Adsorbent Materials in Environmental Remediation

GEopolymer based Adsorbents

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ecosister

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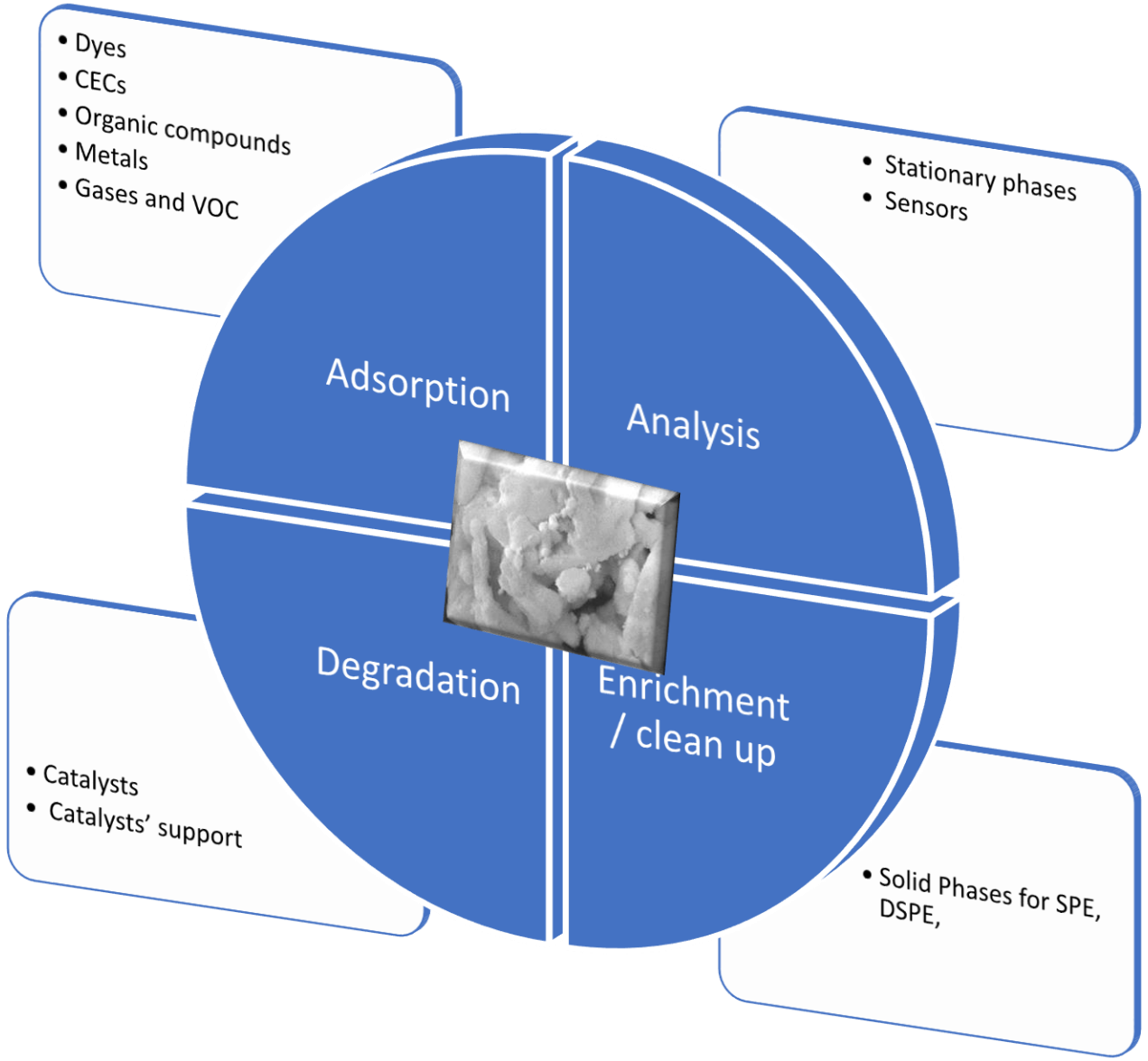
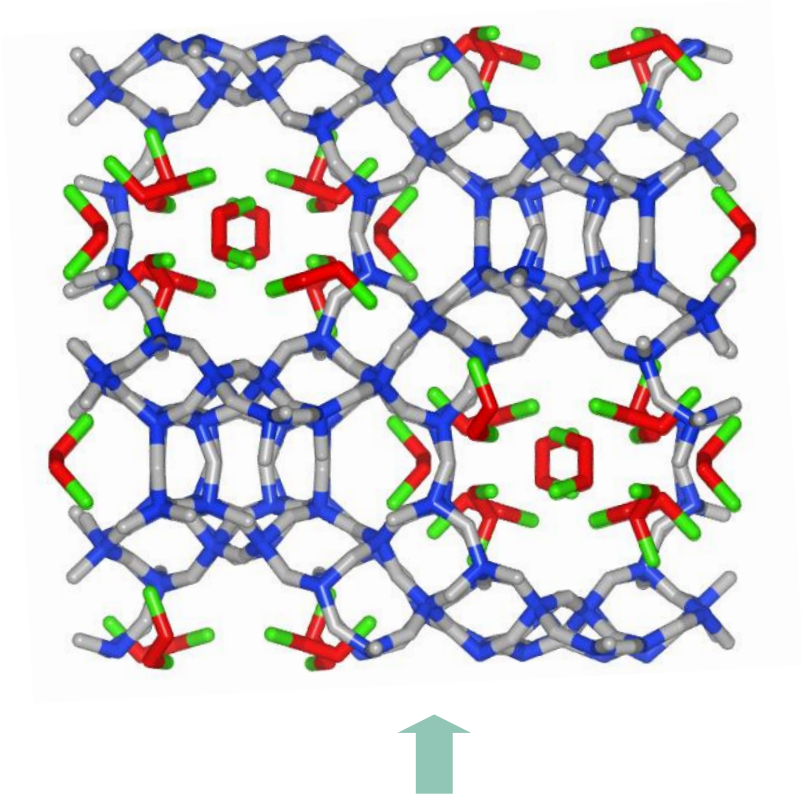
Environmental application of adsorbent materials



Environmental application of adsorbent materials

Study of the absorption (interaction) and kinetics (mobility/diffusion) of organic compounds on different adsorbent materials:

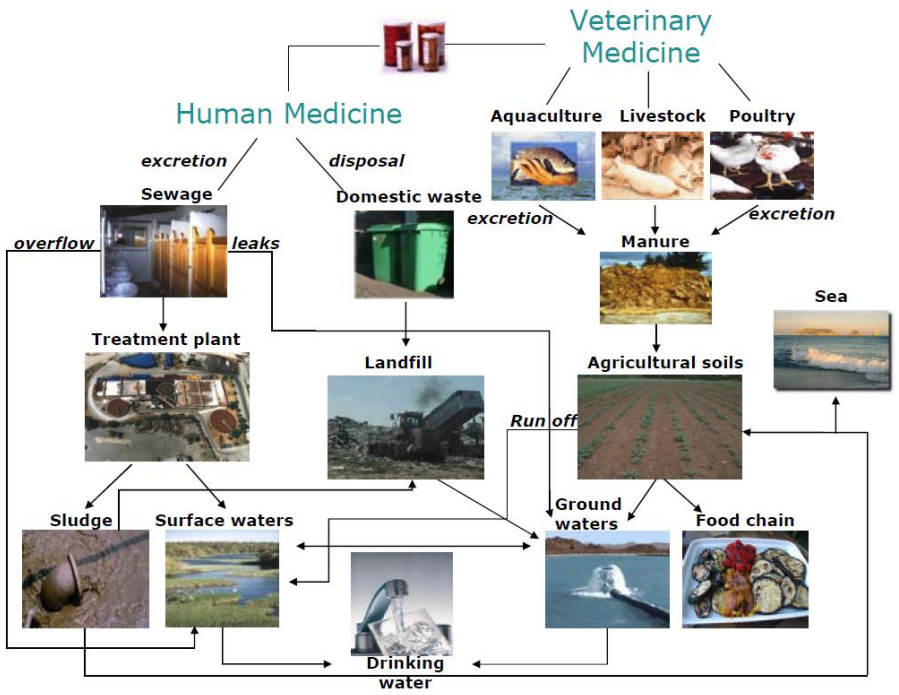
- To measure the adsorption capability of adsorbent materials with respect to aqueous dilute solutions of contaminants
- To quantify aspects of the adsorption process for potential use of adsorbent materials in environmental applications
- To investigate the adsorption mechanisms and to evaluate the factors that can affect the adsorption process, pH, Ionic strength, hydrophobicity.

