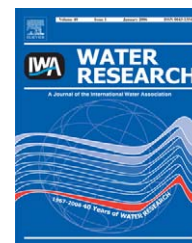


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# Assessment of organic chlorinated compound removal from aqueous matrices by adsorption on activated carbon

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## ABSTRACT

Adsorption on activated carbon is currently the most frequently used technology to remove organic chlorinated pollutants from wastewaters. The present study examines the ability of five commercially available types of activated carbon to remove organic chlorinated compounds from the effluent of a chemical plant. The various types were tested on the basis of Freundlich adsorption isotherms for 14 pure organic chlorinated compounds, of molecular weight ranging from that of dichloromethane ( $MW = 84.93 \text{ g mol}^{-1}$ ) to hexachlorobenzene ( $MW = 284.78 \text{ g mol}^{-1}$ ). The best was selected and used in a laboratory fixed-bed column to assess its removal efficiency with respect to the tested organic chlorinated compounds. Removal efficiency was always higher than 90%. These results provide information necessary to optimize scale-up from the pilot plant to the real one.

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## 1. Introduction

Organic chlorinated compounds are chemicals used on a large scale even in everyday life, and they may be industrial effluent contaminants (Yu and Chou, 2000; Shawwa et al., 2001). Some of them are toxic and are slow to biodegrade, so that they accumulate in the environment. Adsorption on activated carbon is one of the most frequently used and efficient technologies for removing volatile, semi-volatile and non-volatile chlorinated organic pollutants from aqueous industrial sludge, surface waters and drinking water (Sotelo et al., 2002; Yun et al., 1998; Eckenfelder, 1992). The amount and rate of adsorption involve thermodynamic aspects (Chianga et al., 2002) and are functions of the chemical nature of the activated carbon (Chuang et al., 2003; Karanfil and Kilduff, 1999; Kunio et al., 2001; Othman et al., 2000), which depends on the activation method employed (Cheremisinoff, 1980). An equation often used to describe solute/adsorbed equilibrium adsorption capacity  $Q_e$  ( $\text{mg g}^{-1}$ )

isotherms (Eckenfelder, 1992) derives from Freundlich's semi-empirical model:

$$\frac{X}{M} = KC^{1/n}, \quad (1)$$

where  $X$  is the weight of adsorbed compound (mg),  $M$  the weight of adsorbent substrate (g),  $K$  the adsorption constant ( $\text{mg}^{1-1/n} \text{ l}^{1/n} \text{ g}^{-1}$ ),  $C$  the residual compound concentration in solution ( $\text{mg l}^{-1}$ ) and  $n$  the adsorption constant (dimensionless). Non-ideal competitive interactions (Smith, 1991) explain observed deviations from this model. Although Freundlich adsorption isotherms indicate the best activated carbon, they are not sufficient to design a full-scale plant adsorption column that works in non-ideal equilibrium conditions. Inside the column absorbing bed, the thickness of the mass transfer zone (MTZ) in cm (Eckenfelder, 1992; La Grega et al., 1994) depends on various parameters. The relationship between output pollutant concentration  $C_e$  ( $\text{mg l}^{-1}$ ) vs time may be represented by the so-called “breakthrough curve” (Fig. 1).

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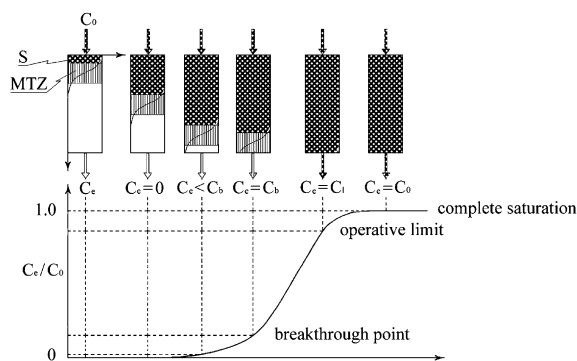
## Nomenclature

