

## THE ADSORPTION ONTO FIBROUS ACTIVATED CARBON APPLICATIONS TO WATER AND AIR TREATMENTS

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### Abstract :

The adsorption of polluted fluids is performed by fiber activated carbon (FAC). The adsorption is carried out in a batch or dynamic reactor. Classic models are applied and kinetic constants are calculated. Results showed that the performances of FAC are significantly higher than that of granular activated carbon (GAC) in terms of adsorption velocity and selectivity. The breakthrough curves obtained with FAC adsorbents are particularly steep, suggesting a smaller mass transfer resistance than GAC. The adsorption zone in the FAC bed is about 3.4 mm and is not really dependent on the water flow rate within the studied range. Applications are developed in water and air treatments. Examples are given in the micropollutants removal of an aqueous solution. Air loaded with VOC or/and odorous molecules is treated by fibers. Regeneration of this material is performed by heating by joule effects or electromagnetic induction. These original approaches to water or air treatment processes are successfully put to use.

### INTRODUCTION

The removal of organic matter in aqueous or gas phases with granular activated carbon (GAC) is commonly performed for the treatment of waters or VOC (Cheremisinoff and Ellerbusch, 1978; Schulhof, 1979; Bansal et al. 1988). GAC adsorbents have been proved effective in removing a large number of organic molecules (Clark and Lykins, 1989).

Fibrous activated carbon (FAC) has received increasing attention in recent years as an adsorbent for purifying water. The raw materials of FAC are polyacrylonitrile (PAN) fibers, cellulose fibers, phenol resin fibers or pitch fibers and their cloths or felts. They are first pyrolysed and then activated at a temperature of 700-1000°C in an atmosphere of steam or carbon dioxide (Seung-Kon Ryu, 1990).

The main objectives of the present paper is to assess the performance of the FAC adsorbents in water and air treatments. Phenol and its derivatives are the basic structural unit of a wide variety of synthetic organics including many pesticides. Then, phenol was the model compound used throughout the adsorption studies in aqueous solutions. The Volatil Organic Compounds (VOC) are well adsorbed on FAC, an exemple is shown. Two new regeneration method are proposed.

### MATERIALS AND METHODS

#### Activated Carbon Materials

Activated carbon materials are commercial products proposed by the PICA Company and Actitex Company (France). The main characteristics of the materials used in the present investigations are presented in Table 1. Scanning electronic microscopy pictures of the different adsorbants have been shown elsewhere (Le Cloirec et al., 1990 b)

#### Water treatments

**Kinetic and equilibrium studies.** Activated carbon (about 0.6 g) in the form of GAC or FAC was continuously stirred with 1 liter of an aqueous solution at  $20 \pm 1^\circ\text{C}$  containing initially 100  $\text{mg.l}^{-1}$  as micropollutants. Samples were withdrawn at regular times and then filtered for analysis until a steady state was obtained, up to 300 minutes for GAC. For the equilibrium studied, the activated carbon mass was varied from 0.05 to 0.5 g in 250 ml of solution. The final solution was then filtered and analysed.

**Continuous Flow Reactor.** A laboratory pilot unit was set up for the continuous flow study (Figure 1). The raw water contained 50  $\text{mg.l}^{-1}$  of micropollutant and was pumped to the adsorption line which was composed of four similar stages. Just one stage is shown on the figure 1. The modules have a diameter of 2.5 cm. The dead volume inside and between the FAC modules was negligible. The water flowed through each FAC module with a given velocity of 0.67 to 2.07  $\text{m h}^{-1}$ . Samples were taken at regular times in the outflow of the FAC modules in order to determine the corresponding breakthrough times.

#### Air treatments

**Adsorption procedure.** A laboratory pilot unit was set up for the continuous flow study. The raw air contained 50  $\text{mg m}^{-3}$  to 50  $\text{g VOC m}^{-3}$  and was sent to the adsorption line. The air velocity through the FAC was in a range between 50 and 1000  $\text{m h}^{-1}$ . Samples were taken at regular times in the outflow of the FAC modules in order to determine the corresponding breakthrough times.

**Regeneration.** Two kinds of regeneration were tested. The heating of FAC was developed by joule effect (Figure 2) or by electromagnetic induction (Figure 3).

## RESULTS AND DISCUSSION

### Water treatments

The results are presented in terms of adsorption velocity and selectivity compared to activated carbon grains.

