ADSORPTION OF ORGANICS IN WATER ONTO ACTIVATED CARBON FIBERS CORRELATION BETWEEN ADSORPTION PARAMETERS AND MOLECULAR STRUCTURE

C. Brasquet [1], E. Subrenat[2] and P. Le Cloirec[1]
1) Ecole des Mines de Nantes, Centre Génie des Procédés de l'Environnement
BP 20722, 4 rue Alfred Kastler, 44307 Nantes cedex 03, France
(2) Actitex, 16 rue de Trézel, 92309 Levallois cedex, France

Introduction

Activated carbon fibers (ACF) in the form of felt or cloth have received an increasing attention in recent years as an adsorbent for purifying water. The first studies on this new material were carried out mainly in gaseous phase and showed that ACF seemed very effective in removing contaminants from air [1]. Thwaites et al. [2] showed that initial adsorption rates are 2.5-10 times larger with fibers than with granules. ACF adsorption seems selective for low molecular weight compounds. For example, Ryu [3] compared adsorption of benzene and cyclohexane on an activated carbon cloth (ACC).
The main objective of the present study is to assess the removal of organics by activated carbon cloths in aqueous solution. Classical models were applied to simulate the adsorption in batch reactor. From experimental results, a correlation (QSAR : Quantitative Structure-Activity Relationship) was developed.

Experimental

Characteristics of cloth and activated carbon cloth are presented in Table 1.

sample identifier	ACF-m	ACF-M	GAC
presentation	cloth	cloth	granules
precursor	rayon	rayon	coconut
BET surface area ($m^2\ g^{-1}$)	1689	1460	1292
micropore surface area (%)	87.5	77.2	76.0
micropore volume (%)	96.3	68.1	94.4
median pore diameter (Å)	6.9	7.3	7.3

Table 1. Characteristics of activated carbon cloth

Activated carbon cloth (25-500 mg) was continuously stirred with 250 mL of an aqueous solution with an organic micropollutant concentration of about 100 mg L^{-1} at 20 ± 1°C. Equilibrium was reached after a contact time of 12 h for the fibers.

All adsorbates were commercially available with a high degree of purity (>98%). The concentration measurements were carried out with an UV-Vis spectrophotometer from SHIMADZU, using the UV region (200-300 nm).

The Quantitative Structure-Activity Relationships (QSAR) are used to develop a quantitative relationship between adsorption properties and molecular characteristics of a set of chemicals. Molecular connectivity indexes are descriptors originally proposed by Randic as branching indexes and later extensively developed and formalized by Kier and Hall [4]. These indexes, fundamental in nature, are calculated from structural information and encode information relating to physicochemical properties. Data are given in Table 2 for aromatic solute used in this study. $^1\chi$ encodes molecular size, molecular surface area and relative degree of branching, whereas $^1\chi^v$ encodes molecular volume and the topology of insaturation and heteroatoms.

Results and Discussion

Table 3 gives adsorption parameters of classical isotherm relations :
- Freundlich equation

$$q_e = K \cdot C_e^{1/n}$$

- Langmuir's relation

$$q_e = \frac{b \cdot q_m \cdot C_e}{1 + b \cdot C_e}$$

where q_e is the adsorption capacity at the equilibrium (mg g^{-1}), C_e the solution concentration at the equilibrium (mg L^{-1}), K a Freundlich parameter (mg$^{1-1/n}$ $L^{1/n}$ g^{-1}), 1/n a Freundlich parameter, q_m the maximum adsorption capacity (mg g^{-1}) and b the Langmuir equilibrium parameter (L mg^{-1}).

n°	adsorbate	$^1\chi$	$^1\chi^v$	log K
1	toluene	3.390	2.410	2.432
2	phenol	3.390	2.130	1.748
3	benzaldehyde	4.340	2.430	2.057
4	benzoic acid	4.300	2.580	1.914
5	dl- tyrosine	6.090	3.850	1.897
6	dl-phenylalanine	5.700	3.720	1.859
7	vaniline	5.270	3.100	2.211
8	aniline	3.390	2.200	1.677
9	p- chlorophenol	3.790	2.130	2.119
10	p- nitrophenol	4.700	2.230	2.273
11	4-terbutyl benzoic acid	6.190	4.250	1.630
12	2-terbutyl 4-methyl phenol	5.410	4.210	2.323
13	3,5- dimetoxy benzoic acid	5.090	3.410	1.641
14	diethylphtalate	6.370	3.960	2.347

