UNIVERSIDAD COMPLUTENSE MADRID

REMTAVARES
Red Madrileña de Tratamientos Avanzados de Aguas Residuales

Workshop REMTAVARES 2020

Application of sludge-based activated carbons for effective adsorption of neonicotinoid pesticides

Eva Sanz Santos, M. Larriba, V. I. Águeda, S. Álvarez-Torrellas, G. Ovejero, J. García

Facultad de Ciencias Químicas
Departamento de Ingeniería Química y de Materiales

evsanz08@ucm.es

1. INTRODUCTION

Surface and ground water are highly contaminated
An **effective** method is urgently required

Persistent

Non biodegradable

~~Conventional WWTP~~

High toxicity

1. INTRODUCTION

Neonicotinoid pesticides are the most widely used insecticides in the world

Negative Environmental Effects

Bee decline

COMMISSION IMPLEMENTING DECISION (EU) 2018/840

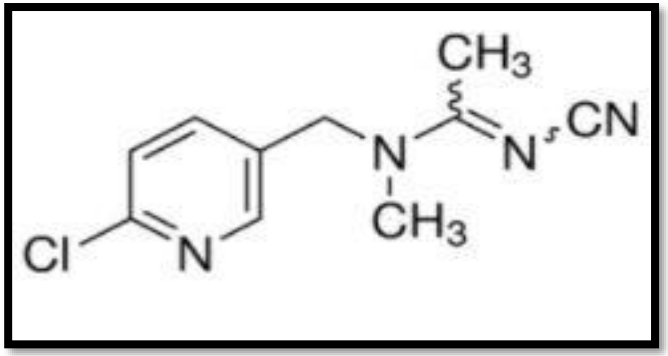
of 5 June 2018

establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council and repealing Commission Implementing Decision (EU) 2015/495

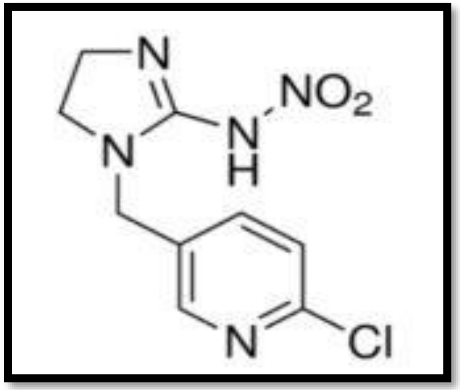
(notified under document C(2018) 3362)

Nombre de la sustancia/grupo de sustancias	N.º CAS (¹)	N.º UE (²)	Método analítico indicativo (³) (⁴)	Límite máximo aceptable de detección del método (ng/l)
17-alfa-etinilestradiol (EE2)	57-63-6	200-342-2	SPE, LC-MS-MS en grandes volúmenes	0,035
17-beta-estradiol (E2), estrona (E1)	50-28-2, 53-16-7	200-023-8	SPE, LC-MS-MS	0,4
Antibióticos macrólidos (⁵)			SPE, LC-MS-MS	19
Metiocarb	2032-65-7	217-991-2	SPE, LC-MS-MS o GC-MS	2
Neonicotinoides (⁶)			SPE, LC-MS-MS	8,3
Metaflumizona	139968-49-3	604-167-6	LLE, LC-MS-MS o SPE, LC-MS-MS	65
Amoxicilina	26787-78-0	248-003-8	SPE, LC-MS-MS	78
Ciprofloxacina	85721-33-1	617-751-0	SPE, LC-MS-MS	89

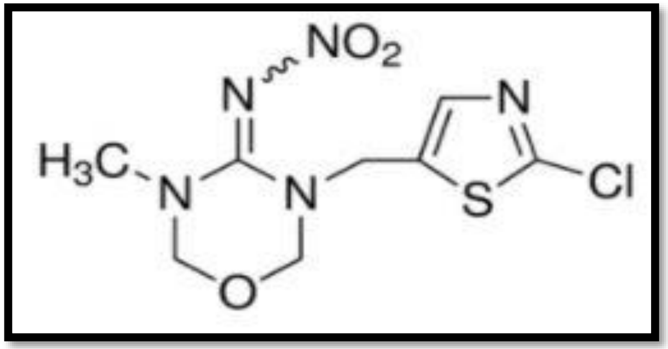
1. INTRODUCTION



Acetamiprid (ACT)
Molecular volume: 266 Å^3



Imidacloprid (IMD)
Molecular volume: 271 Å^3



Thiamethoxam (THM)
Molecular volume: 303 Å^3

1. INTRODUCTION

In Spain, around **1.200.000 tons** of **sewage sludge** (dry solid) are produced annually

↑ industrialization + ↑ urbanization = ↑ sludge production

Agricultural usage, landfilling or incineration are causing secondary pollution problems

How to solve this problem?