$a = \frac{N_0}{C_0 V}$	fixed-bed operative parameter ( $\text{h m}^{-1}$ )
$b = -\frac{1}{KC_0} \ln\left(\frac{C_0}{C_b} - 1\right)$	fixed-bed operative parameter (h)
BDST	bed depth service time (h)
bp	boiling point ( $^{\circ}\text{C}$ )
$C$	residual compound concentration in solution ( $\text{mg l}^{-1}$ )
$C_b$	breakthrough concentration ( $\text{mg l}^{-1}$ )
$C_e$	output pollutant concentration ( $\text{mg l}^{-1}$ )
$C_l$	operative limit concentration ( $\text{mg l}^{-1}$ )
$C_0$	input concentration ( $\text{mg l}^{-1}$ )
$d$	relative density (dimensionless)
$D$	dipole moment (Debye)
$K$	reaction kinetics constant ( $\text{l h}^{-1} \text{mg}^{-1}$ )
$K$	adsorption constant ( $\text{mg}^{1-1/n} \text{l}^{1/n} \text{g}^{-1}$ )
$k$	time constant (h)
LOD	limit of detection ( $\text{ng l}^{-1}$ ) as three times the signal-to-noise ratio
$\log K_{ow}$	logarithm of octanol-water partition coefficient (dimensionless)
LOQ	limit of quantification ( $\text{ng l}^{-1}$ ) as six times the signal-to-noise ratio

$M$	weight of adsorbent substrate (g)
mp	melting point ( $^{\circ}\text{C}$ )
MTZ	mass transfer zone (cm)
MW	molecular weight ( $\text{g mol}^{-1}$ )
$n$	adsorption constant (dimensionless)
$nD_{20}$	refractive index (dimensionless)
$N_0$	activated carbon adsorbent capacity ( $\text{kg m}^{-3}$ ), i.e., mass of contaminant removed per unit of column volume ( $\text{m}^3$ )
$Q_e = \frac{X}{M} = KC^{1/n}$	equilibrium adsorption capacity ( $\text{mg g}^{-1}$ )
$t$	service time (h)
$V$	superficial velocity through column, i.e., flow ( $\text{m}^3 \text{h}^{-1}$ ) per unit section of column ( $\text{m}^2$ )
$X$	weight of adsorbed compound (mg)
$Z$	bed depth (m)
$Z_0 = \frac{V}{KN_0} \ln\left(\frac{C_0}{C_b} - 1\right)$	critical bed thickness (m)

## Greek letter

$$\eta = \frac{Z-Z_0}{Z} \times 100 \text{ percent adsorption efficiency (dimensionless).}$$



**Fig. 1 – Breakthrough curve.** S: saturation zone; MTZ: adsorbing zone;  $C_0$ : input concentration;  $C_e$ : output concentration;  $C_e/C_0$ : ratio between output and input concentrations. Above  $C_b$ , so-called breakthrough concentration,  $C_e$  is no longer acceptable and adsorbing bed needs to be regenerated. In particular, “breakthrough point” here is defined as point reached when concentration is 10–5% of initial one.  $C_l$ : operative limit concentration;  $C_e = C_0$ : complete saturation.

This curve can be fitted by the following equation:

$$\frac{C_{out}}{C_{in}} = \frac{t^n}{k^n + t^n}, \quad (2)$$

where  $t$  is the elapsed time (h), while the constant  $k$  (time constant, h) and the dimensionless exponent  $n$  depend on the system under study. A simplified relationship (Hutchins, 1973), involving the desired “service time  $t$ ” (h) of a filtering unit, its “bed depth  $Z$ ” (m) and the “bed depth service time”

(BDST) (h), allows us to design an adsorbing bed, provided that  $C_0$  and  $C_b$  ( $\text{mg l}^{-1}$ ) are known. At this point, BDST can be used to determine fixed-bed operative parameters  $a$  and  $b$ :

$$t = aZ + b, \quad (3)$$

where  $a = N_0/C_0 V$  “fixed-bed operative parameter” ( $\text{h m}^{-1}$ ),  $N_0$  being the activated carbon “adsorbent capacity” ( $\text{kg m}^{-3}$ ), i.e., mass of contaminant removed per unit of column volume ( $\text{m}^3$ ),  $C_0$  = input concentration ( $\text{mg l}^{-1}$ ) and  $V$  = superficial velocity through the column, i.e., flow ( $\text{m}^3 \text{h}^{-1}$ ) per unit section of column ( $\text{m}^2$ );  $b = -(1/KC_0) \ln(C_0/C_b - 1)$  is the “fixed-bed operative parameter” (h) with  $K$  = reaction kinetics constant ( $\text{l h mg}^{-1}$ ) and  $C_b$  = “breakthrough concentration” ( $\text{mg l}^{-1}$ ).

Considering only the class of chlorinated organic compounds examined here, the aims of the present work are as follows: (1) to study the removal efficiency of five commercial activated carbons by determining their Freundlich adsorption isotherms and choosing the best among them; (2) to verify the removal efficiency of the chlorinated compounds by continuum absorption on a fixed bed of granular activated carbon; (3) to optimize parameters useful for scaling-up from the pilot adsorbing column to the full-scale plant.