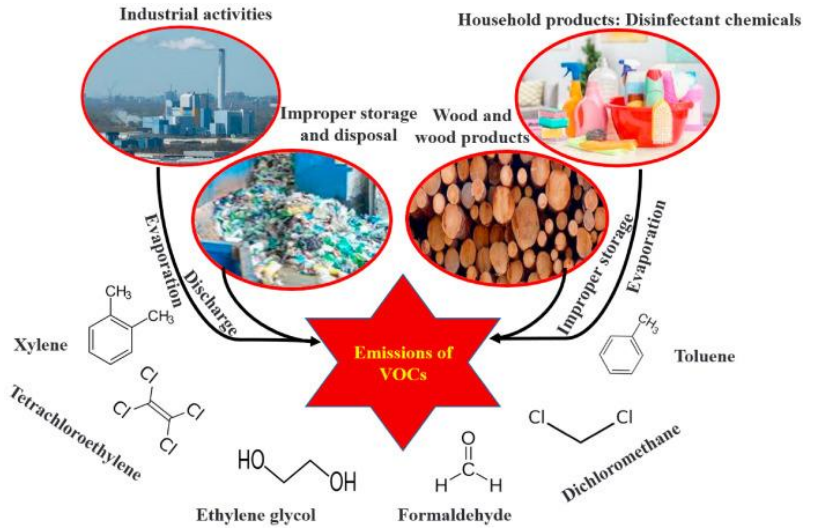


Volatile Organic Compouds (VOCs)
Dichloroethane (DCE)
Toluene (TOL)
Methyl tert-ButylEther (MTBE)
VOC Mixture
PFAs
Drugs
- Floxacin (FLX)
- Erythromycine (ERY)
- Carbamazepin (CBZ)
- Atenolol (ATN)
- Hydrochlorotiazide (HTC)
- Ketoprofen (KTP)

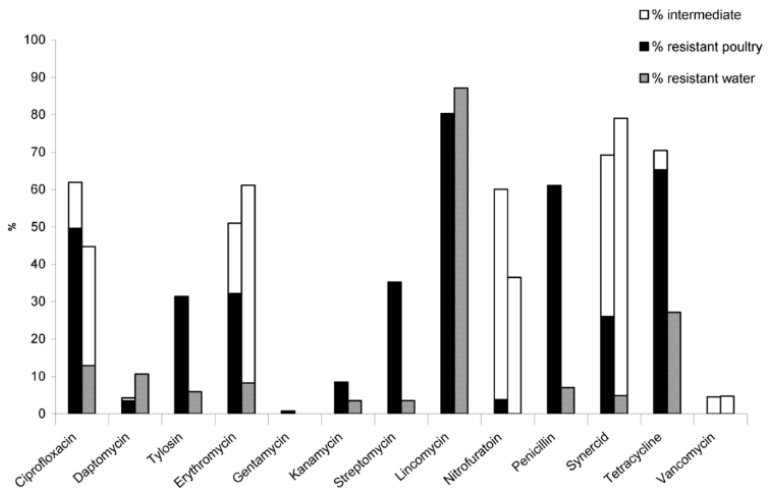
Zeolites (zeolites Y, mordenite, ZSM-5, Beta), Carbonaceous materials, bioadsorbents

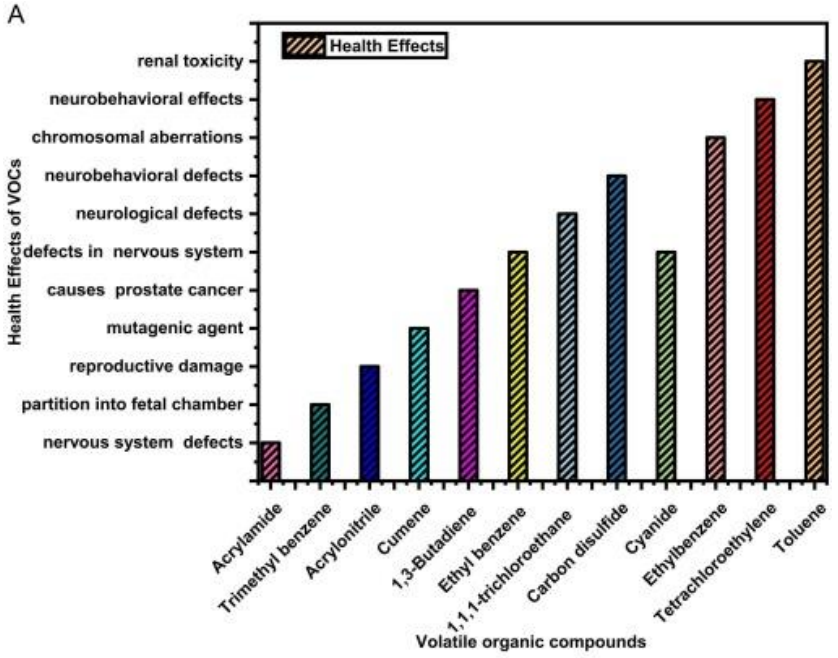
Sources of organic contaminants in surface waters



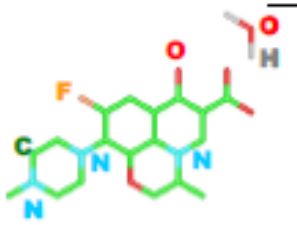
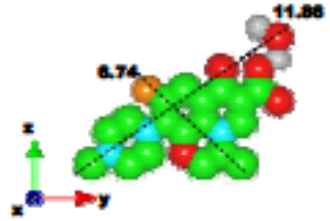
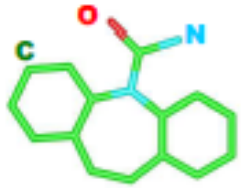
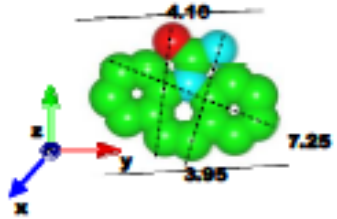
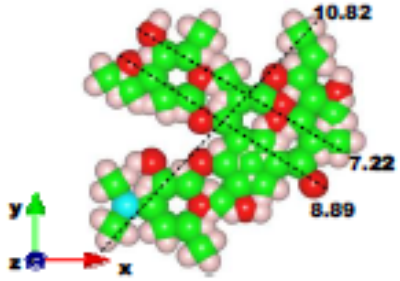


Increase of antibiotics resistance

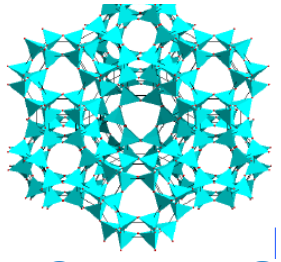
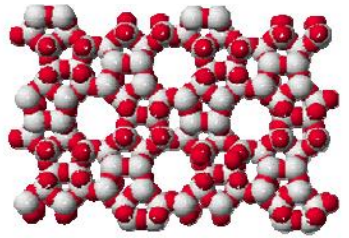
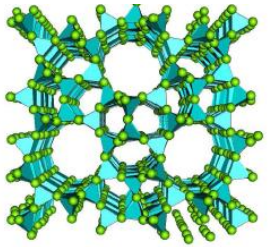




Removal of drugs from water

Structure	Chemical name	Molecular weight (gmol-1)	3D structure[a] and distances (A)	Water Solubility (mg L^{-1})	pK_a	log K_{ow}
	Levofloxacin	361.4		28300[1]	6.05[2] 5.70[3] 8.22[2] 7.90[3]	0.6[4] -0.56[5]
	Carbamazepine	236.3		17.66[6]	13.9[6]	2.25[7] 1.51[8]
	Erythromycin	733.9		2000[9]	8.90[10]	3.06[6]

Martucci, A., Pasti, L., Marchetti, N., Cavazzini, A., Dondi, F., Alberti, A.
Adsorption of pharmaceuticals from aqueous solutions on synthetic zeolites
(2012) Micropor. & Mesopor. Mat. , 148 (1), 174-183.