Valorization

2. EXPERIMENTAL METHOD

Synthesis of the activated carbons

Drying sludge

24h, 105°C

Impregnation

24h, room temperature

$ZnCl_2$, $FeCl_3$, $Fe(NO_3)_3$ and $Fe_2(SO_4)_3$

Drying

24h, 105°C

Pyrolysis

800°C, 2h, N_2 flow

Washing

1º) HCl 5M

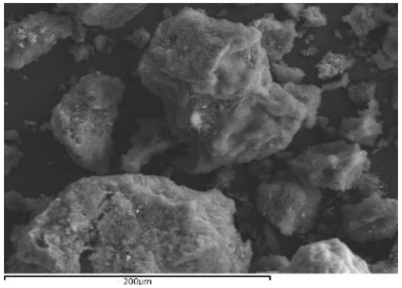
2º) Deionized H_2O

Drying

24h, 105°C

Pyrolysis

800°C, 2h, N_2 flow



2. EXPERIMENTAL METHOD

Experimental adsorption tests

Operation conditions

Orbital shaker

Solution volume: 25 mL

Room temperature

Stirring speed: 250 r.p.m.

Initial pesticide concentration: 50 mg L^{-1}

Adsorbent particle size: 250-50 µm.

Adsorbent load:

- Kinetic tests: 0.3 g L^{-1}
- Equilibrium adsorption tests: 0.06 – 1.5 g L^{-1}

Characterization of the precursor: sludge

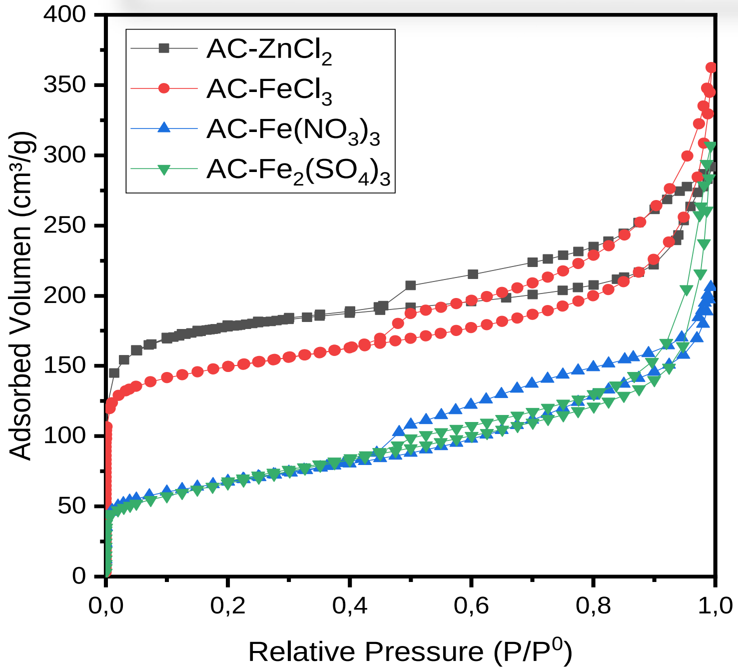
Pharmaceutical industry sludge: Ercros Industrial, Aranjuez (Madrid)

Sludge											
Ultimate analysis (%)											
C	O	H	N	P	S	Cl					
47.89	6.84	6.62	3.38	1.18	0.49	1.13					
Metal content (%)											
Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe	Cu	Zn	Ni
0.15	0.02	0.38	0.17	0.49	7.25	0.02	0.01	0.19	0.01	0.02	0.03
Total solids (g/L)	56.76										
Volatile solids (g/L)	46.24										
Fixed solids (g/L)	10.52										
COD (g O_2/L)	55.36										

80%

3. RESULTS AND DISCUSSION

Characterization of the activated carbons



Micro-mesoporous character of activated carbons: N_2 adsorption-desorption isotherms Type **IV**, according to IUPAC classification *(Thommes, M. et al., 2015)*