## 2. Materials and methods

### 2.1. Materials and reagents

Reagents used for activated carbon adsorption tests were sodium chloride 99.5% RPE (Carlo Erba reagents), sodium hydroxide 98% Arista R<sup>®</sup> (BDH) and Milli-Q water (WP 4100 reagent-grade water purifier-SMEG). Reagents used to wash

**Table 1 – Main characteristics of tested activated carbons**

Activated carbon commercial name	Specific surface (m <sup>2</sup> g <sup>-1</sup> )	Iodine number (mg g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Apparent density (g l <sup>-1</sup> )	Grain size (mm)	Removable substances <sup>a</sup>
GAC 1240	1175	1075	1.0	490	0.4–1.7 <sup>b</sup>	Dyestuffs, dissolved organic compounds
GVC 12 × 40 (now GCN 1240)	1150	1050	0.8	510	0.4–1.7 <sup>b</sup>	Compounds causing unpleasant odors and tastes, organic micro-pollutants
RB 1	1100	1000	0.9	510	1.0 <sup>c</sup>	Compounds causing unpleasant odors and tastes, chlorine, ozone, dissolved organic compounds
pK 1-3	850	750	1.3	290	1–3	Compounds causing unpleasant odors and tastes, chlorine, ozone, organic substances from drinking water or processing water, pesticides
ROW 0.8 SUPRA	1150	1050	1.05	400	0.8 <sup>c</sup>	Compounds causing unpleasant odors and tastes, chlorine, dissolved pesticides and organic substances
Regeneration is always “thermal”.						
<sup>a</sup> According to manufacturer's specifications.						
<sup>b</sup> 12 × 40 mesh.						
<sup>c</sup> Cylinder diameter.						

glassware were concentrated detergent Contrad 2000 (BDH), sulphuric acid 98% AnalAR<sup>®</sup> (BDH) and ammonium persulfate 98% (Aldrich).

## 2.2. Adsorbents

The five types of activated carbons chosen for this work were the most frequently used on the Italian market. Supplied by Norit Italia S.p.A., their main characteristics are listed in Table 1.

The activated carbons were washed in cold Milli-Q water and subjected to three washing cycles in boiling Milli-Q water. At the end of each cycle, the water was analyzed to check for the presence of extraneous interfering substances and then oven-dried overnight at 150 °C.

## 2.3. Adsorbates

Fourteen organic chlorinated compounds were examined, as listed in Table 2, which includes some of their physical-chemical characteristics.

## 2.4. Standards

Freundlich adsorption isotherms were determined for all five activated carbons, using low and high boiling point mixtures

of chlorinated compounds. The standard 8500-6634 “halogenated volatile mixtures” (HVM, Hewlett-Packard) at an average concentration of 100 µg ml<sup>-1</sup> in methanol, was used for low-boiling compounds. A mixture of 1,2,3-trichlorobenzene 99% (Aldrich), 1,2,4-trichlorobenzene 99% (Aldrich), hexachloro 1,2-butadiene 97% (Aldrich) and hexachlorobenzene 99% (Aldrich) at an average concentration of 100 µg ml<sup>-1</sup> in acetone was prepared to study the behavior of high-boiling compounds.

## 2.5. Preparation of standard solutions used to determine removal efficiency of chlorinated compounds

For volatile chlorinated compounds, 0.5 ml of concentrated HVM standard solution was brought to 1 l in Milli-Q water. Starting from this solution, five more standard solutions were prepared: the first one by diluting 200 ml of the solution to 1 l, and the others by further dilutions following the same procedure. For non-volatile chlorinated compounds, the procedure was the same, but 5 ml of concentrated standard in acetone were first diluted to 1 l. Therefore, for volatile chlorinated compounds the concentration range was 10–1.6 × 10<sup>-2</sup> µg l<sup>-1</sup>, while for non-volatile chlorinated compounds the range was 100–1.6 × 10<sup>-1</sup> µg l<sup>-1</sup>.