**Adsorption velocity.** The kinetic coefficients were calculated for the two activated carbon materials into account the initial slopes of the curves. The Freundlich or Langmuir's models are applied (Table 2) the values of initial velocities are shown in Table 3. Adsorption isotherms were performed for the adsorption of phenol from synthetic solutions. All the isotherms demonstrated a favorable adsorption (Weber and Smith, 1987). The Freundlich equilibrium constants were higher for FAC than for GAC probably because of the higher specific surface area and the microporous structure of the activated carbon fibers. Therefore the FAC materials are more interesting than GAC from the standpoint of adsorption capacities. Therefore FAC was used for the breakthrough experiments. The kinetic coefficient for the FAC was found more than 50 times greater than that for GAC. Suzuki (1991) measured similar intraparticle diffusion coefficients with GAC and FAC. On the other hand, Seung-Kon Ryu (1990) came to the conclusion that the superposition of the adsorption forces generated by the opposite walls of the micropores causes an increase in the adsorption potential inside them. FAC seems to have only micropore which are directly connected to the external surface of the fibers (Le Cloirec et al., 1990; Suzuki, 1991; Abe et al., 1992). The pore size distribution for PAN-based activated carbon fibers concentrate around 2.5 to 2.6 nm (Tse-Hao Ko and co-workers, 1992). Thus adsorbates reach adsorption sites through micropore without additional diffusion resistance of macropore which usually is the rate-controlling step in the case of granular adsorbents (Suzuki, 1991). Moreover, the small diameter of the fibers results in the large external surface area exposed to the flowing fluid. Thus FAC adsorbents provide much faster adsorption kinetics compared with GAC (Baudu and co-workers, 1990, 1991).

**Selectivity.** In order to approach the selectivity of the two adsorbents, adsorptions in batch reactor were performed with a mixture of commercial humic substances and phenol. The results are presented in Figure 4. Similar curves are obtained for the two experiments. The FAC presents a selectivity for the low molecular weight molecules (Phenol) compared to macromolecules (Humic Substances). The adsorption capacities are found to be very closed for different waters as shown in Table 4. The micropore distribution could explain this selectivity.

**Dynamic adsorptions.** Breakthrough experiments were carried out for the adsorption of phenol onto FAC material with different flow rates through the FAC modules. Typical breakthrough curves for a given flow rate of 2.07 m.h<sup>-1</sup> are presented in Figure 5. Very steep breakthrough curves were obtained for all the flow rates used in the present investigation. This characteristic shape has already been mentioned in the review by Seung-Kon Ryu (1990). Again, Suzuki (1991) showed drastic differences between the breakthrough curves obtained in the same experimental conditions with GAC and packed FAC. The sharper breakthrough curves observed for the FAC suggested smaller mass transfer resistance than for the GAC. Similarly, Seung-Kon Ryu (1990) concluded that the adsorption rates of FAC are much higher than those of GAC. Therefore the mass transfer zones are much smaller in the case of adsorption onto FAC. The breakthrough times were measured when the phenol concentration (C) reached 0.05 C<sub>0</sub> (initial concentration). The breakthrough time values obtained for the various thicknesses and flow rates used in the study were introduced into the Bed Depth Service Time (BDST) relation developed by Hutchins (1973) and currently used. Parameters of the BDST relation are shown in Table 6. The N<sub>0</sub> (adsorption capacity) and Z<sub>0</sub> (adsorption zone) values were not really strongly dependent on the flow rate within the range 0.62 - 2.07 m.h<sup>-1</sup>. One might hypothesize that the adsorption reaction was not significantly influenced by the external mass transfer of the solutes through the hydrodynamic boundary layer. The main resistance to the mass transfer might be due to the diffusion through micropores inside the activated carbon fibers. The adsorption capacities (N<sub>0</sub>) were recalculated as a function of the activated carbon weight (Table 5). A good adsorption capacity (about 130 mg/g), close to the maximum surface concentrations determined in the batch reactor, is found with this dynamic system.

### Air treatments

**VOC adsorption.** A large number of works were published on the air treatment with activated carbons. Volatil Organic Compounds (VOC) were found to be well adsorbed onto GAC or FAC. During this study, adsorption onto FAC were performed with different VOC. An example is proposed on the figure 6. In this case, the dynamic adsorption capacity is found about 30 %. In order to recover the solvent, an "in situ" regeneration is required.