Adsorbent	**S_{BET} (m^2 g^{-1})**	**S_{ext} (m^2 g^{-1})**	**V_{Total} (cm^3 g^{-1})**	**V_{Micro} (cm^3 g^{-1})**	**V_{Micro}/V_{Total}**	**pH_{PIE}**
AC-$ZnCl_2$	558	145	0.35	0.15	0.43	2.14
AC-$FeCl_3$	468	170	0.56	0.16	0.29	5.40
AC-$Fe(NO_3)_3$	240	158	0.32	0.04	0.13	6.81
AC-$Fe_2(SO_4)_3$	233	203	0.48	0.01	0.02	3.08

Characterization of the activated carbons

AC-$Fe(NO_3)_3$ activated carbon has very strong **magnetic properties.**

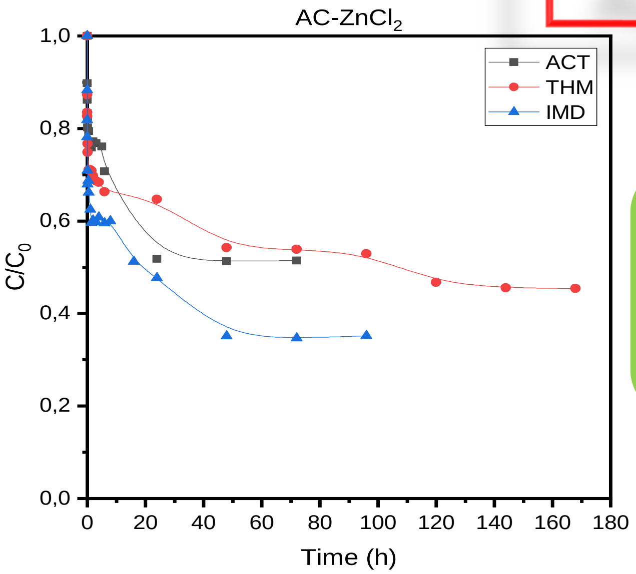
Very interesting as catalyst in heterogeneous Fenton processes (*CWPO*)