**Table 2 – Some physical–chemical characteristics of 14 chlorinated organic compounds (The Merck Index, 1983)**

Substance	MW (g mol <sup>-1</sup> ) <sup>a</sup>	bp (°C) <sup>b</sup>	mp (°C) <sup>c</sup>	nD <sub>20</sub> <sup>d</sup>	Density	log K <sub>ow</sub> <sup>e</sup>	Dipole, D <sup>f</sup>
<b>Volatile</b>							
Dichloromethane	84.93	40.0	–97.0	1.424	1.325	1.15	1.34
Trichloromethane	119.38	61.0	–63.0	1.446	1.492	1.93	1.02
1,1,1-Trichloroethane	133.41	75.0	–35.0	1.436	1.338	2.49	1.57
Carbon tetrachloride	153.82	76.5	–23.0	1.460	1.594	2.73	0.00
1,2-Dichloroethane	98.96	83.0	–35.0	1.445	1.256	1.47	0.00
Trichloroethylene	131.39	86.7	–84.8	1.476	1.463	2.42	0.90
1,1,2-Trichloroethane	133.41	112.5	–35.0	1.471	1.435	2.17	1.25
Tetrachloroethylene	165.83	121.0	–22.0	1.506	1.623	2.88	0.00
1,1,1,2-Tetrachloroethane	167.85	134.5	–70.0	1.481	1.598	2.66	2.33
Trans 1,4-dichloro-2-butene	125.00	155.5	2.0	1.488	1.183	2.37	0.00
<b>Non-volatile</b>							
1,2,4-Trichlorobenzene	181.45	214.0	16.0	1.571	1.454	4.05	1.54
1,2,3-Trichlorobenzene	181.45	218.5	54.0	1.5776	1.690	4.07	3.08
Hexachloro-1,3-butadiene	260.76	215.0	–20.5	1.555	1.665	4.90	0.00
Hexachlorobenzene	284.78	324.5	228.0	1.5743	2.044	5.50	0.00

<sup>a</sup> MW = molecular weight (g mol<sup>-1</sup>).<sup>b</sup> bp = boiling point (°C).<sup>c</sup> mp = melting point (°C).<sup>d</sup> nD<sub>20</sub> = refractive index (dimensionless).<sup>e</sup> log K<sub>ow</sub> = logarithm of octanol-water partition coefficient (dimensionless).<sup>f</sup> D = dipole moment (Debye).

## 2.6. Solid-phase microextraction (SPME)

In the course of our experiments, a SPME fiber (Supelco) and PTFE/silicone septa (Supelco) were used (Boussahel et al., 2002). The fiber holder was a syringe, made up of a stainless-steel barrel with a plunger sliding inside the barrel, holding a needle to which the fiber was attached. The barrel was placed inside an adjustable depth gauge.

## 2.7. Gas-chromatographic (GC) equipment

A CP 9001 gas-chromatograph (Chrompack) was used for GC analyses equipped with an electron capture detector (ECD) (Chrompack). Auxiliary gas was nitrogen, flow rate 35 ml min<sup>-1</sup>, and the septum (i.e., injector) cleaning gas was nitrogen, flow rate 15 ml min<sup>-1</sup>. The carrier gas was helium, flow rate 0.8 ml min<sup>-1</sup>. Volatile compounds were chromatographically separated with medium polarity capillary column DB 624, 60 m × 0.25 (i.d.) mm × 1.4 μm (J & W), and high boiling point compounds with a non-polar capillary column DB 5, 25 m × 0.2 (i.d.) mm × 0.33 μm. Chromatographic data were processed with the Maestro 2.3 program (Chrompack).

## 2.8. Analysis of organic chlorinated compounds

Volatile compounds were determined by SPME fibers in polydimethylsiloxane (PDMS)/carboxen, conditioned for 30 min at 280 °C to avoid the occurrence of spurious GC peaks. As they cannot exceed a certain limit, in order to avoid analyte thermal decomposition, their positions within the sampling vial and GC injector were optimized in conjunction with their adsorbing and desorbing time and temperature.

Two gram of sodium chloride and 10 ml of sample were set in a 20-ml magnetically stirred vial inside a thermostatic cell at 40 °C, together with the SPME holder for 15 min to reach thermal equilibrium between sample and fiber. The fiber was exposed for 45 min to the headspace vapors above the sample, then inserted into the GC and exposed for about 5 min to the carrier gas. GC conditions were: injector temperature: 240 °C; pressure on column head: 120 KPa; temperature program: 35 °C constant for 10 min, then 4 °C min<sup>-1</sup> up to 210 °C, constant for 10 min; detector temperature: 300 °C.

Non-volatile compounds were determined using a SPME fiber made of PDMS conditioned for about 1 h at 250 °C. Four gram of sodium chloride and 20 ml of sample were put in a 20-ml magnetically stirred vial set in a thermostatic cell at 50 °C. The SPME holder was kept inside the solution for 15 min to attain thermal equilibrium; then the fiber was exposed to the sample for 20 min and immediately after to the carrier gas in the GC injector for 5 min. GC conditions were: injector temperature: 240 °C; pressure on column head: 80 KPa; temperature program: 80 °C for 3 min, 20 °C min<sup>-1</sup> up to 165 °C; constant for 18 min, 20 °C min<sup>-1</sup> up to 290 °C; constant for 7 min; detector temperature: 300 °C.

