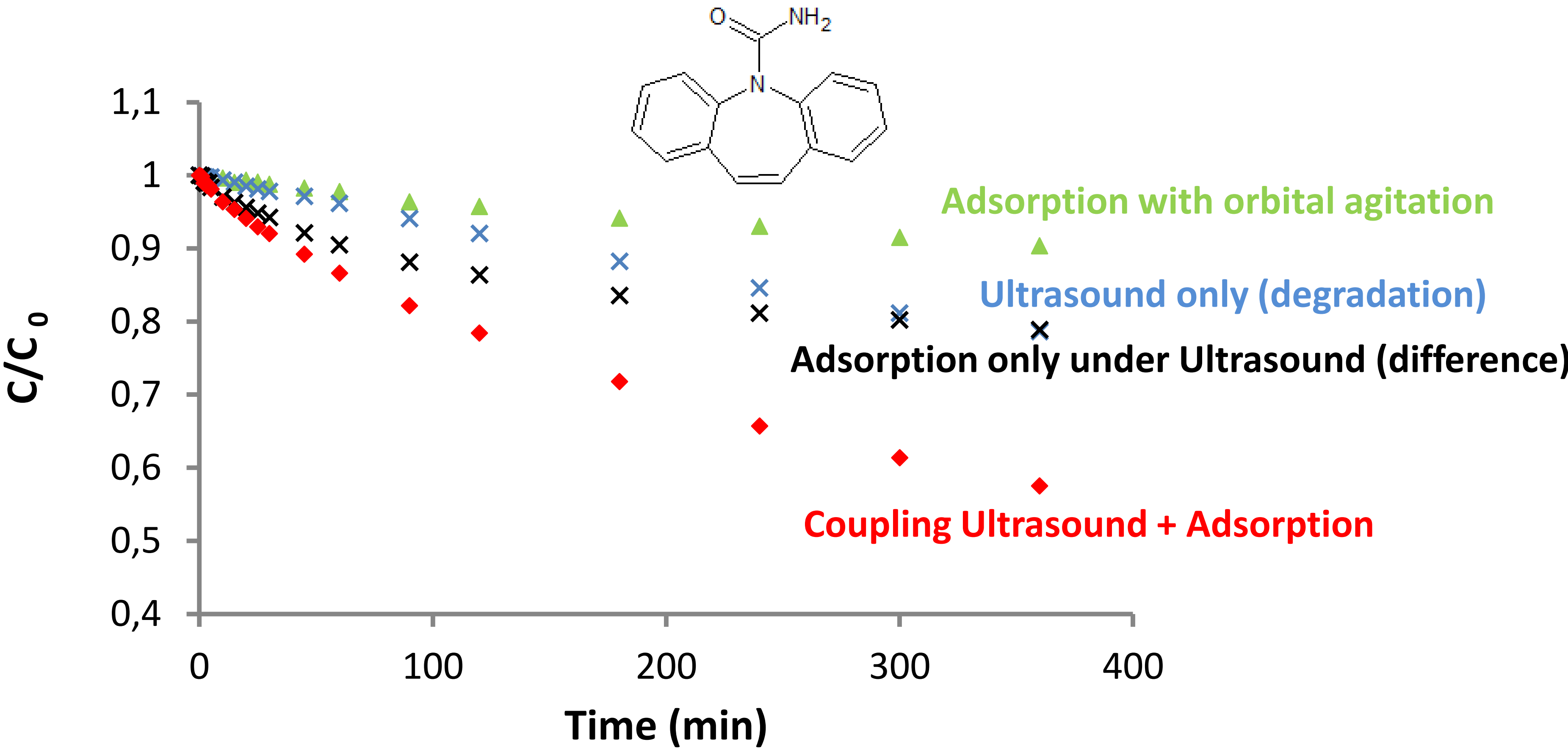
- The ultrasounds of low frequency can induce a degradation of the ibuprofen and carbamazepin by the OH° radicals produced by the water sonolysis .

- The ultrasounds of low frequency and low power (ultrasonic tub) allows the speeding of the diffusion kinetics in macroporous carbon (fabric or granulated AC).

- Kinetics slowdown due to organic matter (OM) competition can be override by ultrasounds treatment.

- Prospect : determination of the self-diffusion coefficients by inelastic neutron scattering.

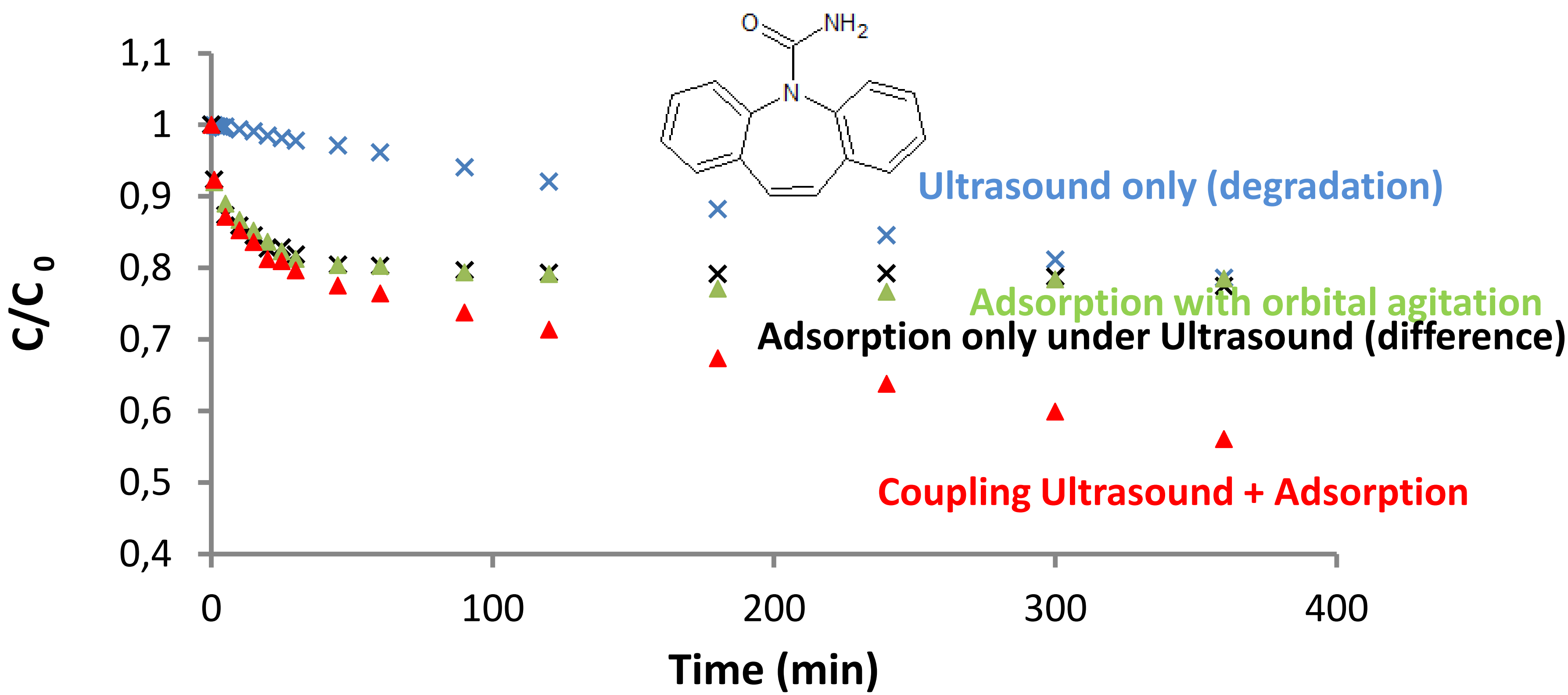
Effect of ultrasound (bath 40 kHz) on carbamazepine adsorption on granulated AC