Zeolites: Constant SAR 200 – variable pore size and structure

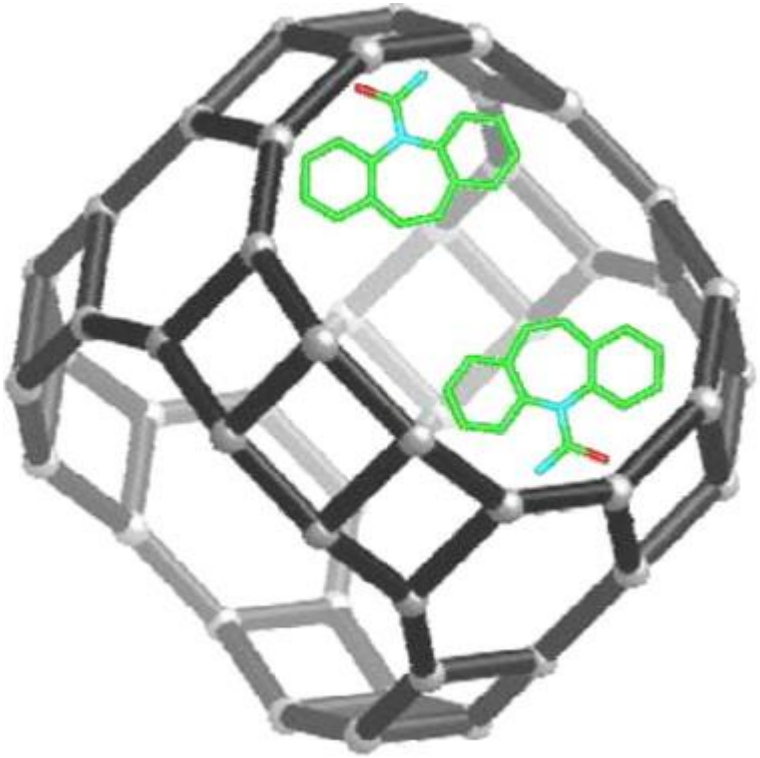
Removal of drugs from water

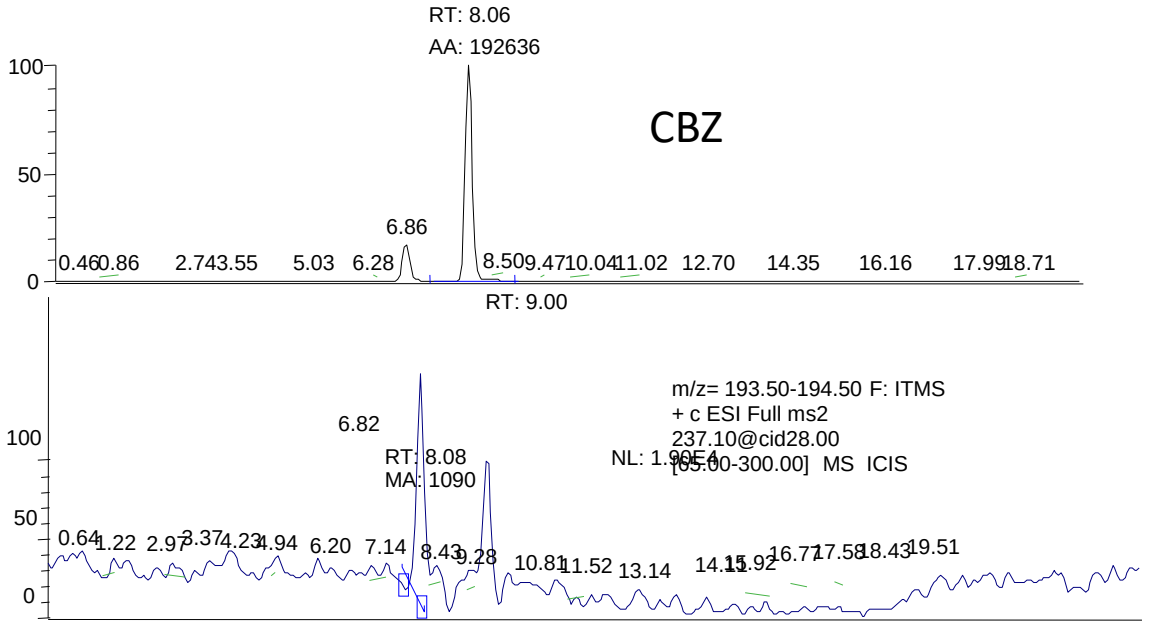
Filtration 0.45 µm

SPE (Strata-X cartige)

HPLC/MS

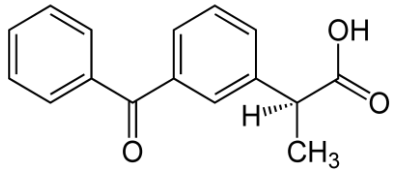
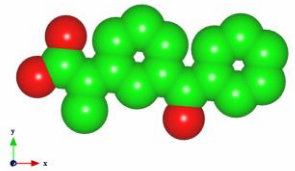
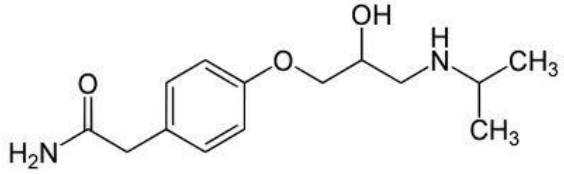
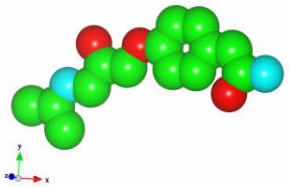
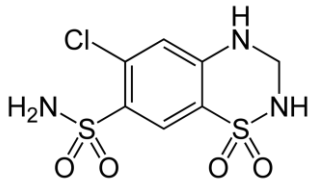
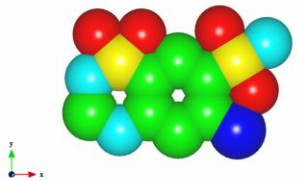
50 x 2.1 mm C18 3 µm
Injection volume 5 µL.
MS : spray voltage 4 kV, capillary temperature 350 C, capillary voltage 29 V and, tube lens 55 V positive ESI condition

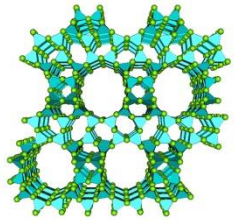




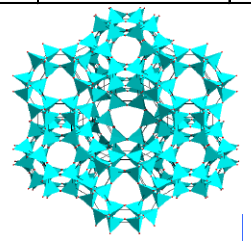
	WW (µg/L)	WW + Y (µg/L)	% removal
CBZ	7.13	< lod	100%
ERY	1.10	< lod	100%
FLX	8.46	0.34	96%

Factors affecting adsorption onto BETA and Y zeolite

Analyte	Formula	Water Solubility	pK_a	Log K_{ow}
Ketoprofen (Non-steroidal anti-inflammatory)	 	0.5 mg/ml [1]	4.45 [2]	3.12 [2]
Atenolol (β-blocker)	 	13.3 mg/ml [3]	9.6 [3]	0.16-0.50 [3]
Hydrochlorothiazide[2] (Diuretic)	 	0.6-1 mg/ml [4]	pK_{a1}=7.9 pK_{a2}=9.2 [2]	-0.07 [2]



Beta (BEA)



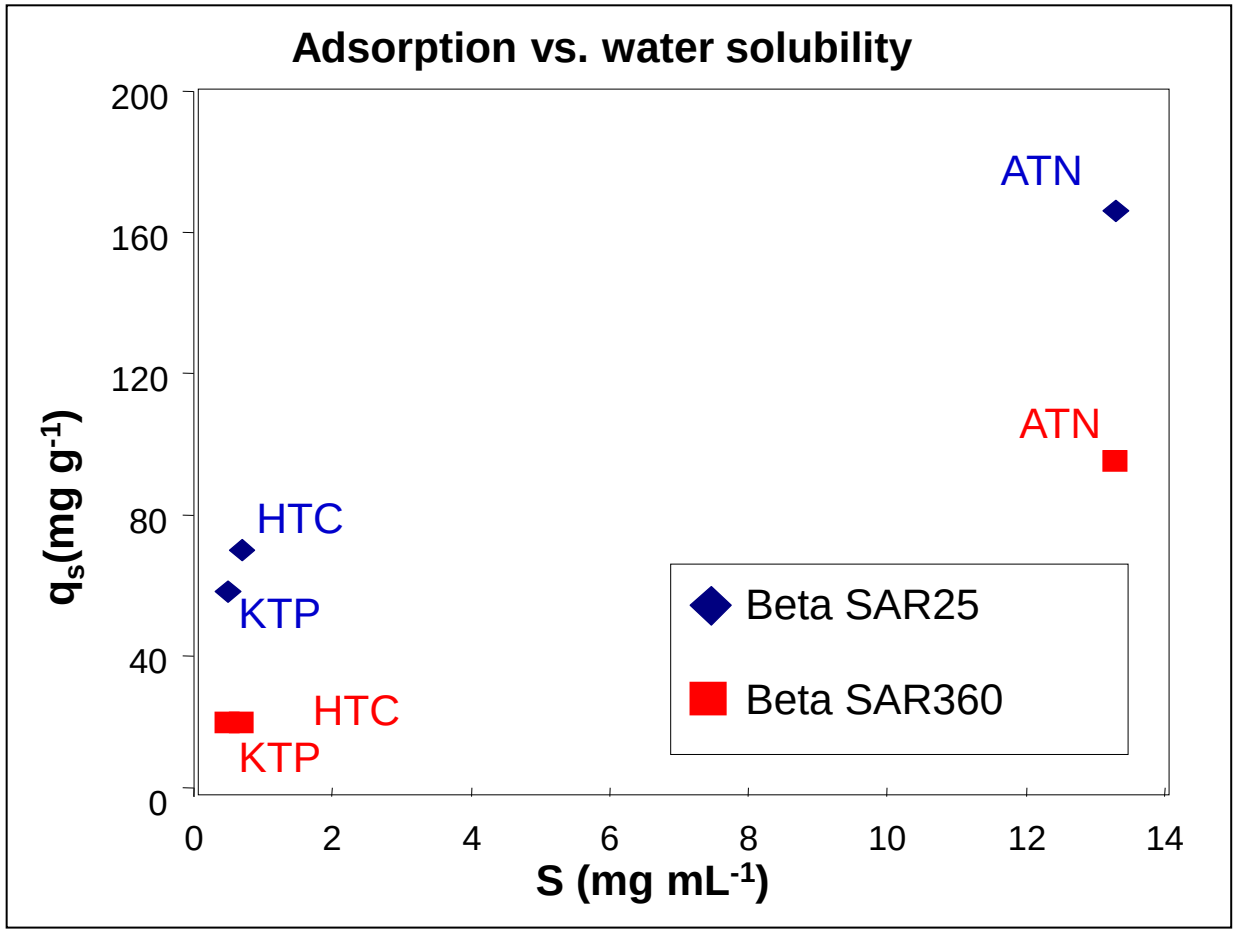
Y

Variable SAR (25, 38, 360), thermal treatment, Solution: pH, ionic strength

Pasti, L., Sarti, E., Cavazzini, A., Marchetti, N., Dondi, F., Martucci, A. Factors affecting drug adsorption on beta zeolites (2013) J. Sep. Sci., 36 (9-10), 1604-1611.