## 2.9. Detection limits and reproducibility

For both volatile and non-volatile organic compounds, calibration curves were determined by repeating the same injection of the standard for each point four times. The same experimental conditions were also maintained for sample analysis. Limits of detection (LOD) were calculated as a signal-to-noise ratio equal to 3, whereas limits of quantification

**Table 3 – Limits of detection and quantification of selected compounds**

	PDMS/carboxen			
	Immersion		Headspace	
	LOD (ngl <sup>-1</sup> )	R <sup>2</sup>	LOD (ngl <sup>-1</sup> )	R <sup>2</sup>
Volatile				
1,1,1-Trichloroethane	0.9	0.991	0.3	0.991
Carbon tetrachloride	0.1	0.999	0.01	0.999
Trichloroethylene	0.9	0.983	0.2	0.969
1,1,2-Trichloroethane	2.0	0.999	0.4	0.997
Tetrachloroethylene	0.8	0.996	0.1	0.997
1,1,1,2-Tetrachloroethane	0.8	0.999	0.2	0.981
PDMS				
	LOD (ngl <sup>-1</sup> )		R <sup>2</sup>	
Non-volatile				
1,2,4-Trichlorobenzene	10		0.991	
1,2,3-Trichlorobenzene	30		0.999	
Hexachloro-1,3-butadiene	9.0		1.00	
Hexachlorobenzene	0.4		0.997	
LOD = limit of detection (ngl <sup>-1</sup> ).				
Detection limit has been calculated 3 times the signal-to-noise ratio.				

(LOQ) were set at twice the LOD. Values for some selected compounds are listed in Table 3.

## 2.10. Adsorption procedures

### 2.10.1. Adsorption isotherm test equipment

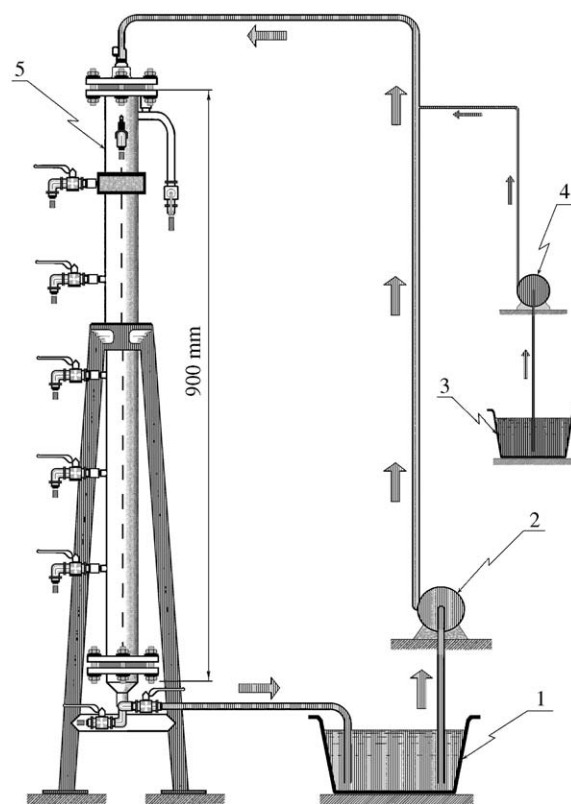
Freundlich adsorption isotherms were obtained by using a thermostatic bath (Haake 3M) to control the temperature of the magnetically stirred organic chlorinated compound solutions within a  $\pm 1^\circ\text{C}$  range.

### 2.10.2. Laboratory pilot plant

The activated carbon laboratory column was fed with a solution, hereafter called as matrix solution, having a composition similar to the fluid discharged from a full-scale plant (water Millipore Milli-Q, 1% NaCl, NaOH to adjust pH to  $\sim 12$ ) (La Grega et al., 1994). The column containing the fixed activated carbon bed (GAC 1240) used during these tests was made of PVC, was about 900 mm high and had an internal diameter of about 40 mm. Five collecting points were set along the column. The column was fed from the top by a peristaltic pump (Zeromax JK1), whose flow was controlled by a flowmeter, and the standard was added to the matrix by an HPLC pump in order to guarantee constant flow rate and feed composition. To assure homogeneous feeding, the first 100 mm of column were filled with glass beads. Fig. 2 shows a sketch of the system.