pH = 7.4 ; T = 25±2°C ; C_0 = 20 ppm ; m_{Fabric} = 20 mg

- Degradation of carbamazepin in the ultrasonic bath (12 W/L acoustic power)
- Acceleration of the adsorption kinetics in the presence of ultrasound (40 kHz)

Effect of ultrasound (bath 38 kHz) on carbamazepin adsorption on powdered AC



pH = 7.4 ; T = 25±2°C ; C_0 = 20 ppm ; m_{Fabric} = 20 mg

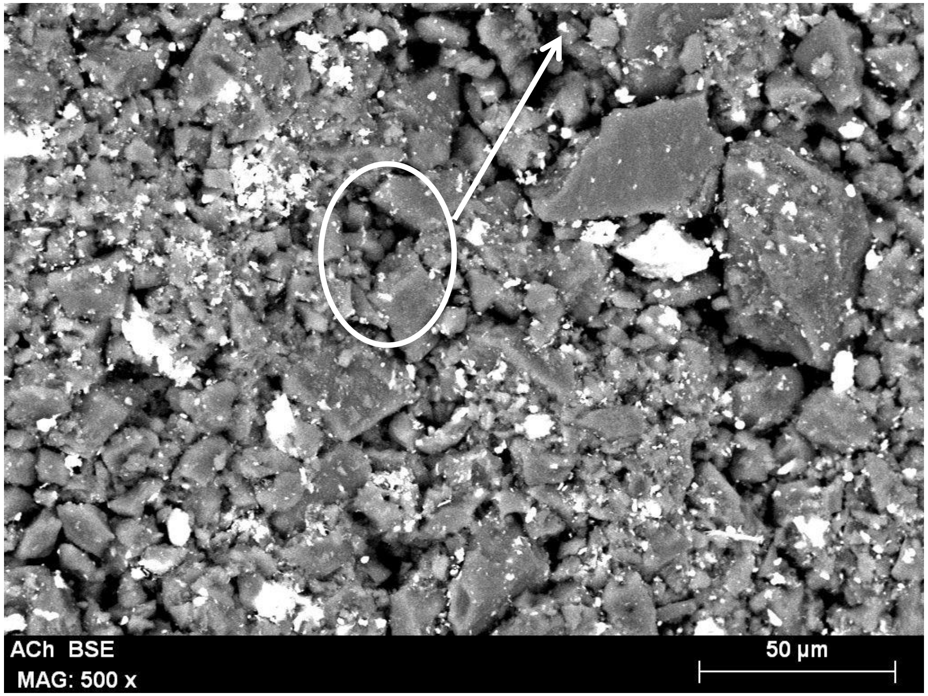
- Adsorption kinetics is similar in silent conditions (orbital agitation) and in the presence of ultrasound (38 kHz)

Structural parameters of the activated carbon fabric

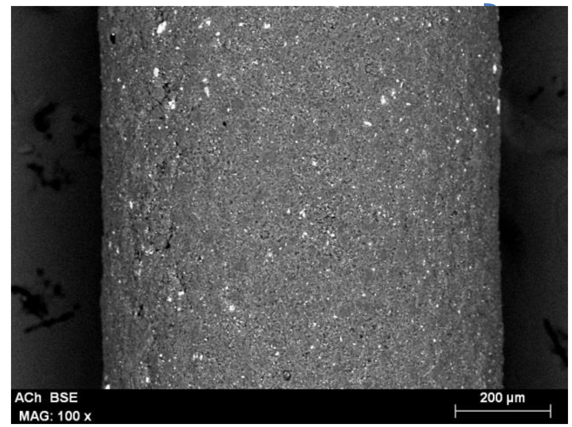
Parameter	d µm	R_{pore} m	Total Porous volume V_{μ} $mL.g^{-1}$	ρ_{app} $kg.m^{-3}$	ρ_s Squeleton density $kg.m^{-3}$	Porosity in which diffusion occur ε
Fiber	12.5	$1.4.10^{-9}$	V_{micro}=0.54	760	1289	0.41
Yarn	295	$0.8 – 60.10^{-6}$	$1.54(V_{micro})+ 1.24(V_{macro})$	391	1289	0.485
Braid	750	60.10^{-6}	$1.54(V_{micro})+ 1.24(V_{macro})$	391	1289	0.485

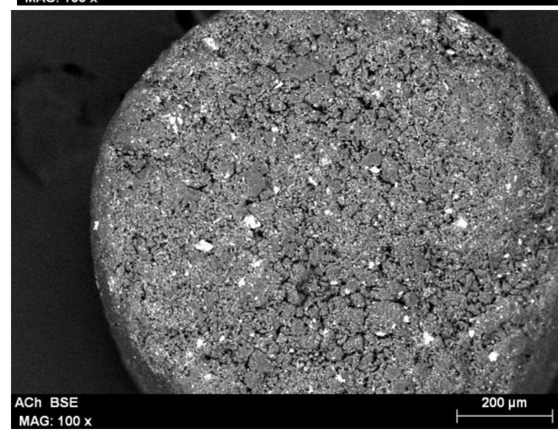
Granulated activated carbon

Presence of macropores



Granulated AC (from China)
Mean particle size : 3 µm





Cylindrical form Ø=915 µm
lenght=3.5 mm

Structural characteristics of the different elements of Extruded: particles, and grain (made of agglomeration of particles)

	d	R_{pore}	V_p	ρ_p	ρ_{sk}	ε_p
unity	(µm)	(m)	($mL.g^{-1}$)	($kg.m^{-3}$)	($kg.m^{-3}$)	(v/v)
Particles	3$	$<2\times10^{-9}$*	0.39#	1155	2100*	0.45
Grain	915*	$0.2\times10^{-6}<$ $<2.5\times10^{-6}$	0.59	894*	1880*	0.53