Beta zeolite: SAR effect

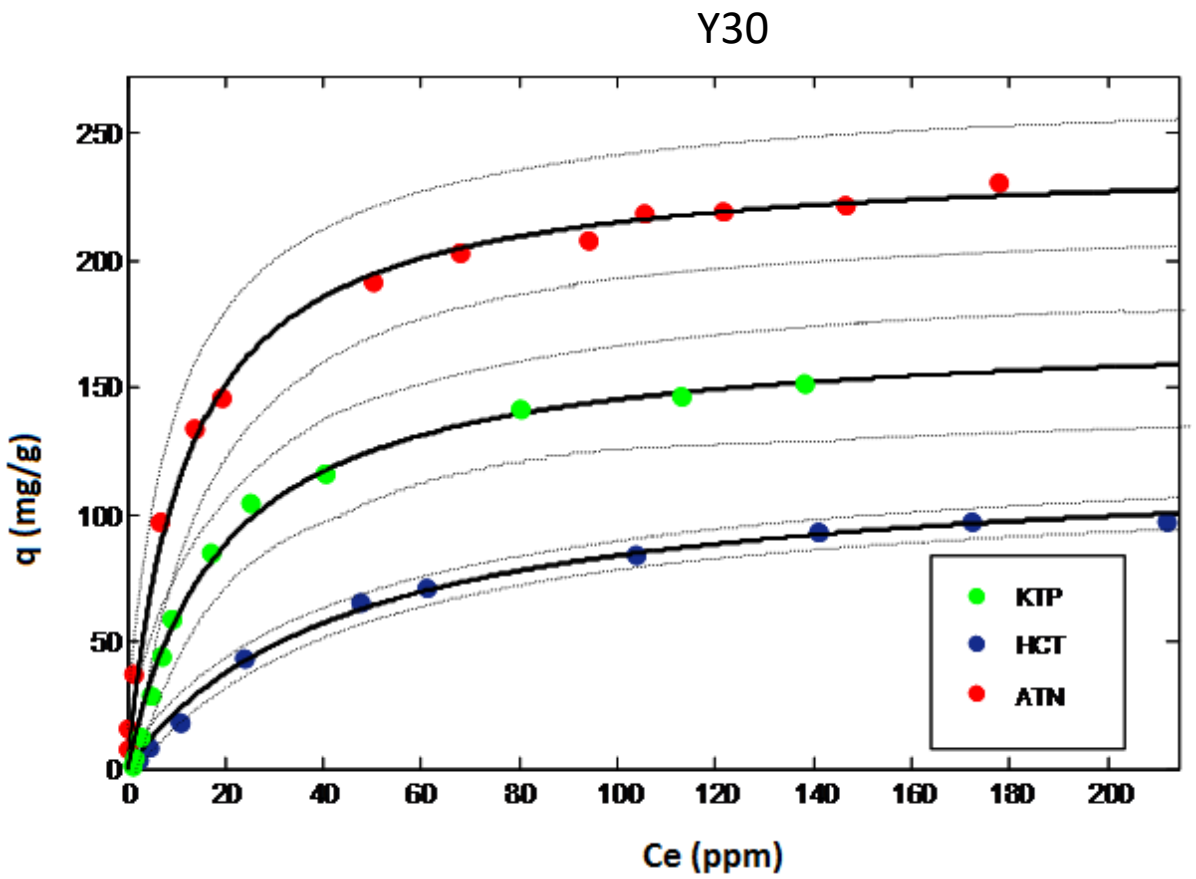
Drug_zeolite	b ($L\ mg^{-1}$)	q_s ($mg\ g^{-1}$)	R^2
KTP – Beta25c	7.0 (5.1, 8.9)	145 (134, 156)	0.9758
KTP – Beta360c	6.4 (5.3, 7.2)	39 (32, 46)	0.9521
HCT – Beta25c	0.6 (0.47, 0.76)	93 (85, 101)	0.9826
HCT – Beta360c	0.061 (0.046, 0.076)	33 (24, 42)	0.9642
ATN – Beta25c	5.8 (3.0, 8.6)	160 (151, 170)	0.9832
ATN – Beta360c	1.9 (0.98, 2.9)	98 (89, 107)	0.9743



- **Both SAR 25 and SAR 360: Saturation capacity ATN > HCT > KTP**
- **Saturation capacity SAR 25 > SAR 360**

Y zeolite: SAR effect

Drug-zeolite	b ($L\ mg^{-1}$)	q_S ($mg\ g^{-1}$)	R^2
KTP – Y200	0.90 (0.76; 1.05)	188 (162; 194)	0.9887
HCT – Y200	0.17 (0.09; 0.24)	180 (168; 192)	0.9856
ATN – Y200	0.21 (0.18; 0.24)	193 (171; 195)	0.9737
KTP – Y30	0.052 (0.035; 0.069)	163 (148; 197)	0.9756
HCT – Y30	0.022 (0.018; 0.026)	98 (84; 112)	0.9957
ATN – Y30	0.084 (0.058; 0.110)	235 (213; 257)	0.9727



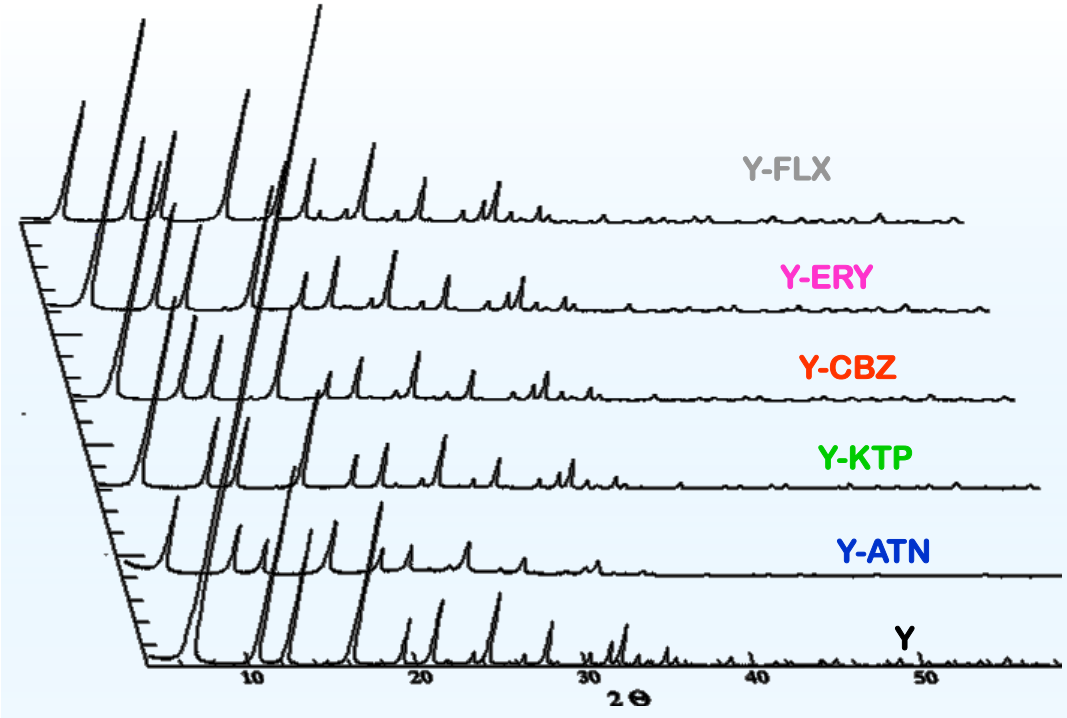
- **Saturation capacity Y > Beta**
- **Y SAR 30: saturation capacity ATN > KTP > HTC**
- **Y SAR 30 > Y SAR 200 (ATN)**

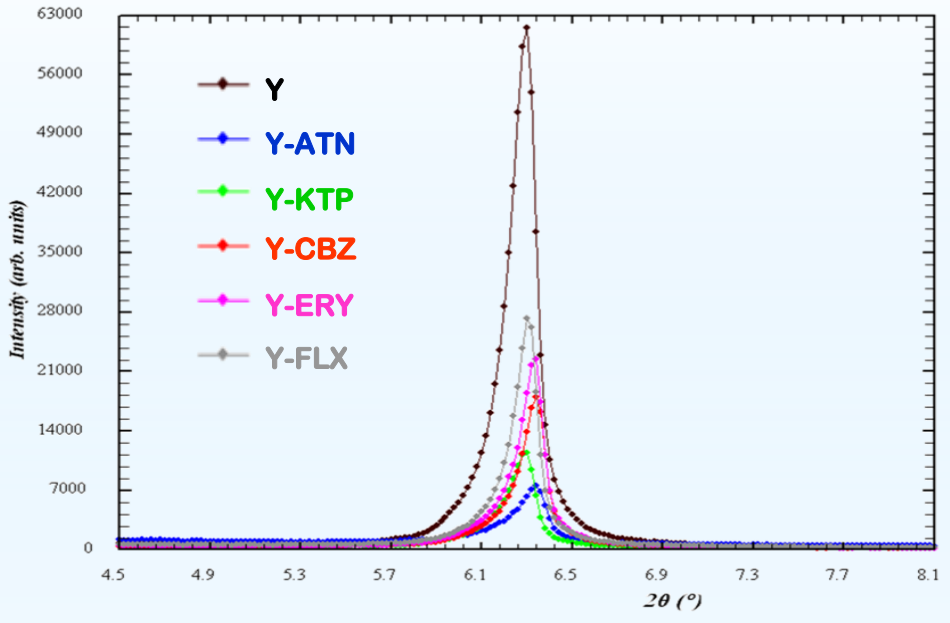
Y zeolite: Structural investigation

Comparison of the X-ray powder diffraction patterns of Y zeolite before and after drugs adsorption:

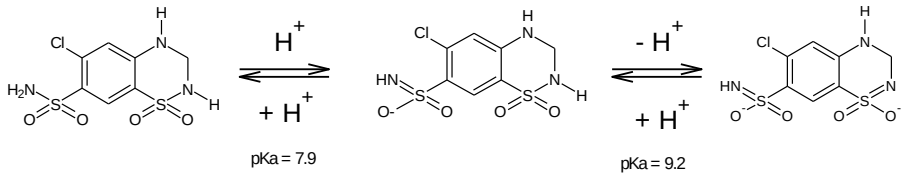
peak intensities in the patterns are markedly different mainly in the low 2θ region.
position of diffraction peaks in the two patterns are slightly different.
spatial symmetry distortion after adsorption

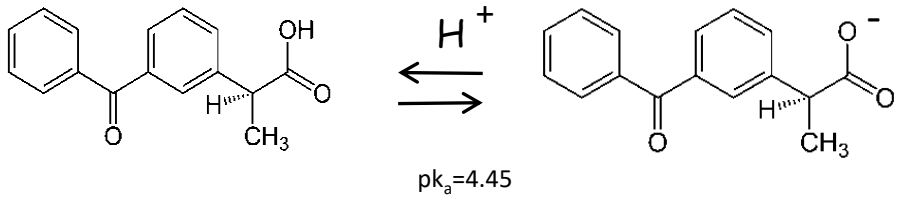
Effective location of host molecules was obtained from Rietveld refinements.