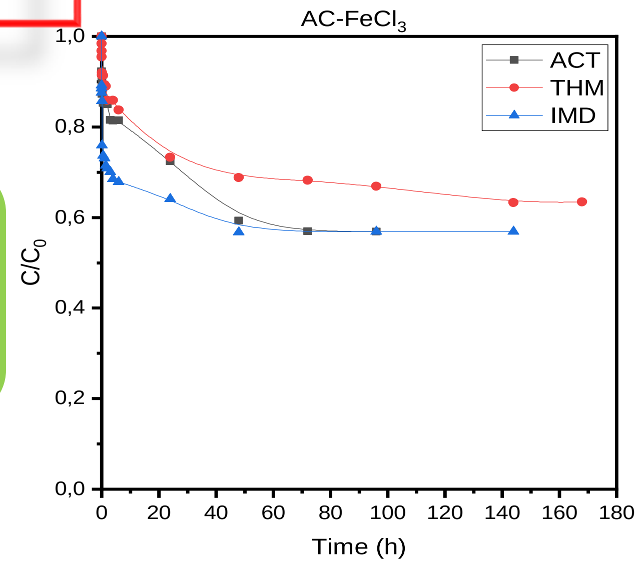
=> <u>FUTURE WORK</u>

Determination of magnetic hysteresis loop

3. RESULTS AND DISCUSSION

Adsorption kinetics

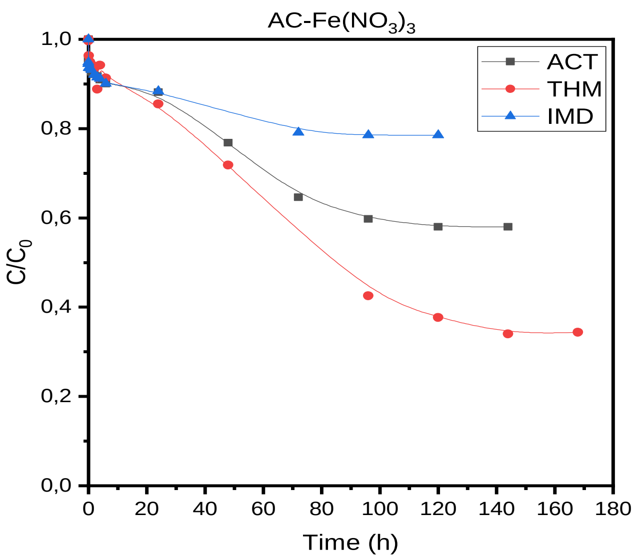


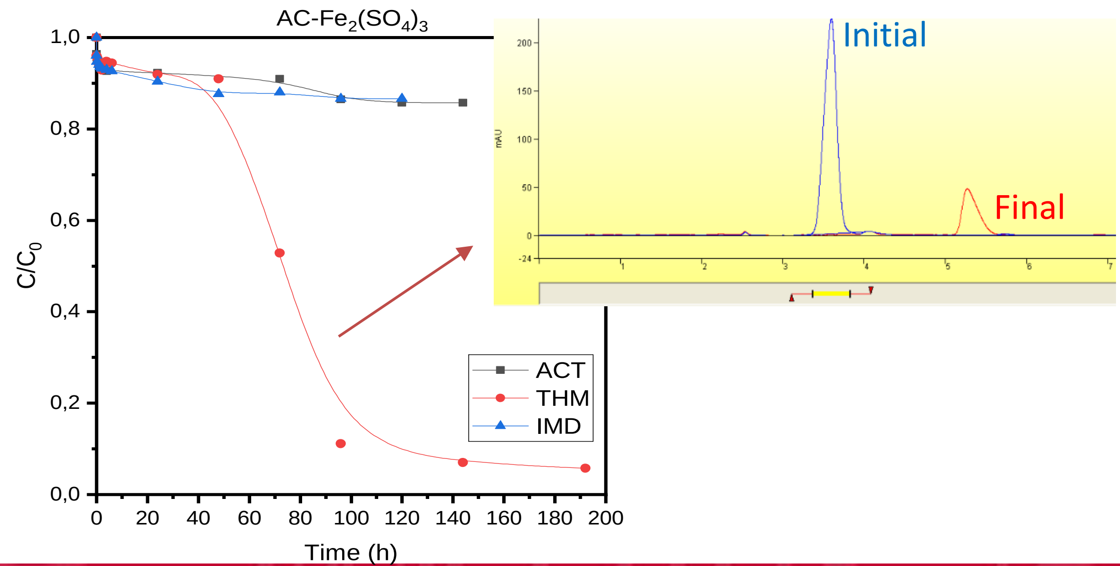


↑t_e ↑molecular volume

266 Å^3 ≈ 271 Å^3 < 303 Å^3

ACT IMD THM





3. RESULTS AND DISCUSSION

Adsorption kinetics

Adsorbent	Pesticide	Parameters	
		t_e (h)	q_e (mg g^{-1})
$AC\text{-}ZnCl_2$	ACT	24	84
	THM	144	97
	IMD	48	106
$AC\text{-}FeCl_3$	ACT	48	70
	THM	144	66
	IMD	48	76
$AC\text{-}Fe(NO_3)_3$	ACT	96	66
	THM	144	135
	IMD	72	35
$AC\text{-}Fe_2(SO_4)_3$	ACT	96	23
	THM	144	195
	IMD	72	22

Adsorbent	S_{BET} (m^2 g^{-1})
$AC\text{-}ZnCl_2$	558
$AC\text{-}FeCl_3$	468
$AC\text{-}Fe(NO_3)_3$	240
$AC\text{-}Fe_2(SO_4)_3$	233

Generally, ↑S_{BET} ↑q_e

Adsorption + Reaction contributions in THM removal

3. RESULTS AND DISCUSSION

Modelling of adsorption kinetics

Pseudo-first order model $$\ln(q_e - q) = \ln q_e - k_1 \cdot t$$

Pseudo-second order model $$\frac{t}{q} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$$

			Pseudo-first order model			Pseudo-second order model		
Adsorbent	**Micropollutant**	**q_e Exp. (mg g^{-1})**	**q_e (mg g^{-1})**	**k_1 (min^{-1})**	**R^2**	**q_e (mg g^{-1})**	**K_2 x10^{-4} (g mg^{-1} h^{-1})**	**R^2**
AC-$ZnCl_2$	**ACT**	84.31	84.21	0.0047	0.8700	78.81	1.18	0.8670
	THM	96.93	96.93	0.0233	0.8042	96.74	5.93	0.8403
	IMD	105.71	105.71	0.0228	0.8242	105.01	4.92	0.8611
AC-$FeCl_3$	**ACT**	70.06	70.04	0.0029	0.9290	65.09	0.65	0.9311
	THM	66.09	66.09	0.0027	0.9688	93.81	1.80	0.8633
	IMD	75.96	64.33	0.3789	0.9431	59.04	117.00	0.9639
AC-$Fe(NO_3)_3$	**ACT**	66.40	60.38	0.0004	0.9671	55.69	1.36	0.9418
	THM	135.00	124.48	0.0003	0.9848	111.99	0.04	0.9646
	IMD	35.42	35.41	0.0021	0.8870	33.04	0.91	0.8993
AC-$Fe_2(SO_4)_3$	**ACT**	23.29	23.29	0.0046	0.8538	39.83	49.10	0.9332
	THM	194.87	156.15	0.0002	0.9129	138.73	0.01	0.9040
	IMD	21.54	21.54	0.0044	0.8886	64.45	4.25	0.9466