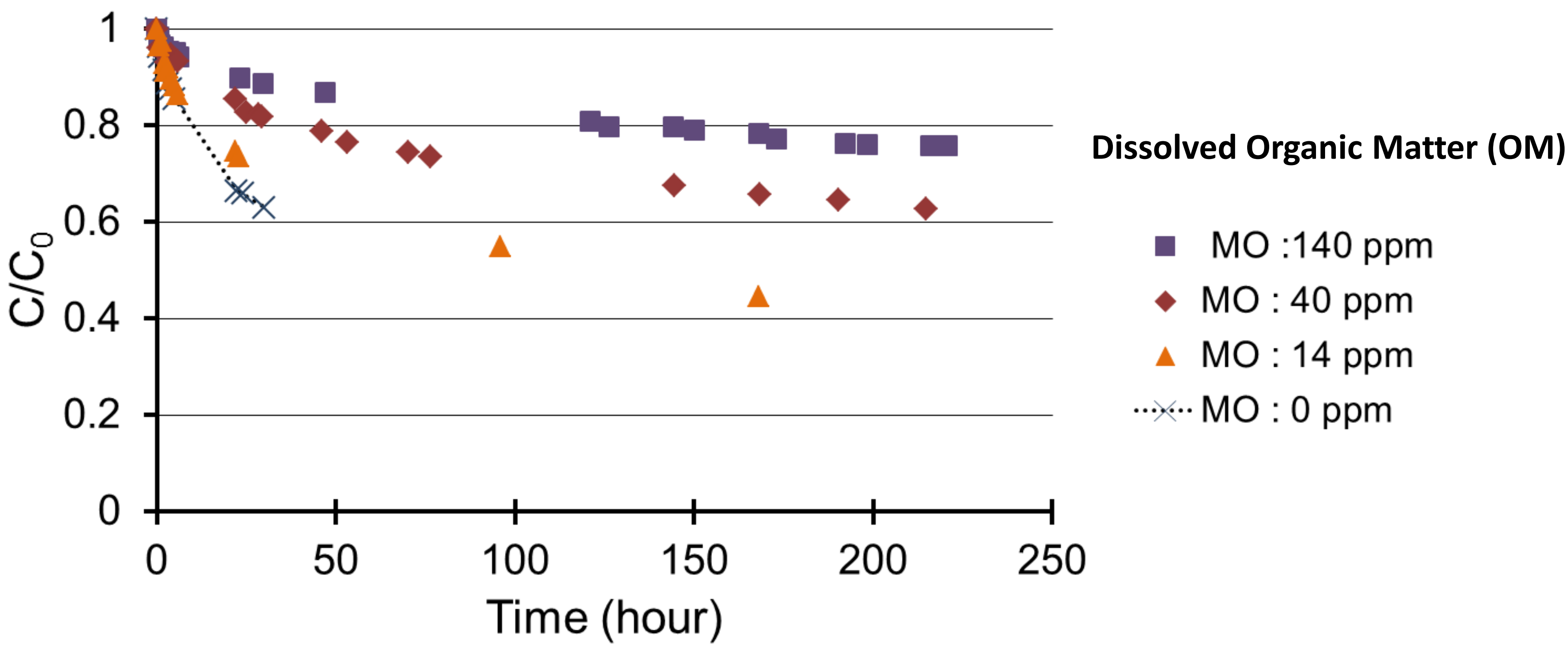
#Values deduced from nitrogen adsorption measurements at 77 K

*Values deduced from pycnometry or lenght measurements

$ mean value from SEM image

Effect of the organic matter (OM) on the adsorption kinetics of ibuprofen

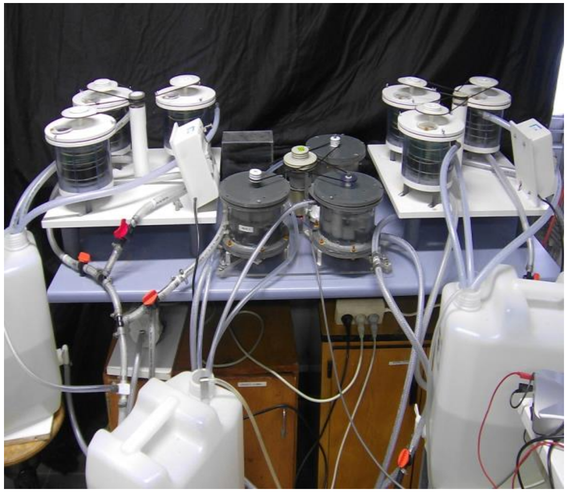
Variation of the humic acids concentration (Aldrich) under Agitation (250 rpm)

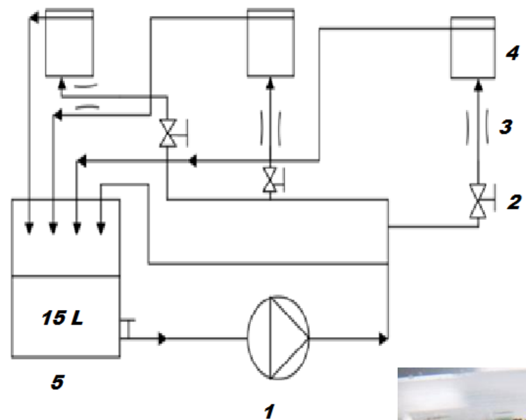


[IBP] = 4 ppm, T = 25°C, m_{Fabric} = 12 mg, V=500mL, pH = 7,4 ; tyndallized water 4h

- Diminution of the adsorption speed because of the competition with OM
- OM-Ibuprofen Complex and adsorption of a part of OM

Growth of biofilm on activated carbon cloth





Legend

1) *Pump*
2) *valve*
3) *Reduction tube*
4) *Carousel*
5) *Water container*

- ***2 kinds of fabric : raw and oxidized in hydrogen peroxide***
- ***Renewal Chambérys' WWTP water from secondary treatment :***