### 2.10.3. Determination of Freundlich adsorption isotherms

According to the ASTM D 3860-89a protocol, the following procedure was applied to determine Freundlich adsorption isotherms and to test the efficiency of the five types of



**Fig. 2 – Experimental setup: 1—matrix reservoir; 2—peristaltic pump; 3—concentrated standard reservoir; 4—HPLC pump; 5—activated carbon column.**

activated carbon. For every type tested, different quantities of activated carbon powder, i.e., 1.0, 2.5, 5.0, 7.5, 10.0, 25.0 and 50.0 mg, were added to seven contaminated water samples of



550 ml each. One extra contaminated water sample was used as a blank (without activated carbon). Each flask was vigorously stirred magnetically in a thermostatic bath at 20 °C for 2 h, and the water phase was then analyzed.

#### 2.10.4. Laboratory “activated carbon” column

Norit GAC 1240 granulated activated carbon was the adsorbent chosen to be further tested for abatement of organic chlorinated compounds on a fixed bed. In order to obtain a bed 480 mm high inside the 900 mm × 40 mm laboratory pilot plant column, about 400 g of activated carbon were used. Liquid samples of about 30 ml each were withdrawn every 24 h and the storage reservoir reintegrated with the matrix solution. During adsorption tests, starting concentrations of the chlorinated organic compounds were ca. 70 µg l<sup>-1</sup> for low-boiling compounds and about 7 µg l<sup>-1</sup> for high-boiling ones. The matrix solution flow rate was kept constant at 0.77 mms<sup>-1</sup>. All filtering tests were performed at room temperature. Volatile compounds were analyzed by diluting the samples 10 times.

### 3. Results and discussion

The Freundlich adsorption isotherms of five activated carbons were compared in order to select the best for adsorbing the examined organic chlorinated compounds. Results are shown in Table 4.

The adsorption values show that volatile chlorinated compounds are best adsorbed by RB 1 and non-volatile ones by pK 1-3. GAC 1240 absorbed both volatile and non-volatile compounds very efficiently and was thus selected among the five types to verify its removal efficiency on a fixed bed at 20 °C. Some preliminary sorption experiments were carried out to establish the time necessary to attain equilibrium conditions at 20 °C. This temperature was chosen because

filtering tests on fixed beds are normally carried out at room temperature. The resulting trends showed that 90% of each compound was adsorbed within the first 15 min and the remaining 10% after about 1.5 h. These two different adsorption velocities are due to the presence of the activated carbon surface of macro-, meso- and micro-pores. Diffusion is very fast through macro- and meso-pores but slow through micro-pores, because of their smaller size (Peel and Benedek, 1980). For convenience, the selected equilibrium time was set at 2 h.

For GAC 1240, breakthrough curves were determined by representing the percentage of pollutant remaining in solution as a function of the service time of the activated carbon bed. Breakthrough concentration was set at 10% of the starting concentration (Hutchins, 1973).  $C_e/C_0$  was shown to be 0.1 and then 0.9 at different bed depths (160, 320 and 480 mm) by interpolating points corresponding to the breakthrough lines. This was accomplished using Eq. (2). The results are reported in Table 5 where  $R^2$  represents the goodness of fit.

These data were used to determine the linear relationship between column service time and activated carbon bed thickness.

To evaluate activated carbon bed adsorption efficiency, parameters used were the constants  $K$  and  $N_0$ , defined in Eq. (3), and  $Z_0$ , defined as “critical bed thickness” (m), which represents the minimum bed thickness necessary to prevent  $C_e > C_b$  at  $t = 0$ , due to the fact that, initially, the first few bed layers are immediately saturated by a certain pollutant.  $Z_0$ , which differs for each specific compound, may be determined by

$$Z_0 = \frac{V}{KN_0} \ln \left( \frac{C_0}{C_b} - 1 \right), \quad (4)$$

where  $V$ ,  $C_0$ ,  $C_b$ ,  $K$  and  $N_0$  are already defined in Eq. (3). Table 6 reports  $Z_0$  together with the parameters of the BDST introduced in Eq. (3) and calculated by considering first  $C_e/C_0 = 0.1$  and then  $C_e/C_0 = 0.9$ .