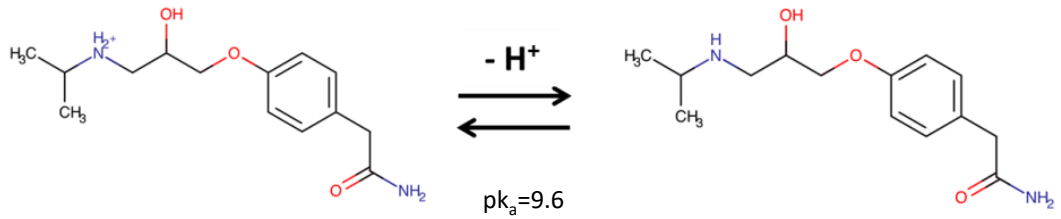


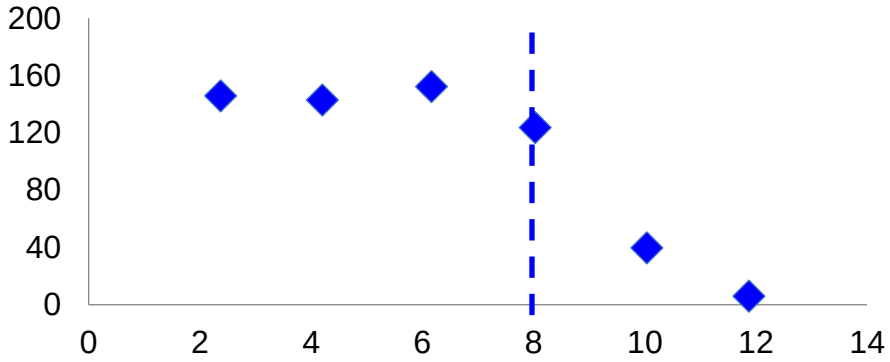


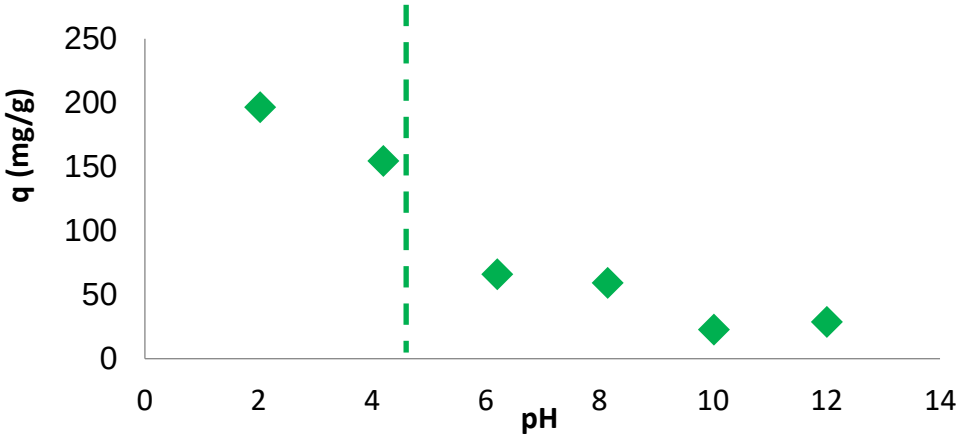
Y zeolite: pH

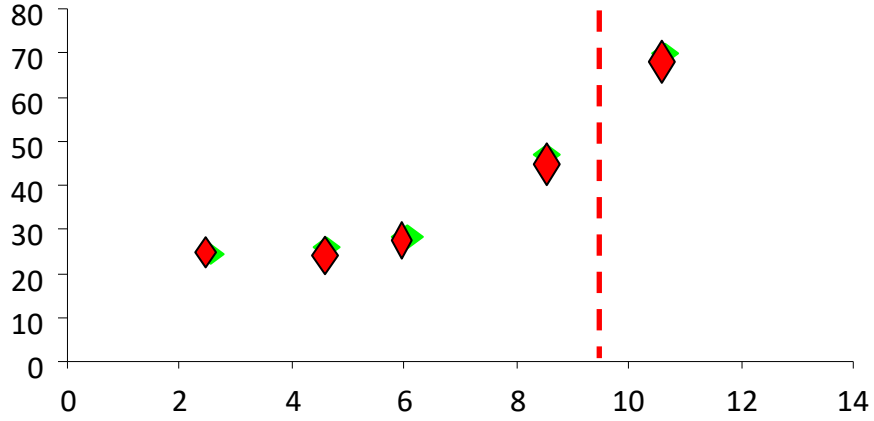

H+
+ H+
pKa = 7.9
- H+
+ H+
pKa = 9.2


H+
pka=4.45

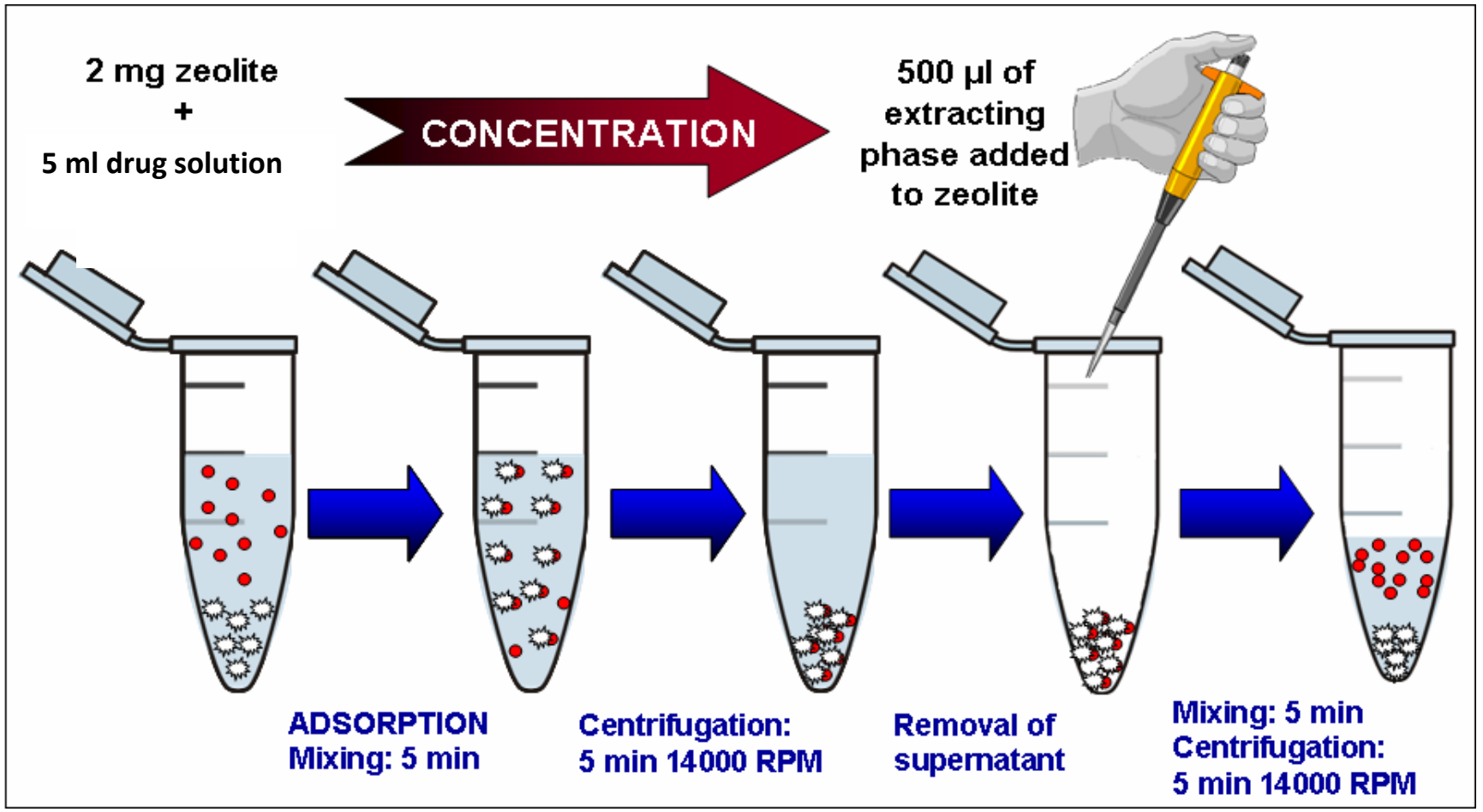

- H+
pka=9.6


200
160
120
80
40
0
0
2
4
6
8
10
12
14


q (mg/g)
250
200
150
100
50
0
0
2
4
6
8
10
12
14
pH


80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
14

Sample preparation: Enrichment



Sample preparation: Enrichment

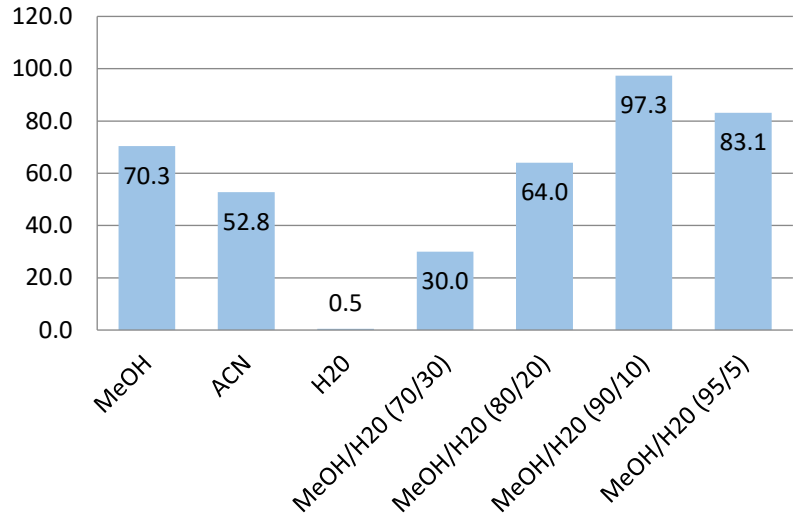
Parameters influencing the extraction efficiency such as:

1) Desorption time,
2) Desorption solvent
3) Extraction volume

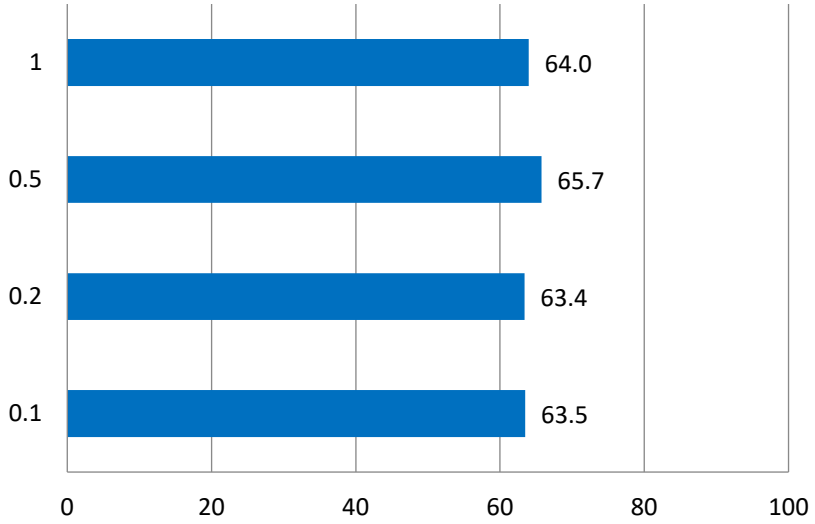
$$\%R = \frac{C_f V_f}{C_i V_i} 100$$

KTP-Y200

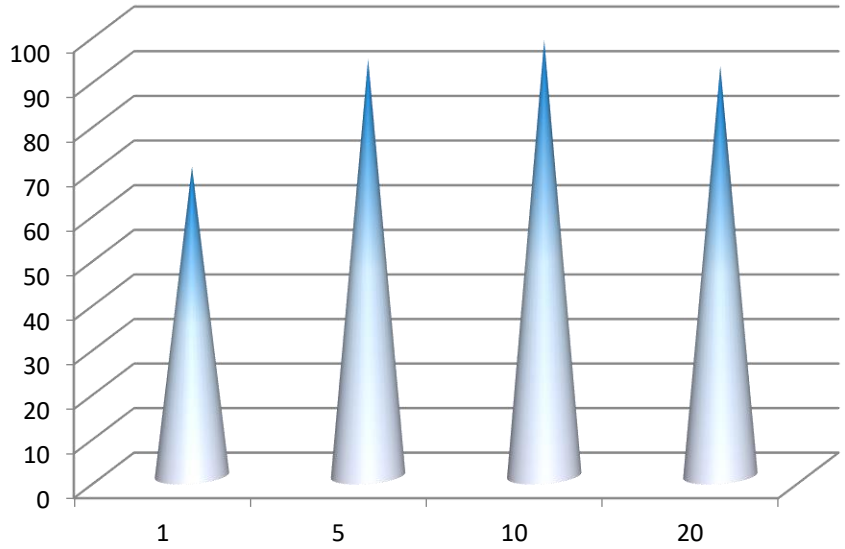
Solvent composition



Extraction volume



Desorption time



Sample preparation: Enrichment

HCT:

Zeolite	Solvent	pH	R %
Y 200	H_2O	5.5	2 %
Y 200	H_2O	10	75 %
Y 200	$MeOH/H_2O$ (70) / (30)	5	95 %

KTP:

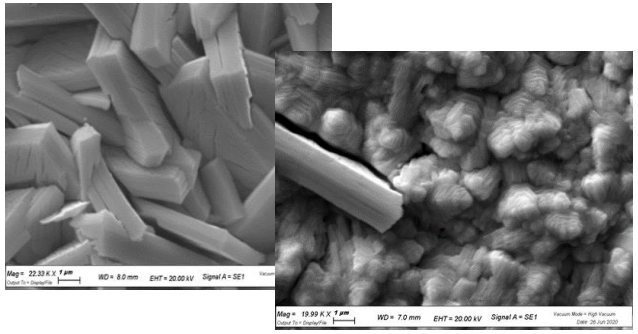
Zeolite	Solvent	pH	R %
Y 200	H_2O	5.5	0.10 %
Y 200	H_2O	10.5	79 %
Y 200	$MeOH/H_2O$ (70) / (30)	3	94 %

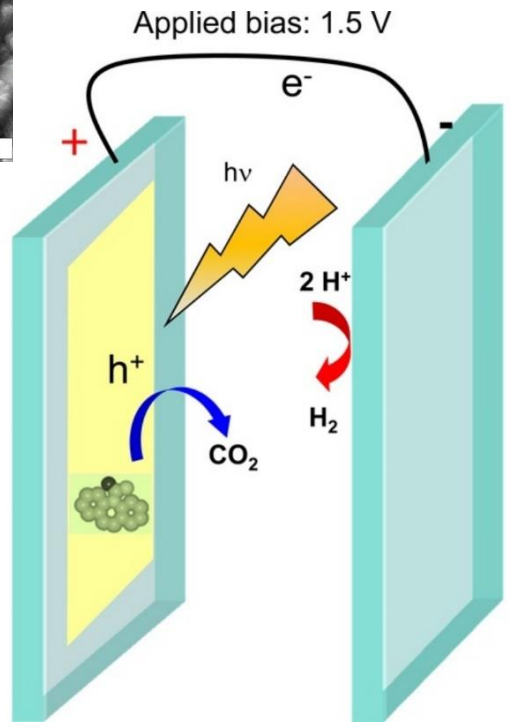
ATN:

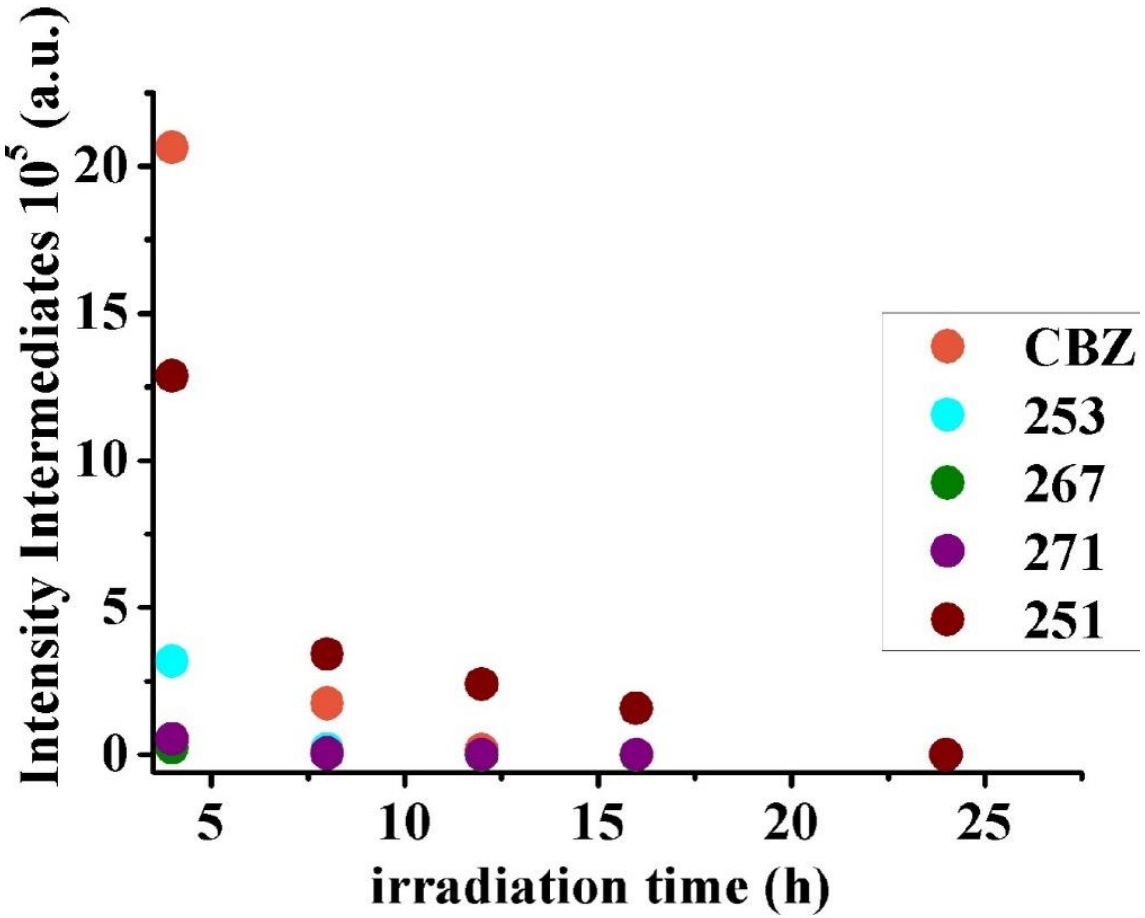
Zeolite	Solvent	pH	R %
Y 200	H_2O	5.5	0.10 %
Y 200	H_2O	10.5	29 %
Y 200	$MeOH/H_2O$ (70) / (30)	10.5	94 %