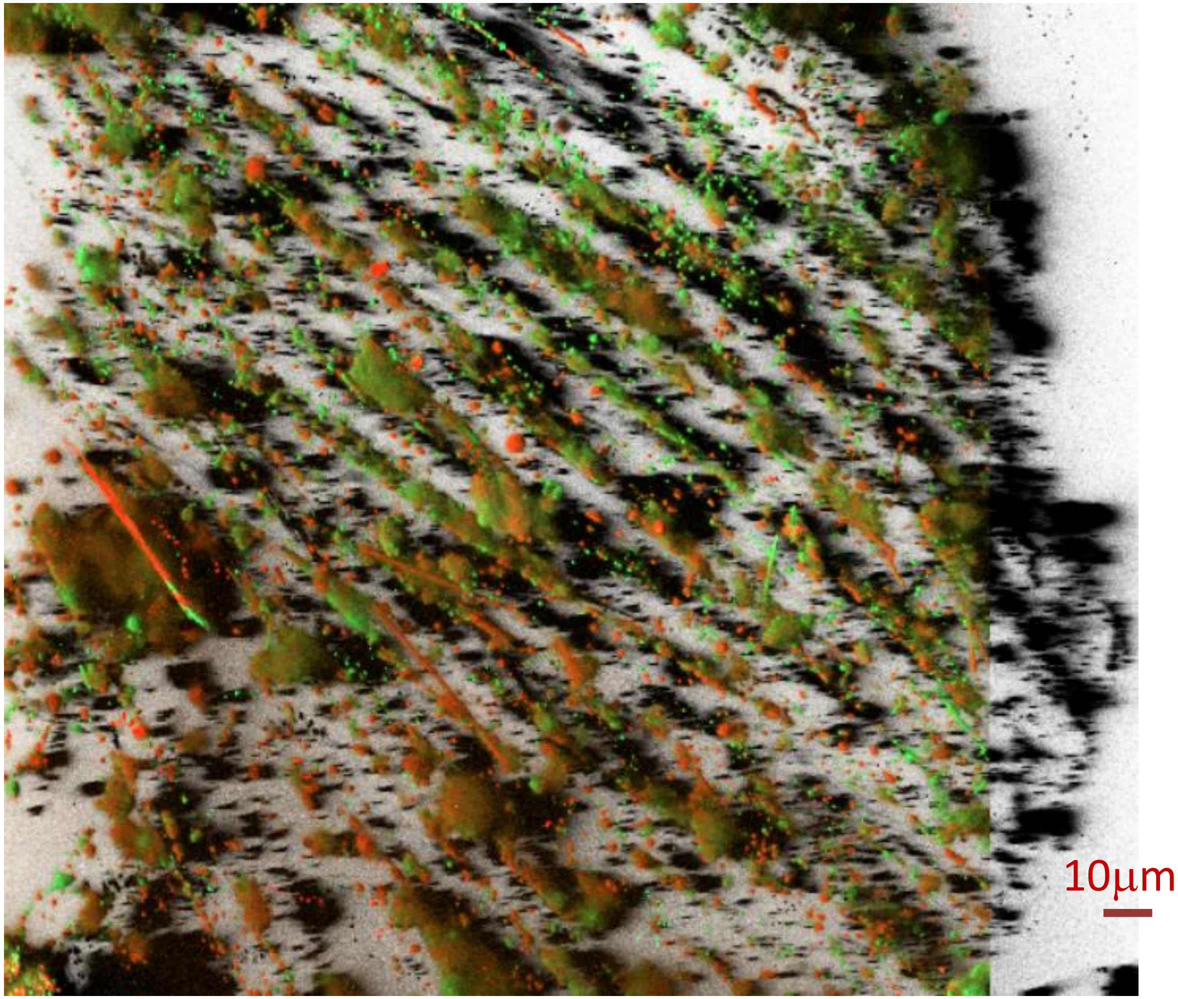
T0, +6 days, +13 days, +20 days, +28 days, +34 days, +42 days, +55 days,

TOC=12-20 mg/L

Characterization by confocal microcopy

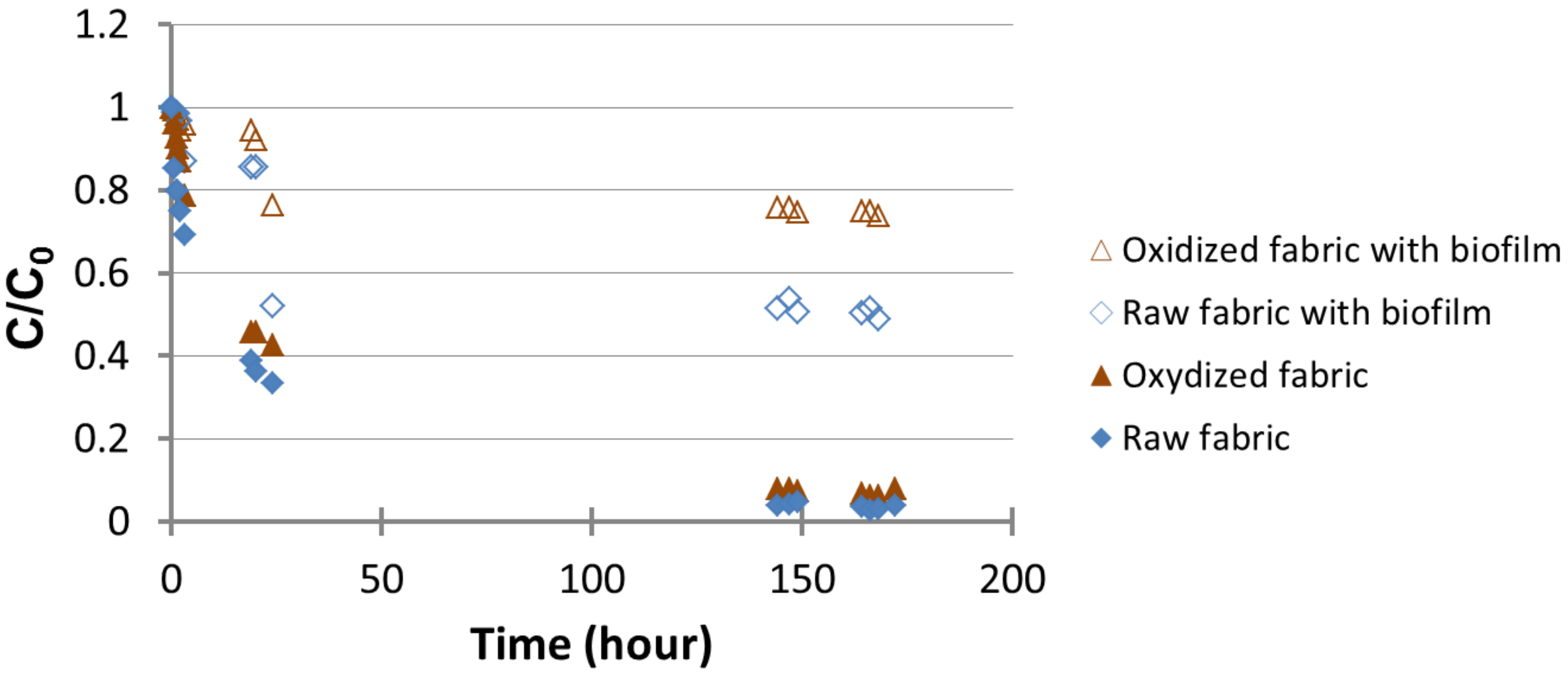
<u>Fluorescence coloration</u> :
- red Syto9
- green propidium iodide

- Bacteria red dead
- Bacteria green : unspoilt



The bacterias are arranged in a biofilm, in the voids between the carbon fibers, they block up these spaces.