**Table 4 – Equilibrium adsorption capacity ( $Q_e$ ) of activated carbons**

Substance	RB 1 (mg g <sup>-1</sup> )	GAC 1240 (mg g <sup>-1</sup> )	GVC 12 × 40 (mg g <sup>-1</sup> )	PK 1–3 (mg g <sup>-1</sup> )	ROW 0.8 SUPRA (mg g <sup>-1</sup> )
Dichloromethane	1.37	0.666	0.793	0.169	0.0273
Trichloromethane	1.34	0.619	0.665	0.232	0.413
1,1,1-Trichloroethane	1.88	1.14	0.893	0.262	0.547
Carbon tetrachloride	1.66	1.52	9.82	1.09	10.6
1,2-dichloroethane	6.53	4.59	4.03	1.27	2.99
Trichloroethylene	4.37	1.54	0.746	0.576	5.17
1,1,2-Trichloroethane	2.31	1.54	0.921	0.425	0.406
Tetrachloroethylene	42.2	3.55	3.01	3.55	43.6
1,1,1,2-Tetrachloroethane	2.05	0.758	1.56	0.456	0.489
Trans 1,4-dichloro-2-butene	3.21	7.65	8.89	2.12	0.896
1,2,4-trichlorobenzene	2.56	4.56	2.48	15.2	1.98
1,2,3-trichlorobenzene	0.758	4.56	3.25	7.69	2.01
Hexachloro-1,3-butadiene	0.989	0.924	0.889	2.12	0.898
Hexachlorobenzene	0.306	0.797	0.501	1.09	0.567

**Table 5 – Breakthrough values of tested organic chlorinated compounds**

Substance	Bed depth (cm)	Time ( $C_e/C_0 = 0.1$ ) (h)	Time ( $C_e/C_0 = 0.9$ ) (h)	$R^2$
Dichloromethane	16	192	343	0.992
	32	395	527	0.995
	48	589	712	0.990
Trichloromethane	16	190	340	0.991
	32	390	530	0.996
	48	590	700	0.989
1,1,1-Trichloroethane	16	197	313	0.991
	32	433	565	0.989
	48	620	760	0.978
Carbon tetrachloride	16	191	230	0.994
	32	455	550	0.988
	48	625	680	0.986
1,2-Dichloroethane	16	99	199	0.957
	32	336	443	0.986
	48	532	631	0.983
Trichloroethylene	16	162	227	0.980
	32	448	470	0.994
	48	600	680	0.986
1,1,2-Trichloroethane	16	168	195	0.988
	32	359	526	0.995
	48	670	700	0.991
Tetrachloroethylene	16	182	284	0.994
	32	430	580	0.989
	48	670	753	0.976
1,1,1,2-Tetrachloroethane	16	168	185	0.996
	32	395	478	0.999
	48	680	700	0.998
Trans 1,4-dichloro-2-butene	16	168	242	0.988
	32	397	479	0.990
	48	590	650	0.989
1,2,4-Trichlorobenzene	16	176	272	0.987
	32	441	519	0.993
	48	680	760	0.978
1,2,3-Trichlorobenzene	16	255	400	0.998
	32	540	610	0.969
	48	790	920	0.987
Hexachloro-1,3-butadiene	16	170	220	0.977
	32	272	380	0.980
	48	480	514	0.978
Hexachlorobenzene	16	160	262	0.989
	32	309	443	0.996
	48	514	638	0.989

$R^2$  is the squared determination coefficient, which quantifies the percentage of total variance explained by the model obtained by interpolating data with Eq. (2).

In this way, it was also possible to calculate percent adsorption efficiency  $\eta$  (dimensionless) as follows:

$$\eta = \frac{Z - Z_0}{Z} \times 100, \quad (5)$$

where  $Z = 480$  mm. This efficiency depends on the pollutant in question and represents the net amount of available absorbing bed  $Z - Z_0$  related to total bed thickness  $Z$ . In fact, after  $t = 0$ , only  $Z - Z_0$  is effectively able to remove a specific compound. The results of these calculations are listed in Table 7.

With the aim of explaining our laboratory findings, a statistical study was carried out to verify if any quantitative

relationship exists among absorption efficiency, available active carbon characteristics and/or some of the physical–chemical properties of the compound. A preliminary study searched for a relationship between: (1) the observed carbon efficiency of the studied compounds (dependent variable  $y$ ); (2) a group of independent variables  $X_1$  and  $X_2$ , defined as follows:

- (a) compound characteristics ( $X_1$ ), i.e., their physical–chemical properties: molecular weight (MW), boiling point (bp), melting point (mp), refractive index ( $n_{D20}$ ), density ( $d$ ), logarithm of octanol–water partition coefficient ( $\log K_{ow}$ ) and dipole moment ( $D$ ).