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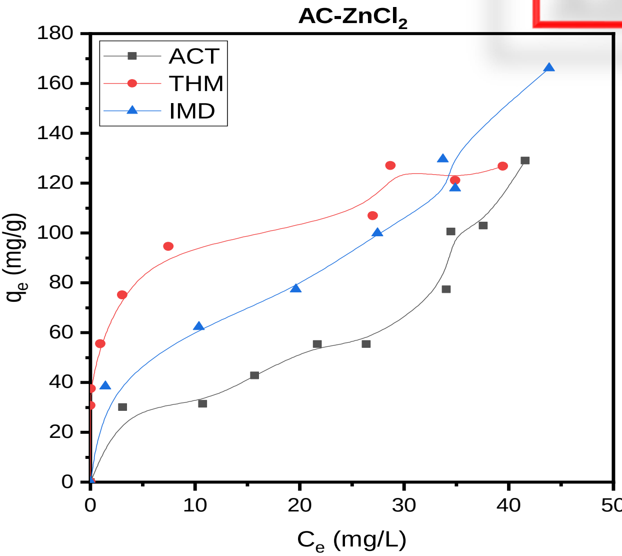
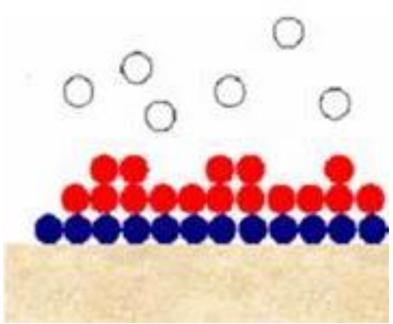
3. RESULTS AND DISCUSSION