Effect of biofilm on the adsorption under orbital agitation



pH = 7.34 ; T = 24±2°C ; C_0 = 4 ppm ; V=250 mL, m_{Fabric} = 12 mg

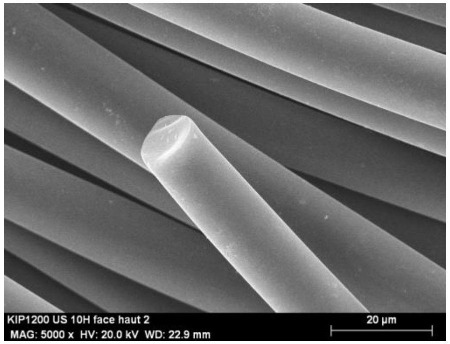
The biofilm strongly slows the adsorption kinetics, it forms a barrier to the ibuprofen access

Influence of ultrasound (probe 20 kHz) on the fabric texture

Sonication 10h probe 20KHz, 500 mL of buffer solution, disk 12 mg

SEM Analyses

Sonicated Fabric (×200)

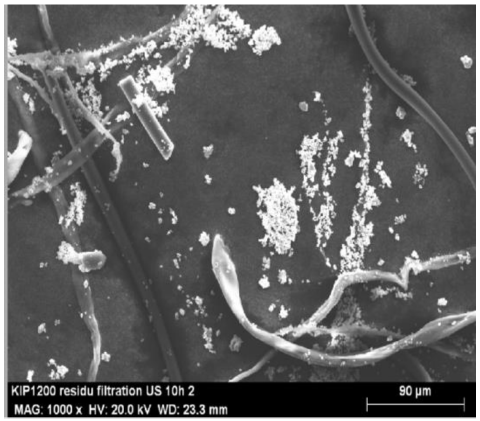


Sonicated Fabric

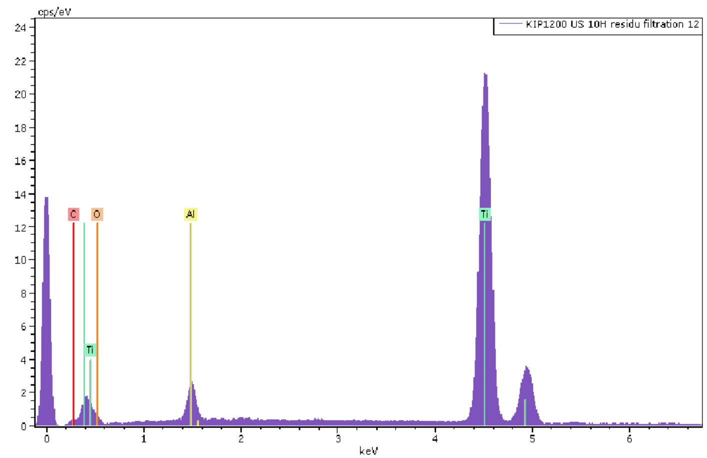
	Raw Fabric	**Sonicated Fabric 10h**
BET Surface area (m^2/g)	1520	1480
Surface Micropores (m^2/g)	1320	1310
External Surface	190	170
Volume micropores (cm^3/g)	0,50	0,50

- No change in sonicated fabric
- No detectable disorder compared to raw fabric.

Influence of Ultrasounds on the structure of Fabric



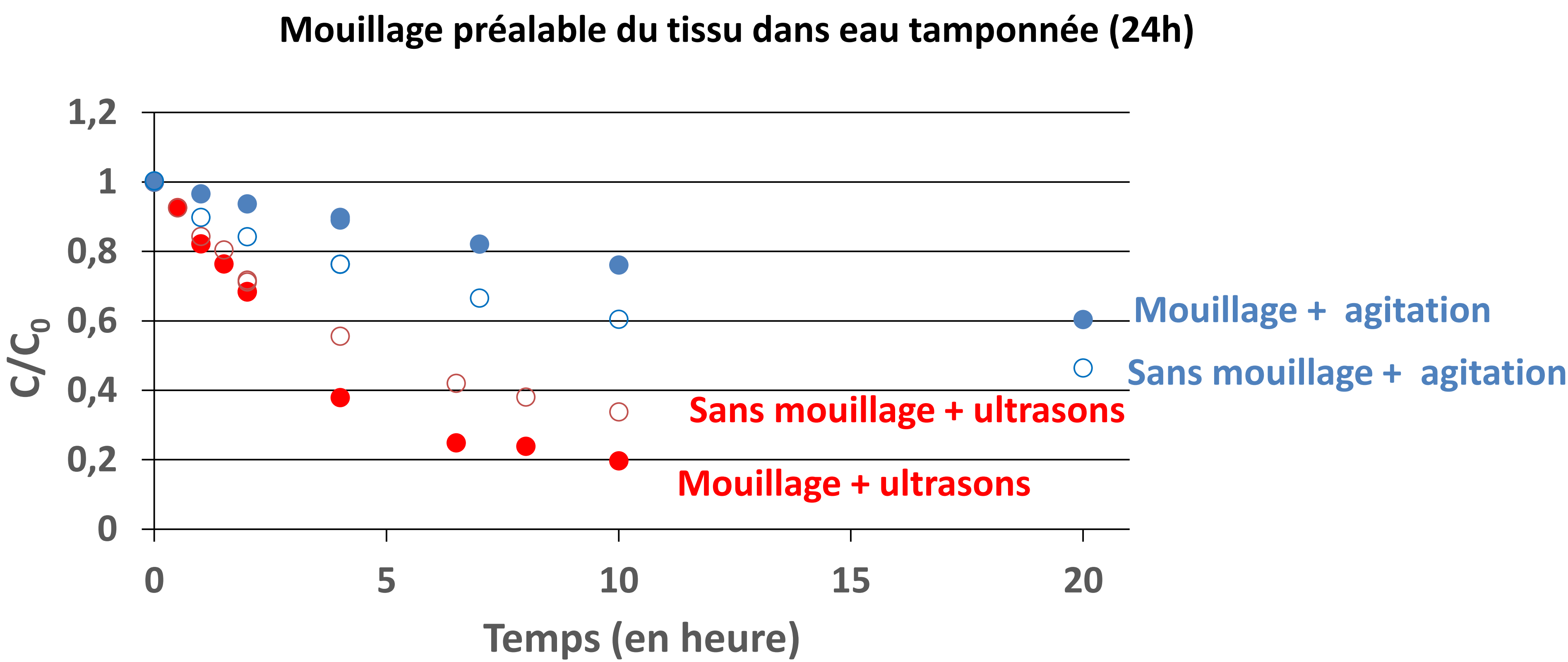
SEM image of residual solid after filtration (*1000)



EDS Spectra of rounded shape particles

- Présence of filaments (carbone fibers)
- Presence of more rounded shape particles made of Ti from probe erosion