Sarti, E.; Chenet, T.; Stevanin, C.; Costa, V.; Cavazzini, A.; Catani, M.; Martucci, A.; Precisvalle, N.; Beltrami, G.; Pasti, L. High-Silica Zeolites as Sorbent Media for Adsorption and Pre-Concentration of Pharmaceuticals in Aqueous Solutions. Molecules 2020, 25, 3331. https://doi.org/10.3390/molecules25153331

Contaminants Degradation

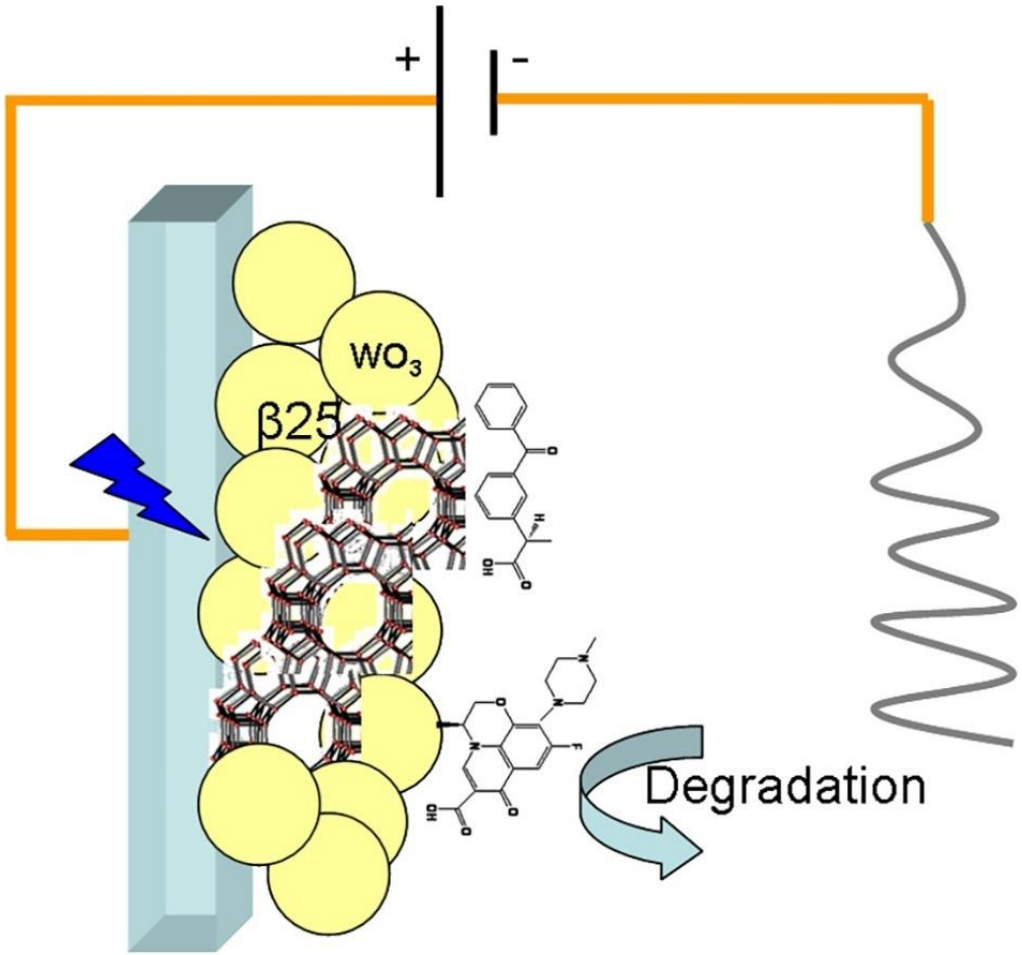


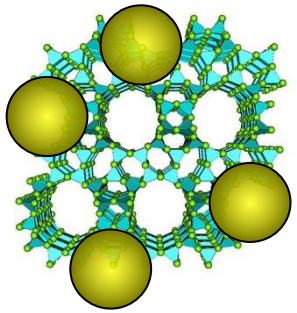


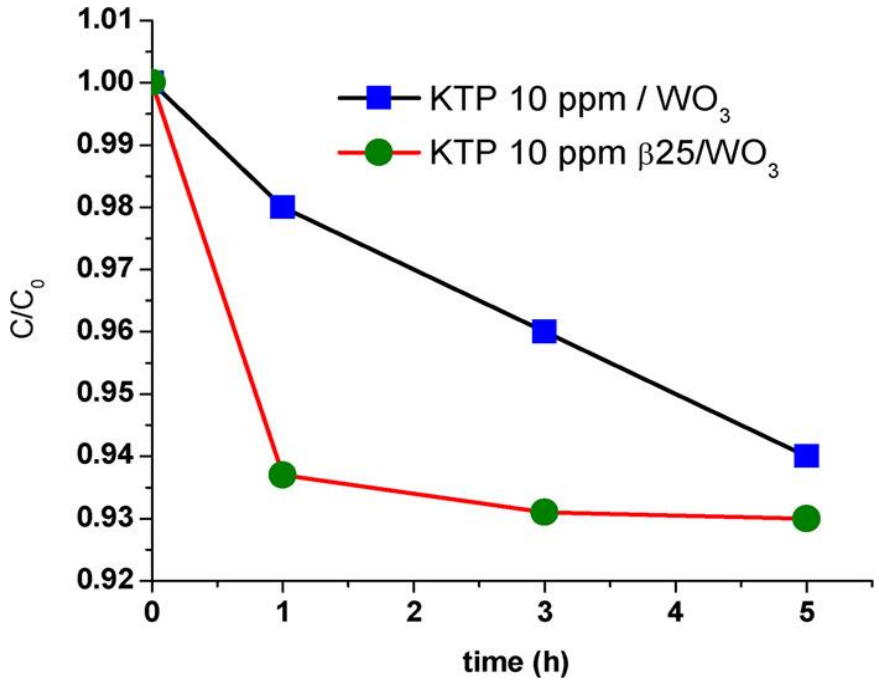


G. Longobucco, L. Pasti, A. Molinari, N. Marchetti, S. Caramori, V. Cristino, R. Boaretto, C. A.Bignozzi, Photoelectrochemical mineralization of emerging contaminants at porous WO3 interfaces, Applied Catalysis B: Environmental, 204, 2017, 273-282.

Contaminants Degradation







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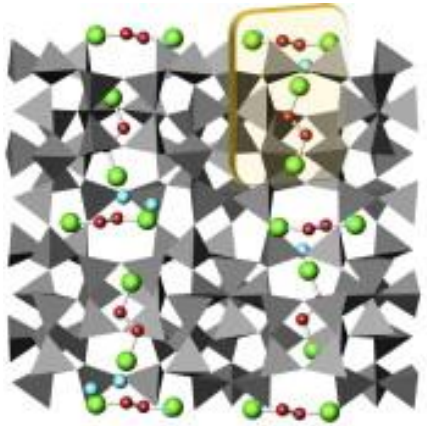
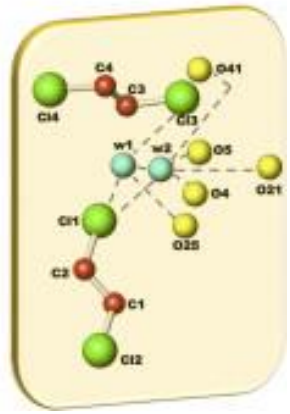
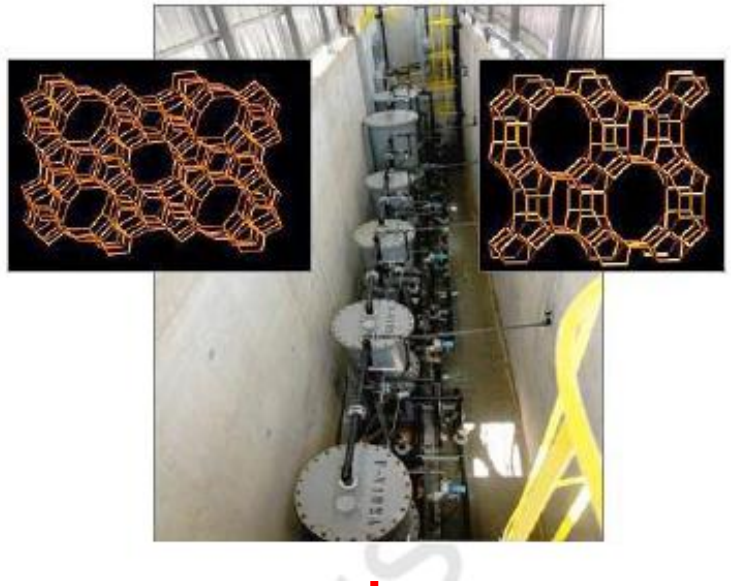
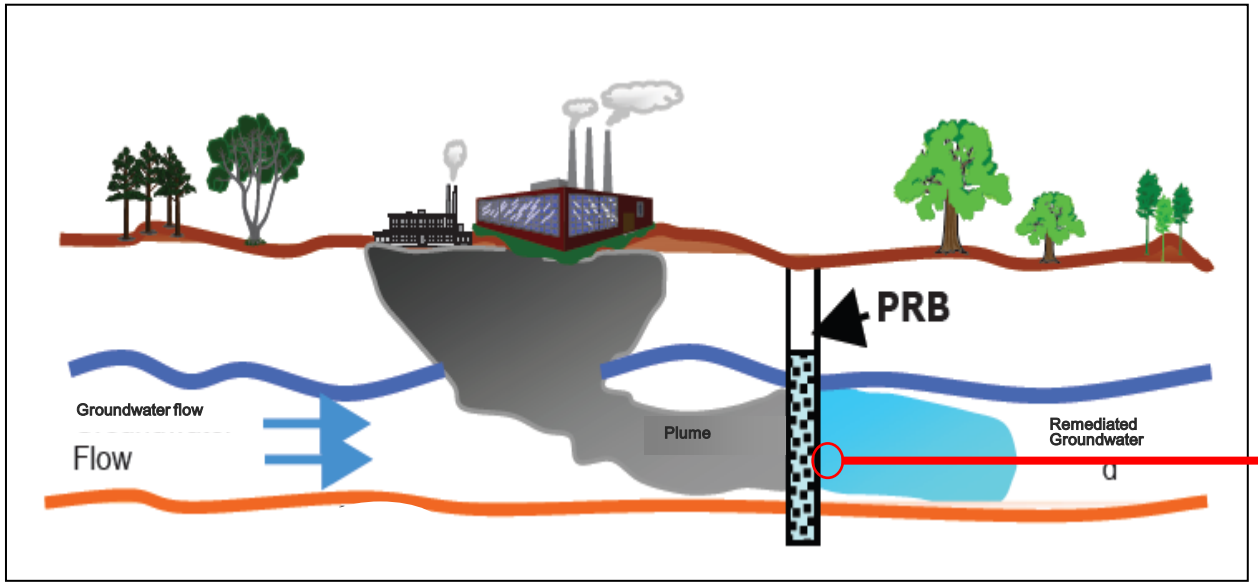
Adsorption of organic contaminants in ground water