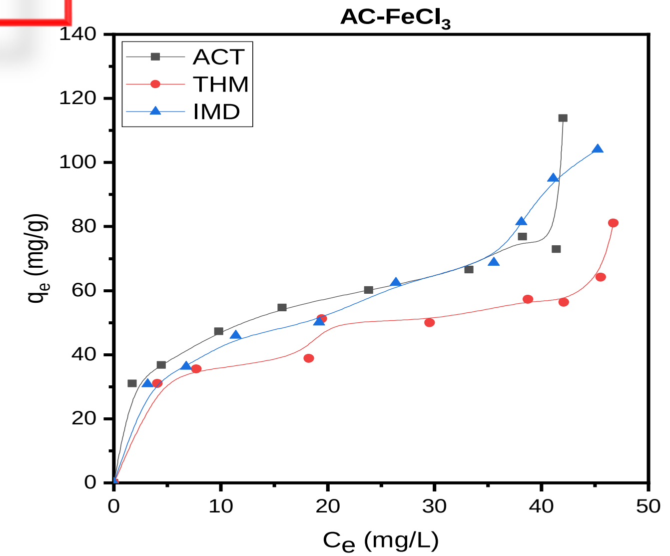
Adsorption isotherms

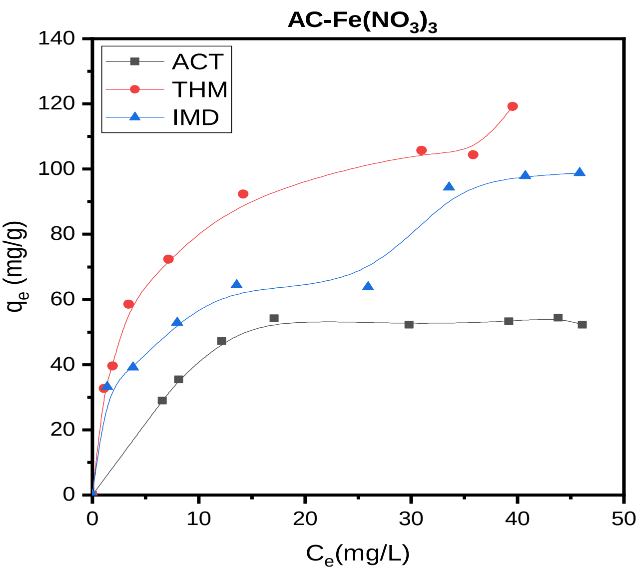


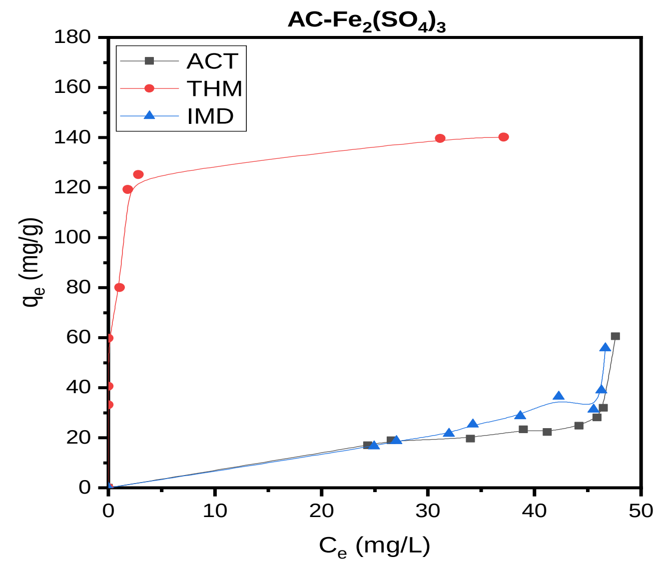
Adsorption isotherms type **S3** and **S4,** according to Giles and col. classification

Multilayer adsorption









3. RESULTS AND DISCUSSION

Modelling of adsorption isotherms

Langmuir $$q_e = \frac{q_{sat} \cdot b \cdot C_e}{1 + b \cdot C_e}$$

Freundlich $$q_e = K_F \cdot C_e^{1/n_F}$$

		Langmuir					Freundlich			
Adsorbent	**Pesticide**	**q_{exp} (mg g^{-1})**	**q_{teor} (mg g^{-1})**	**q_{sat} (mg g^{-1})**	**b (L mg^{-1})**	**R^2**	**q_{teor} (mg g^{-1})**	**K_F (L g^{-1})**	**n_F**	**R^2**
AC-$ZnCl_2$	**ACT**	128.94	112.94	886713	3.06	0.9555	115.32	1.98	0.92	0.9590
	THM	126.76	149.45	899454	4.21	0.8755	126.25	59.16	4.85	0.9786
	IMD	166.13	164.55	884860	4.24	0.9756	149.40	12.82	1.54	0.9728
AC-$FeCl_3$	**ACT**	113.88	95.89	884860	2.58	0.8899	85.05	16.24	2.26	0.9226
	THM	81.08	82.20	884860	1.72	0.8154	65.64	15.81	2.70	0.9501
	IMD	104.09	103.61	884860	2.59	0.9604	92.33	11.71	1.85	0.9692
AC-$Fe(NO_3)_3$	**ACT**	60.55	34.19	886713	0.81	0.7685	37.60	0.04	0.57	0.7930
	THM	140.19	160.52	899455	4.81	0.6790	143.31	100.95	10.31	0.9318
	IMD	55.82	39.04	884860	0.95	0.8998	42.64	0.06	0.59	0.9256
AC-$Fe_2(SO_4)_3$	**ACT**	60.55	34.19	884860	0.81	0.7685	37.09	0.06	0.60	0.7916
	THM	140.19	160.52	899455	4.81	0.6789	143.31	100.95	10.31	0.9318
	IMD	55.82	38.67	884860	0.94	0.8998	42.38	0.08	0.61	0.9254

4. CONCLUDING REMARKS

- Activated carbons show heterogeneous textural properties, characteristic of biomass-based activated carbons and maybe attributed to the heterogeneous character of sludge precursor.

- By using $Fe(NO_3)_3$ salt as an activating agent, an activated carbon with strong magnetic properties has been obtained.

- High adsorption capacity values have been obtained despite the slow adsorption kinetics, as a consequence of diffusional/steric hindrance effects.

- Generally, adsorption isotherms showed a bi-layer profile.

- For the removal of THM pesticide on AC-$Fe(NO_3)_3$ and AC-$Fe_2(SO_4)_3$ activated carbons, two simultaneous contributions, e.g., adsorption and reaction, have been observed.

Thanks!

Contact:

Grupo de Catálisis y Procesos de Separación

Universidad Complutense de Madrid
Web: www.ucm.es/gcyps
e-mail: evsanz08@ucm.es