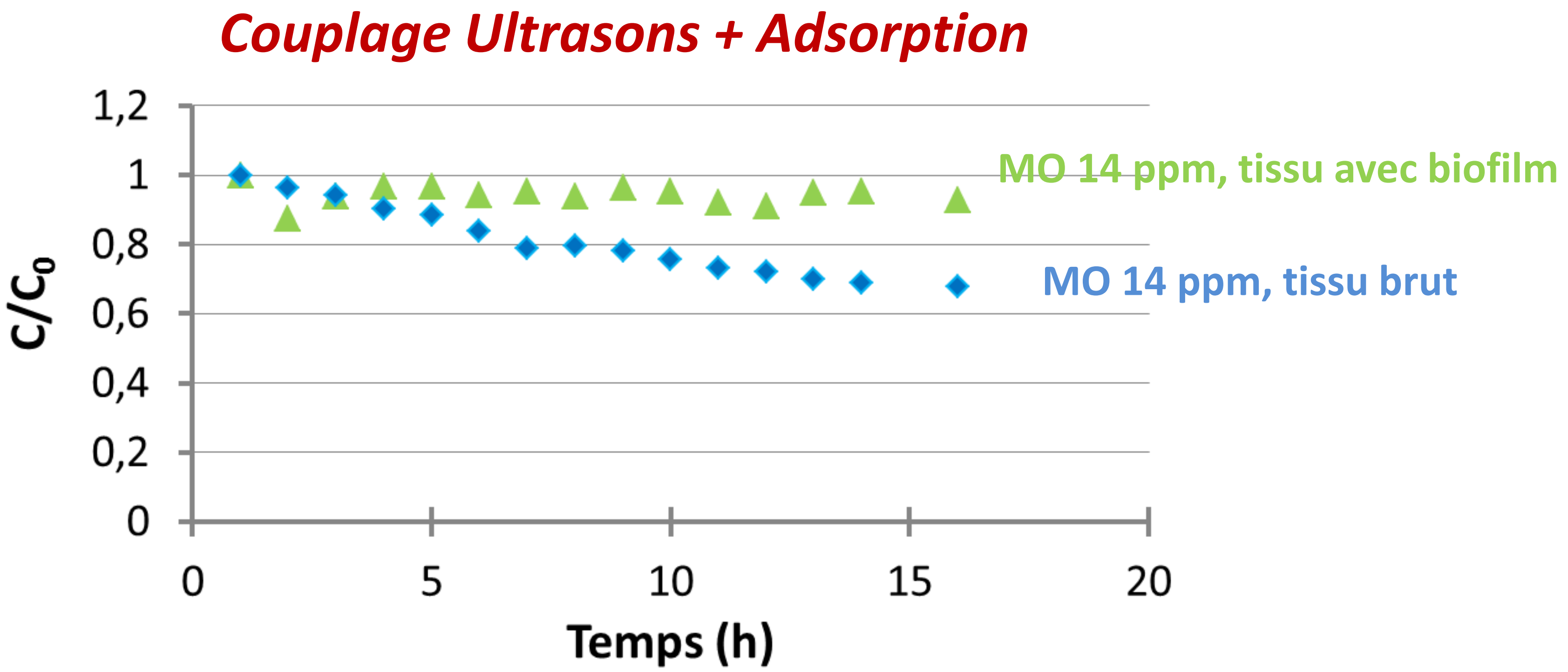
Effet du mouillage avec et sans ultrasons



[IBP] = 4 ppm, T = 25°C, m_{Tissu} = 12 mg, V=250mL, pH = 7,4

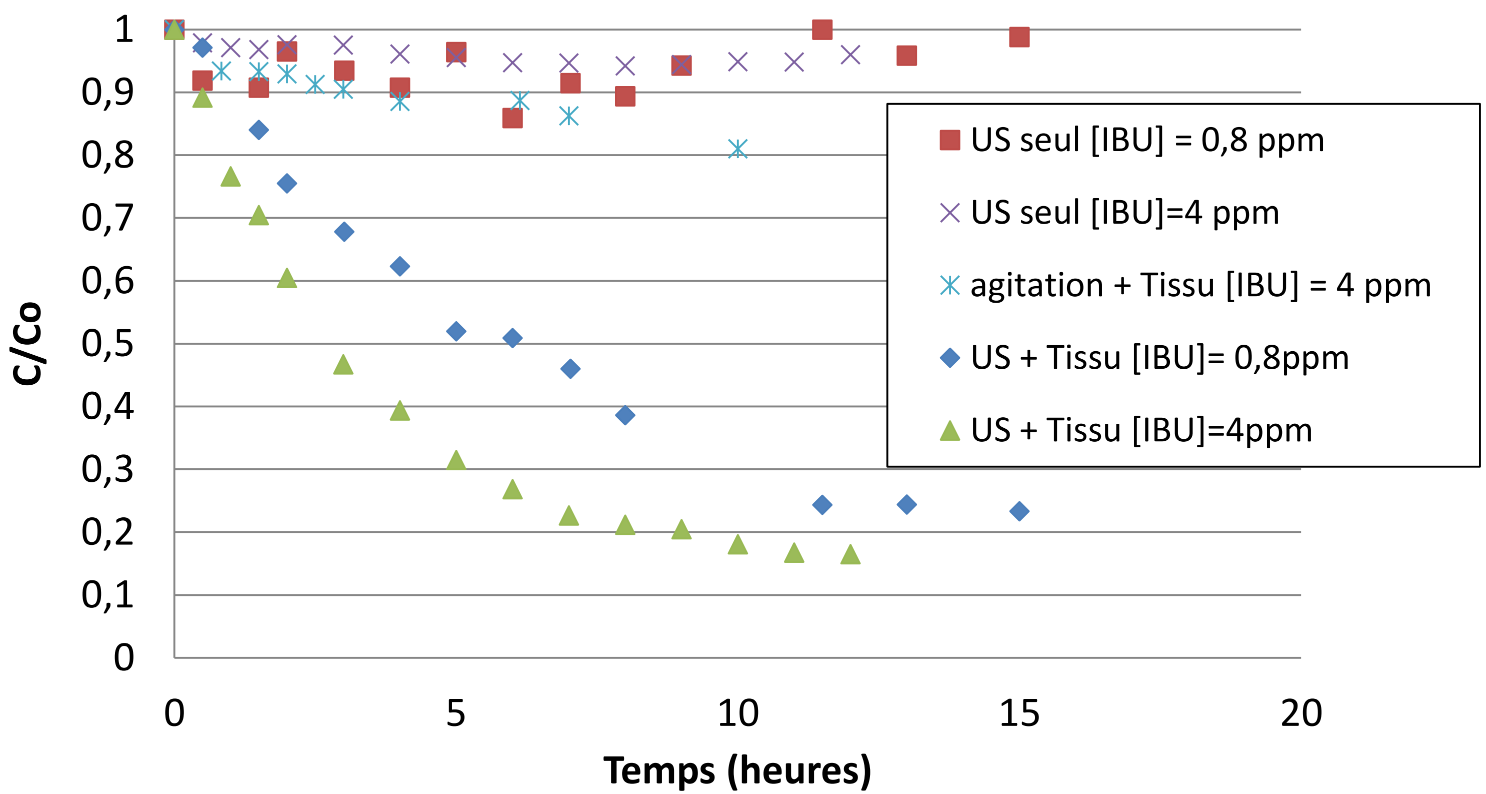
- L'absence de mouillage a un effet bénéfique sous agitation
- Compétition de l'eau tamponnée et de l'ibuprofène?