**Regeneration of FAC.** Two conventionnal methods are currently used to desorb VOC from activated carbon by high pressure steam or preheating fluid (air, nitrogen...). In order to overcome problems found with conventionnal methods, new processes usefull with FAC were considered.

**Regeneration by joule effect.** Recently, a new thermal regeneration process has been used. It consists of submitting the carbon to the passage of an electric current. the carbon can be either granular (Baudu et al., 1992) or fibrous (Le Cloirec et al., 1991). the activated carbon structure is akin to a semi-conductor. Laboratory scale experiments on solvent desorption are very promising. The advantage of such a process is that it can be easily implemented in-situ. Examples of regeneration by joule effect on fibrous carbon is given in the Table 6.

The regeneration by induction heating (Le Cloirec, 1993; Mocho, 1994). Induction heating can be used to regenerate activated carbon for the purpose of recycling volatile organic carbon. As the technological possibilities offered by induction on an industrial scale have to be taken into account, the FAC was presented as cylinders. Figure 4 shows the activated carbon heating equipment. Experiments developed with ethyl acetate show the best frequency is in a range of 1 to 100 kHz. A regeneration rate of 100% is reached for the activated carbon at the end of an hour. At this time, this kind of regeneration is developed at a laboratory scale for a treatment by FAC of air loaded by solvents.

## CONCLUSIONS

The objective of this study was to determine the efficiency of adsorption of fibrous activated carbon in water and air treatments. Results showed that performance of FAC is significant. FAC have a fast adsorption kinetics and selectivity. Thus, FAC well adsorbed VOC and new regeneration processes were proposed. For air and water treatments new reactors could be developed.

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	GAC	FAC
Commercial name	Pica NC 60	Actitex 1501
Size (mm)	3	-
Origin	coconut	viscose
Porosity	microporous	microporous
Specific area (m <sup>2</sup> .g <sup>-1</sup> )	1200	1550

Table 1 : Main Characteristics of Activated Carbons  
(PICA Company, Levallois France for GAC and Actitex, Levallois, France for FAC)

	GAC	FAC
1/n	0.39	0.428
k	0.06	27.7
qm	117	183
b	0.03	0.083

Table 2 : Langmuir and freundlich model parameters of phenol adsorption

	GAC	FAC
$\gamma$ (l. mg <sup>-1</sup> .min <sup>-1</sup> )	5.8 10 <sup>-6</sup>	4.5 10 <sup>-5</sup>

Table 3 : Initial adsorption velocity for phenol removal

Water	Phenol only	HS only	Phenol in the mixture	HS in the mixture
Deionised	40.1	1	34.3	0
Drinking Water	40.3	0.5	32.6	0
River water	44	0	40.2	0

Table 4 : Adsorption capacity (mg g<sup>-1</sup>) of phenol and humic substances (HS) in different waters

U (m/h)	Z <sub>0</sub> (mm)	N <sub>0</sub> (mg.l <sup>-1</sup> )	N <sub>0</sub> (mg.g <sup>-1</sup> )
0.62	3.5	9210	134
1.02	3.3	8925	130
2.07	3.4	8625	126

Table 5 : Adsorption zone and capacity at different flow velocities

Experiment	P (w)	Time to be at 100°C	Regeneration yield (%)
1	240	3 min 45 s	95
2	340	1 min 20 s	100
3	440	55 s	100

Table 6 : Thermal regeneration of fibrous activated carbon by joule effect (Baudu et al., 1992)