TOLUENE
MTBE
DCE
MTBE-TOL
DCE-TOL
MTBE-DCE
HEXANE
Cl-BENZENE





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Competitive Adsorption of organic contaminants

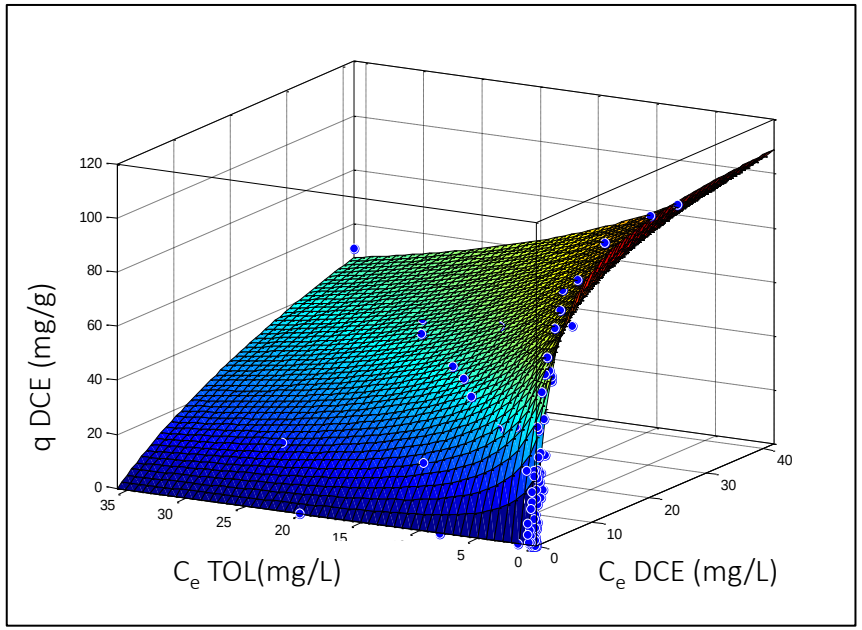
TOL-DCE su ZSM-5

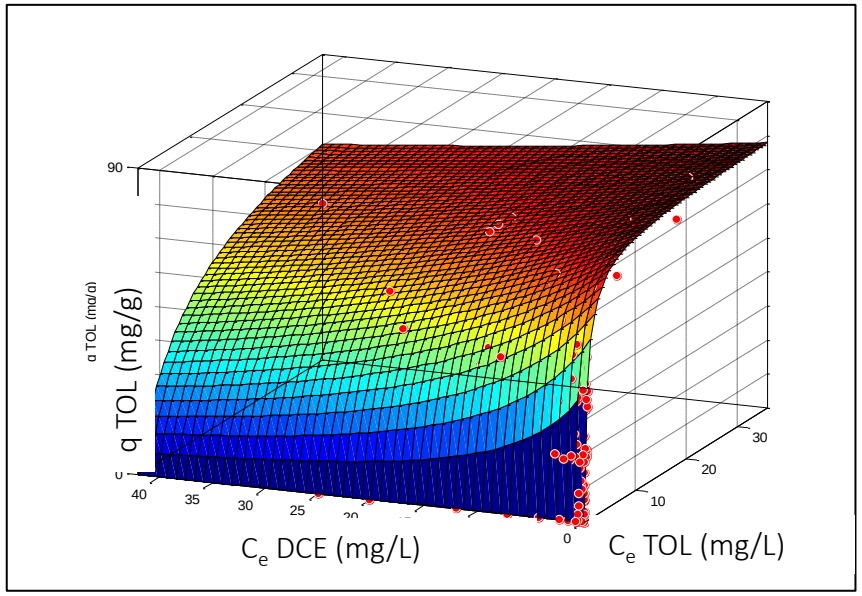
	TOL	DCE
q_s (mg/g)	79	116
b (L/mg)	2.11	0.21
R^2		0.9122

Saturation capacity ZSM-5 DCE > TOL

B ZSM-5 TOL > DCE

$$q_{s,1} = \frac{q_s b_1 C_{e,1}}{1 + b_1 C_{e,1} + b_2 C_{e,2}}$$





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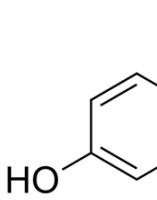
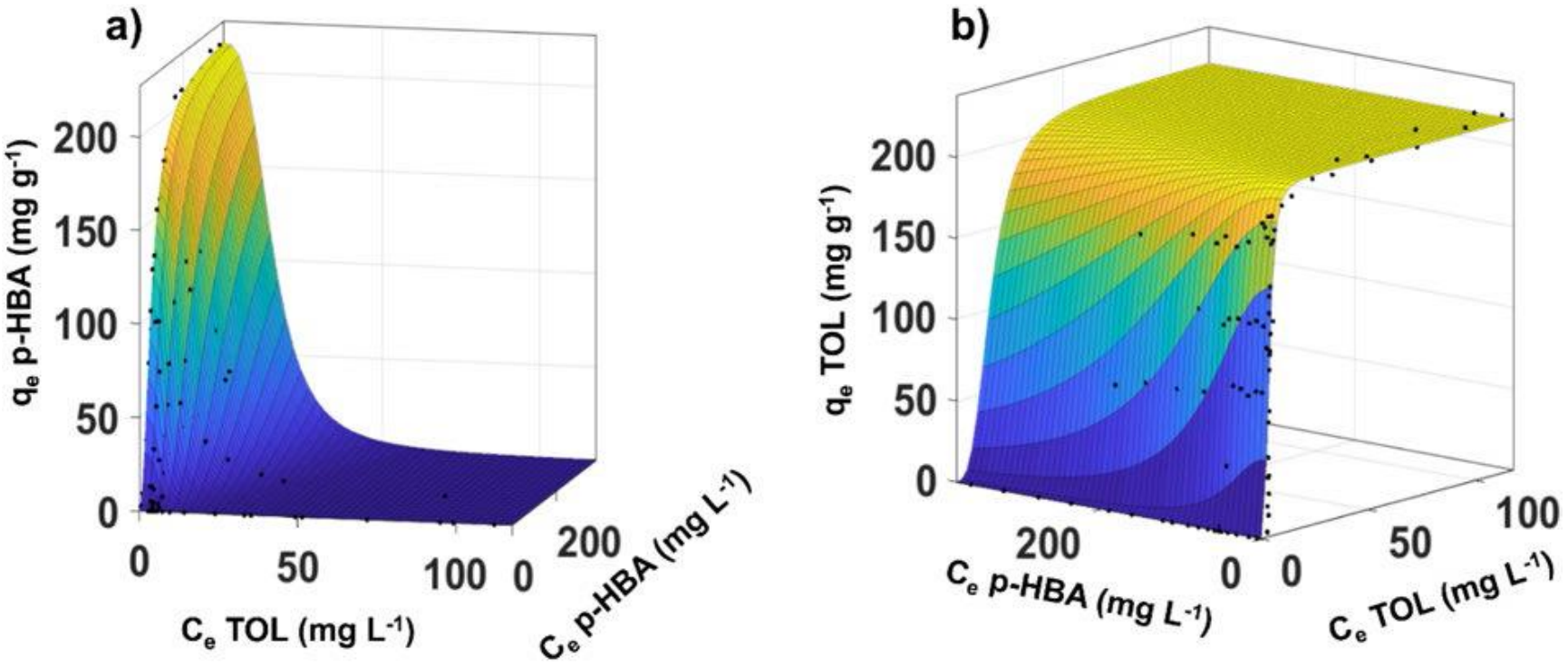
Natural Organic matter

Natural organic matter (NOM) is present in surface and ground waters 40-80% of which is composed of humic substances with a concentration range of 1-25 mg L^{-1}). Monomers of humic substances have molecular dimensions similar to those of some organic contaminants could compete with contaminants in the adsorption process.





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Thank you !!!