Effet des ultrasons sur un tissu recouvert de biofilm en présence de matière organique dissoute



En présence de matière organique, les ultrasons sont inefficaces pour accélérer l'adsorption de l'ibuprofène sur un tissu recouvert de biofilm. Il n'y a plus aucune d'adsorption sous ultrasons.

Influence de la concentration en ibuprofène sur la cinétique d'adsorption en présence US



Léger ralentissement de la cinétique lorsque l'on passe de 4 ppm à 0,8 ppm

Supports étudiés

Caractéristiques physicochimiques : Porosité (adsorption N_2 et CO_2)

	Surface BET (m^2/g)	Volume µcropores (<0,7 nm) (cm^3/g) DFT	Volume supermicropores (cm^3/g) DFT	Volume mésopores (cm^3/g) DFT	Volume poreux total (cm^3 /g)
Tissu KIP1200	1560	0,40 (74%)	0,14 (26%)	0	

Chimie de surface : Titrage de Boehm et pH_{pzc}

Tissu KIP1200	0,02	**0,03**	**0,05**	**0,37**	**0,47**	**0,21**	**8,75**

Dacarb, France

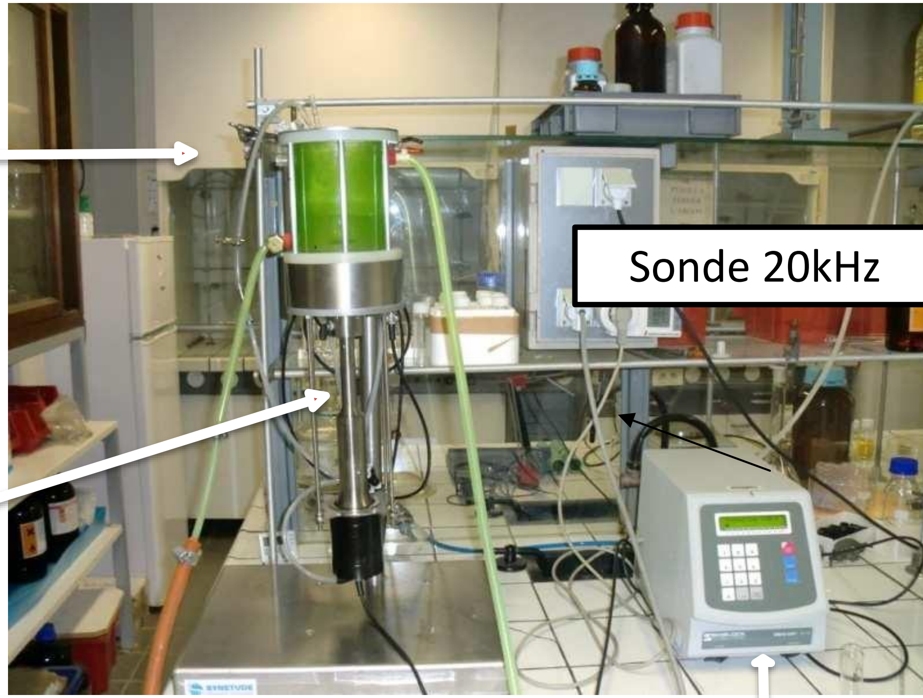
Réacteur US

Réacteur

Ultrasons

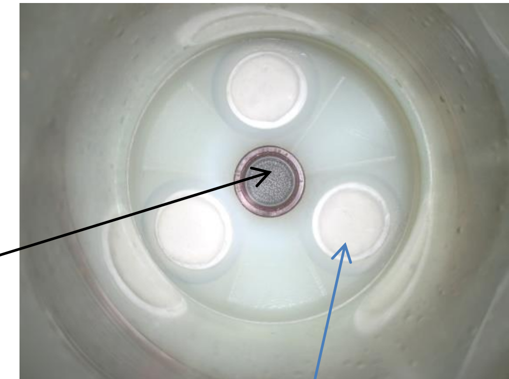
$V_{Réacteur} = 1L$

$\phi_{Int} = 6,1$ cm



Sonde 20kHz

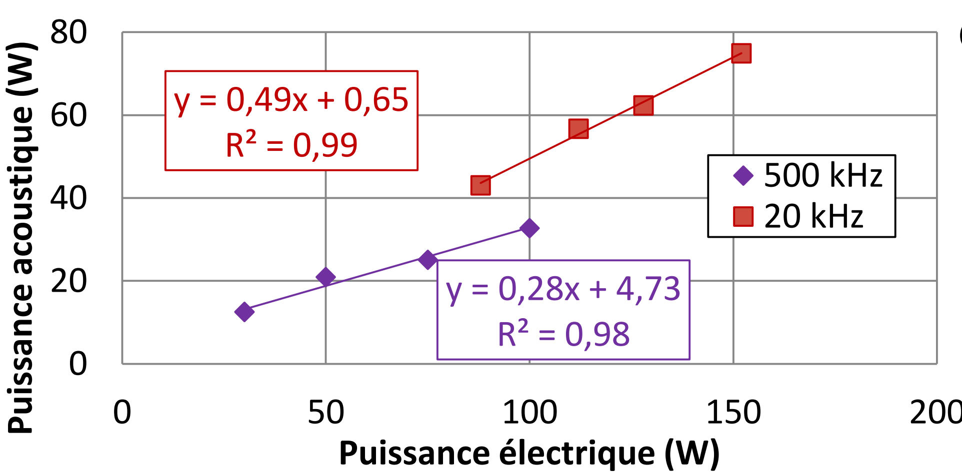
Sonde 20kHz