**Table 6 – Values of mass transfer zone (MTZ) thickness,  $K$ ,  $Z_0$ , and  $N_0$** 

Substances	$C_0$ ( $\mu\text{g l}^{-1}$ ) <sup>b</sup>	MTZ (cm) <sup>a</sup>	$Z_0$ (cm)	$N_0$ ( $\text{mg l}^{-1}$ )	$K$ ( $\text{l mg h}^{-1}$ )
Dichloromethane	70	13.90	0.80	241	3.17
Trichloromethane	70	11.48	0.67	231	3.12
1,1,1-Trichloroethane	70	7.99	0.481	183	6.97
Carbon tetrachloride	70	2.80	0.476	196	6.71
1,2-Dichloroethane	70	7.69	8.26	341	0.223
Trichloroethylene	70	2.97	2.53	348	0.699
1,1,2-Trichloroethane	70	4.57	6.57	341	0.277
Tetrachloroethylene	70	7.94	4.03	213	0.711
1,1,1,2-Tetrachloroethane	70	1.94	6.10	350	0.291
<i>Trans</i> 1,4-dichloro-2-butene	70	6.52	2.81	284	0.778
1,2,4-Trichlorobenzene	7	7.02	0.402	53.5	28.7
1,2,3-Trichlorobenzene	7	6.39	4.55	46.8	2.87
Hexachloro-1,3-butadiene	7	8.26	0.281	24.5	90.6
Hexachlorobenzene	7	8.81	2.37	22.8	11.3

<sup>a</sup>  $V$  = velocity through column =  $0.077 \text{ cm s}^{-1}$ .<sup>b</sup>  $C_0$  = starting concentration.**Table 7 – Values of adsorption efficiency**

Substances	Percentage of adsorption efficiency (%)
Dichloromethane	98.3
Trichloromethane	98.8
1,1,1-Trichloroethane	99.0
Carbon tetrachloride	99.0
1,2-Dichloroethane	82.8
Trichloroethylene	94.7
1,1,2-Trichloroethane	86.3
Tetrachloroethylene	91.6
1,1,1,2-Tetrachloroethane	87.3
<i>Trans</i> 1,4-dichloro-2-butene	94.2
1,2,4-Trichlorobenzene	99.2
1,2,3-Trichlorobenzene	90.5
Hexachloro-1,3-butadiene	99.4
Hexachlorobenzene	95.1

(b) active carbon characteristics ( $X_2$ ): specific surface, iodine number, pore volume, apparent density and grain size.

Variables were first standardized (i.e., normalized to average = 0, and standard deviation = 1). Statistical techniques applied were multiple regression and partial least squares in latent variables (PLS, Simca-P software, Umetrics). Both procedures, which were applied to a model made up of all independent variables  $X_1 + X_2$ , i.e., collecting the physical-chemical characteristics of both compound and carbon, gave unsatisfactory results. Specifically, in the case of multiple regression, the variance explained by our model was lower than 10% ( $r^2 < 0.1$ ) whereas in PLS analysis, no significant component emerged. Explained variability of 30% was

obtained by the regression involving carbon absorption efficiency, i.e.,  $y$  and  $X_1$ , the set of independent variables concerning the physical-chemical characteristics of the 14 studied compounds. The same result was not obtained when the regression involved carbon absorption efficiency and  $X_2$  (i.e., the set of independent variables concerning carbon physical-chemical characteristics).

It thus appears that the currently available physical-chemical descriptors cannot properly explain the behavior of the tested carbons when they interact simultaneously with varying compounds. Consequently, at this state-of-the-art, no practical method of forecasting  $Z_0$  values and MTZ fluctuations is available. Therefore, while deeper understanding of the activated carbon absorption mechanism is developing, no reliable alternative seems to exist for empirical laboratory experiments.

#### 4. Conclusions

In this work, Freundlich adsorption isotherms were used to reveal the best of five commercially available activated carbons suitable for abating chlorinated organic compounds in aqueous matrices. An attempt to explain the relationship between compound properties in conjunction with active carbon characteristics on one hand and absorption efficiency on the other, despite the powerful up-to-date statistical method employed, gave poor results. Further research is probably needed to improve our understanding of active carbon absorption mechanisms before the results of empirical laboratory experiments can be predicted. For the timebeing, experiments appear to be the only reliable means of obtaining useful parameters. During our fixed-bed column experiments, removal efficiency was always higher than 90%. Optimization of operative conditions was necessary for scaling-up to a real plant column. Based on this technology,



a  $50\text{ m}^3\text{ h}^{-1}$  real plant was built to remove chlorinated organic compounds from industrial effluents in June 2004.

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