

ADSORPTION OF 4-CHLOROPHENOL ON ACTIVE CARBON GRAINS AND CARBON FABRICS.

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Introduction

A process allowing elimination of chlorophenols from polluted water has been developed in our laboratory [1, 2]. This process proceeds through two steps : first, the pollutant is adsorbed on active carbon, then, the adsorbed species are catalytically hydrogenated by means of a noble metal present on the active carbon. (this catalytic step is not described in the present work). In order to optimize the process we have studied 4-chlorophenol adsorption on two types of carbon supports : grains and fabrics (carbonized viscose).

Experimental

Adsorption experiments have been carried out in a stirred reactor (determination of adsorption capacity) or in a column (determination of adsorption isotherms and breakthrough curves). Chlorophenol concentrations were measured by UV absorption at 282 nm (Jasco MD-910 detector). Textural characteristics have been evaluated from nitrogen adsorption-desorption isotherm at 77 K (Micromeritics ASAP 2010)

Three adsorbents have been studied : granulates of active carbon (Picactif TE80), woven carbon fabrics (Actitex RS1301) and non woven carbon fabrics (Actitex FC1201). These carbon fabrics result from the carbonization and activation treatments of viscose fabrics. The textural characteristics of adsorbents are described in table 1.

Table 1 : Pore characteristics of adsorbents

	Active carbon (TE80)	Carbon fabrics (RS1301)	Non woven (FC1201)
S_{BET} (m ² /g)	1098	1348	999
S_{micro} (m ² /g)	495	1004	889
V_{total} (cm ³ /g)	0.55	0.731	0.44
V_{micro} (cm ³ /g)	0.215	0.462	0.411
D_{pores} (nm)	2	2.2	1.8
D_{micro} (nm)	0.7	0.5	0.6

These adsorbents are microporous, with narrow pores.

Results and Discussion

Adsorbent behavior can be depicted by the breakthrough curve which gives the pollutant concentration at the outlet of the adsorption column as a function of time. From this curve a critical time (time for which the pollutant

concentration becomes higher than the maximum value allowed for pollutant rejection - 0.1 ppm for 4-chlorophenol) is measured as well as the corresponding critical amount of adsorbed pollutant.

A preliminary study led to select Picactif TE80 (PICA) which presents a large adsorption capacity and a high adsorption rate.

Modelling of 4-chlorophenol adsorption on TE80 :

From experiments at laboratory scale the adsorption, in fixed bed, of 4-chlorophenol has been modelled. The model must allow to predict the behaviour of a fixed bed during the adsorption of 4-chlorophenol from a solution having a pollutant concentration C_0 , flowing through the adsorbent bed with a constant flow rate Q . The objective was to derive, from the initial pollutant concentration, the liquid flowrate and the reactor dimensions, the amount of adsorbed pollutant and its concentration in the liquid phase as a function of time in every point of the adsorbent bed. The model must allow to foresee the capabilities of an extrapolated industrial unit.

The obtained model is based on a non linear adsorption isotherm conjugated to a significant resistance to the mass transfer [3]. Pollutant molecules diffuse through a thin motionless liquid film surrounding the adsorbent particles. The local concentration gradient existing at the particle surface is the leading force for pollutant molecule movement considered as purely diffusional and which can be described by the first Fick law.

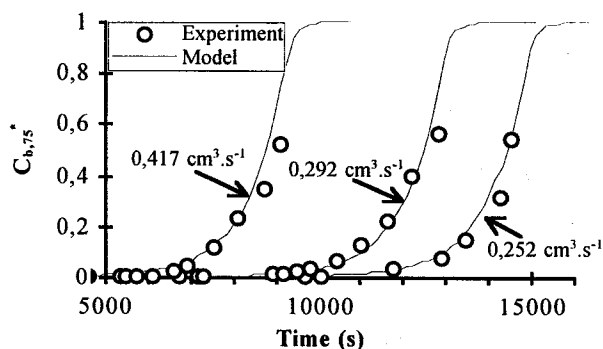


Figure 1 : Experimental and modeled breakthrough curves at different flow rates.