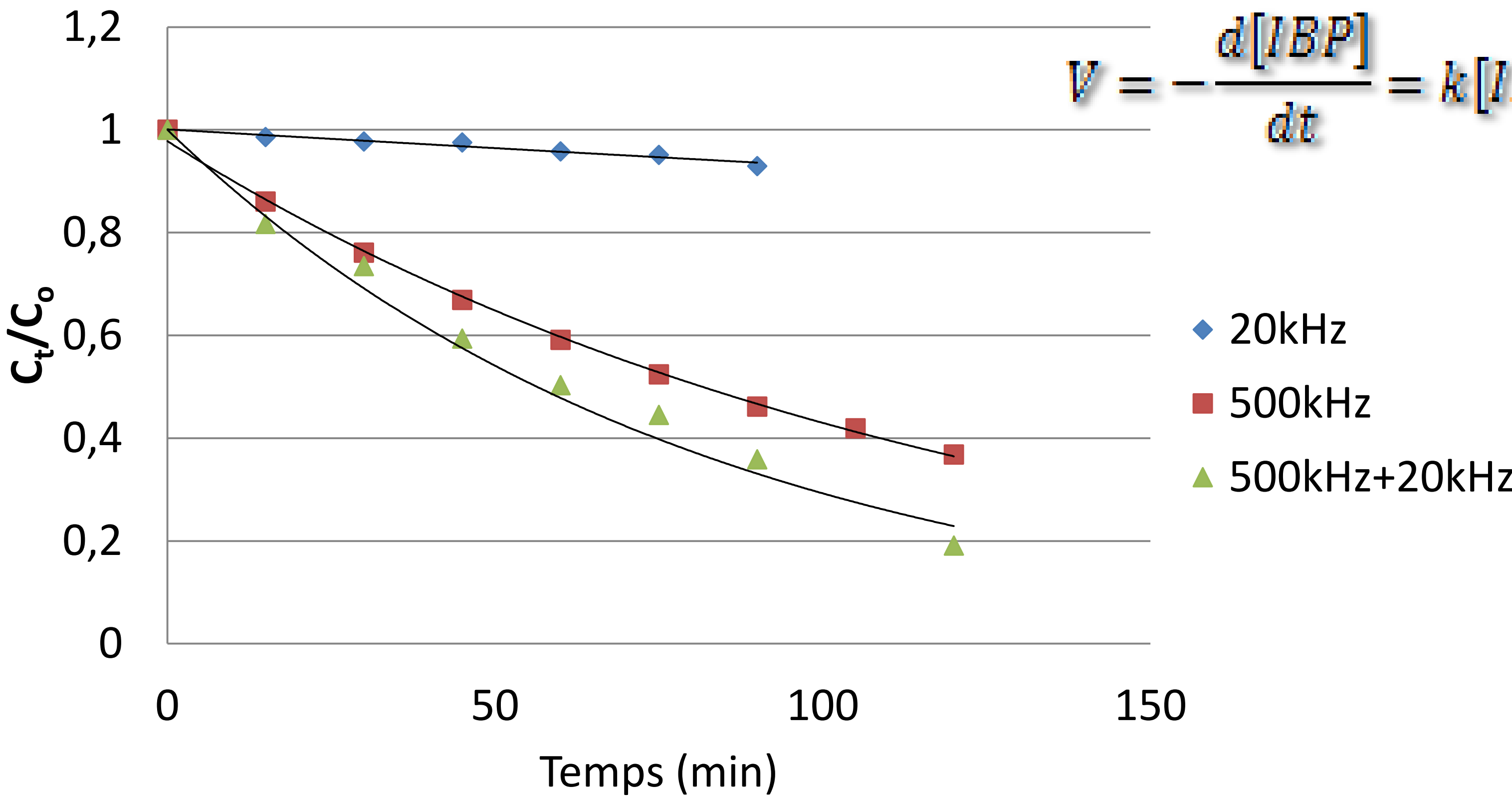
Piézoélectrique

500 kHz

Générateur 20kHz



Dégradation sonochimique de l'ibuprofène



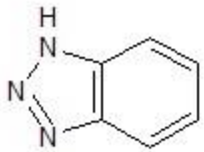
$$V = -\frac{d[IBP]}{dt} = k[IBP]$$

[IBP] = 50mg/L ; pH = 7,34 ; T = 24±2°C ; $V_{solution}$ = 0,5 L
f = 500 kHz, $P_{acoustique}$= 32 W ; f = 20 kHz,$P_{acoustique}$ = 62 W

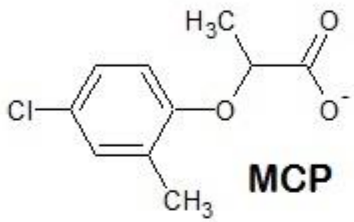
- Meilleure dégradation de l'IBU à 500 kHz qu'à 20 kHz pour une puissance malgré la faible puissance acoustique (plus de radicaux produits)
- Additivité des cinétiques en double fréquence : 500 + 20 kHz

Formula	$C_{13}H_{18}O_2$
Molar mass	206.28 g/mol
Solubility (pH = 7,4)	110 ppm
pK_A (25°C)	4.91
Log K_{ow}	3.87
Dimensions (Å)	13.57×7.96×5.2

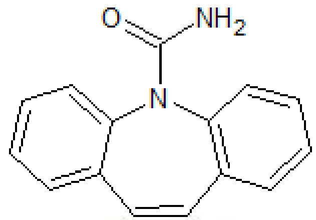
Physico-chemical characteristics



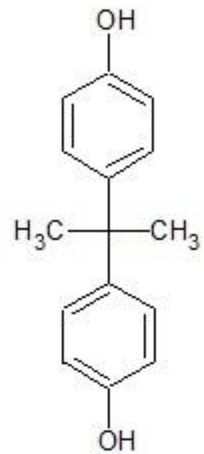
BZT



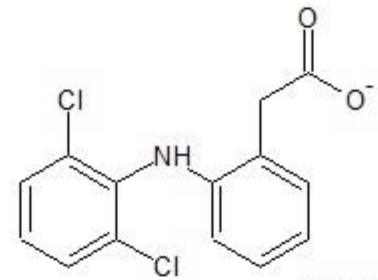
MCP



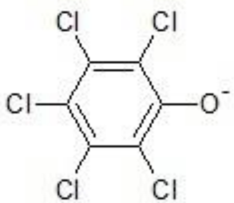
CBZ



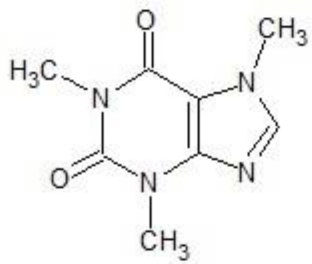
BPA



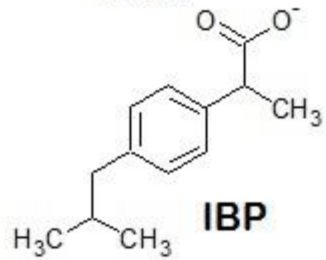
DFN



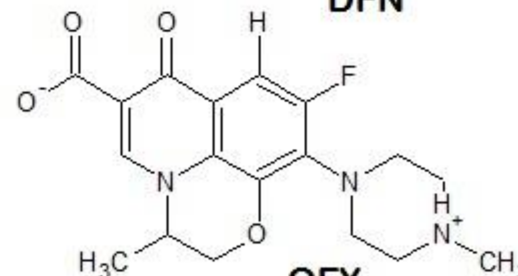
PCP



CAF



IBP



OFX