Table 2 : Molecular connectivity parameters and adsorbability of aromatic compounds

As a decriptor of adsorbability on the sample ACF-m, "log K" was used, K being the Freundlich parameter. Various molecular connectivity indexes were calculated, the values are given in table 1.
The following equation was found :

$$\log K = 1.266 + 0.863\ ^1\chi - 1.166\ ^1\chi^v$$

The correlation coefficient being high (0.9216).

Conclusions

This study produces the following conclusions :
- ACF were shown to be good adorbents for a large set of aromatic organic compounds.
- QSAR was successfully used to predict adsorption.

		Freundlich			Langmuir		
N°	AC	1/n	K	r	b	q_m	r
1	ACF-m	0.182	270.4	0.92	0.07	699.0	0.89
	ACF-M	0.204	206.4	0.99	0.344	476.0	0.98
2	ACF-m	0.354	56.0	0.96	0.193	208.0	0.92
	ACF-M	0.300	43.9	0.99	0.520	118.1	0.94
	GAC	0.289	50.3	0.99	0.116	184.2	0.98
3	ACF-m	0.276	114.1	0.98	0.557	277.0	0.94
	ACF-M	0.255	75.6	0.97	0.258	207.5	0.99
	GAC	0.278	82.4	0.99	0.217	253.2	0.95
4	ACF-m	0.384	82.0	0.99	0.096	422.0	0.97
	ACF-M	0.245	88.5	0.99	0.129	274.0	0.99
	GAC	0.391	53.7	0.97	0.046	371.7	0.97
5	ACF-m	0.272	78.9	0.99	0.373	209.5	0.95
	ACF-M	0.346	46.3	0.98	0.103	204.5	0.97
	GAC	0.258	35.2	0.95	0.115	111.9	0.94
6	ACF-m	0.205	75.2	0.96	0.547	163.0	0.97
	ACF-M	0.124	83.9	0.95	1.000	132.1	0.92
	GAC	0.348	66.6	0.95	0.395	198.0	0.96
7	ACF-m	0.184	162.4	0.93	5.500	227.8	0.93
	ACF-M	0.095	188.7	0.98	3.200	261.1	0.99
	GAC	0.168	131.6	0.99	1.240	224.7	0.95
8	ACF-m	0.330	47.5	0.98	0.135	182.5	0.98
	ACF-M	0.373	43.8	0.99	0.111	205.3	0.99
	GAC	0.332	43.3	0.98	0.111	177.9	0.99
9	ACF-m	0.206	131.6	0.99	2.350	207.9	0.95
	ACF-M	0.271	141.2	0.99	2.270	233.1	0.96
	GAC	0.220	122.7	0.98	1.160	233.1	0.96
10	ACF-m	0.110	187.5	0.97	1.390	280.9	0.99
	ACF-M	0.153	196.2	0.97	1.200	333.3	0.98
	GAC	0.150	174.7	0.99	0.840	301.2	0.94
11	ACF-m	0.309	42.7	0.95	0.073	232.6	0.97
	ACF-M	0.655	21.3	0.98	0.021	534.8	0.99
	GAC	0.381	12.8	0.95	0.039	86.2	0.92
12	ACF-m	0.117	301.0	0.99	0.549	427.4	0.94
	ACF-M	0.167	207.7	0.98	1.060	343.6	0.95
	GAC	0.328	74.5	0.99	0.164	273.2	0.97
13	ACF-m	0.096	43.8	0.86	0.196	70.9	0.93
	ACF-M	0.235	30.3	0.98	0.086	96.2	0.98
	GAC	0.241	45.3	0.99	0.221	121.8	0.99
14	ACF-m	0.226	222.3	0.95	0.255	602.4	0.99
	ACF-M	0.121	215.1	0.95	0.750	350.9	0.93

Table 3 : Freundlich and Langmuir parameters of organics adsorption onto various activated carbons

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