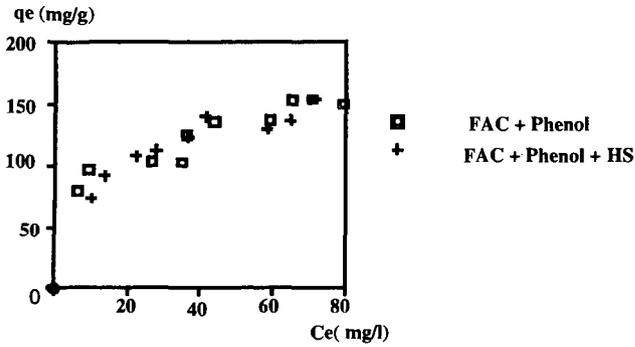


Figure 4 : Adsorption of mixture of humic substances (HS) and Phenol onto FAC

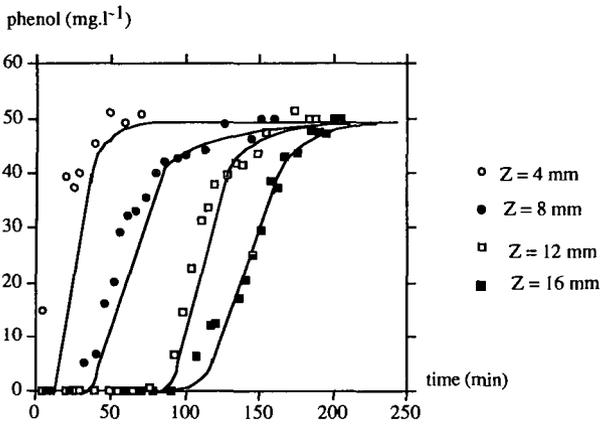


Fig.5 : Breakthrough curves for different thicknesses of FAC (flow rate: 2.07 m.h<sup>-1</sup>; raw water concentration: 50 mg phenol.l<sup>-1</sup>).

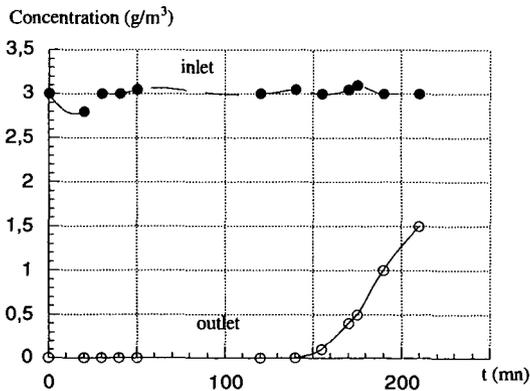


Figure 6 : Breakthrough curve on FAC. Air loaded with perchlorethylene, Velocity : 522 m/h; FAC weight : 7 kg (Baudu et al., 1992)

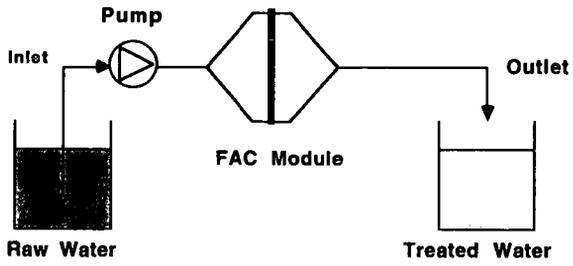


Figure 1 : Continuous flow reactor used in water treatment

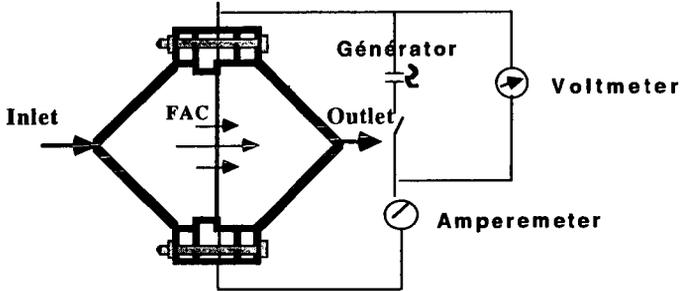


Figure 2 : Heating by joule effect, experimental equipment

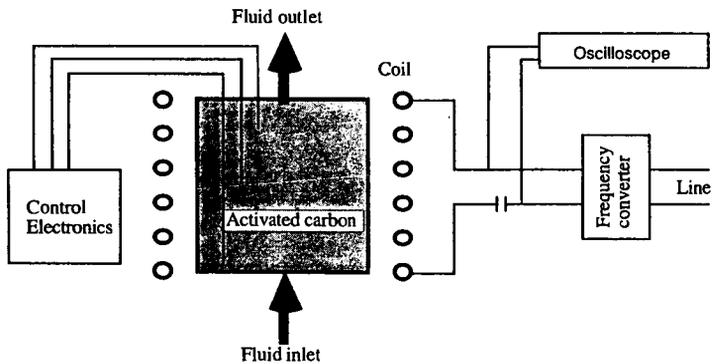


Figure 3 : Heating by electromagnetic induction. Experimental equipment