For modelling purposes, the adsorbent column is described as N identical cells considered as perfectly stirred reactors. The value of N is optimised to fit our operating conditions and is set at the value $N= 75$. Then, the equations describing the mass balances, the diffusion in a carbon particle, the symmetry at the particle center and the

fluid flux at the particle periphery are derived and lead to a five equation system with five unknowns. The numerical resolution of this system is carried out using the orthogonal collocation method [4].

Figure 1 shows the good agreement achieved between experimental and calculated breakthrough curves.

Table 2 allows to compare experimental and calculated critical time (t_c) values for different flow rate of the solution. M is the mass of adsorbent and $q_{c \text{ exp}}$ is the experimental critical amount of adsorbed pollutant (per gram of adsorbent). Whatever the flow rate a large difference is noted between the two values. Although the validity of the model has been established, we cannot explain these differences. Among all the coefficients only the external mass transfer coefficient, K_m , has an influence on the critical time value.

Table 2 : Comparison of experimental and calculated values of the critical time

$Q \text{ (cm}^3 \text{ s}^{-1}\text{)}$	0.1236	0.2078	0.3247	0.4217	0.5739
$M \text{ (g)}$	31	31.18	30.99	31.85	31.44
$t_{c \text{ exp}}$	24300	14100	8190	5610	2910
$t_{c \text{ sim}}$	15900	7380	3200	1620	0
$q_{c \text{ exp}}$	86.1	83.5	76.4	66	47.2

Comparison of the adsorption of 4-chlorophenol on TE80 and on carbon fabrics :

When used in a fixed bed small carbon grains present some drawbacks : high pressure drop , irregular filling of the reactor, grain erosion. To minimize these effects, structured adsorbents which are under the form of active carbon fabrics (RS1301 and FC1201; see table 1), have been tested. Their adsorptive properties have been compared to these of TE80.

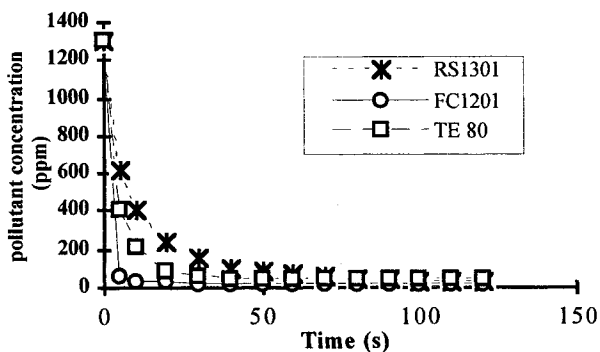


Figure 2 : Chlorophenol concentration versus time in a stirred reactor (initial concentration : 1300ppm; adsorbent mass : 0,5 g; temperature : 20 °C)

Figure 2 presents the rate of adsorption (stirred batch reactor) of 4-chlorophenol on each adsorbent. In each case the mass of adsorbent is 0.5 g and the initial concentration of 4-chlorophenol is 1300 ppm. Although the non woven fabrics has the highest rate of adsorption the differences between the three adsorbents remain slight and thus the adsorption rate alone does not allows for picking out the best one.

In order to determine the breakthrough curves for each adsorbent (figure 3) a 4-chlorophenol solution is passed through a cylindrical adsorbent bed and its concentration is measured at the outlet. TE80 and RS1301 exhibit quite similar behavior. In the case of FC1201 the outlet concentration remains below the limit value for a longer time (table 3) and then rises more stiffly than for the other adsorbents. This means a better performance, since with this adsorbent, the 4-chlorophenol adsorption could be carried out with a higher flow rate.

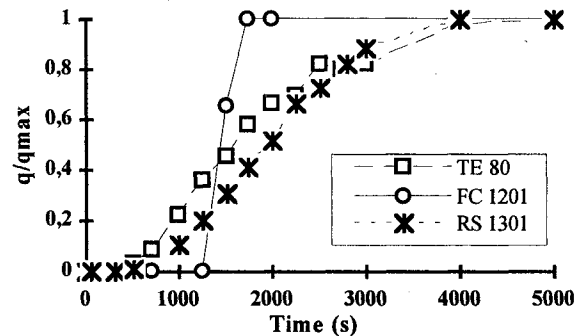


Figure 3 : Breakthrough curves of adsorbents (adsorbent mass : 3 g; flow rate : 1 l/h; initial concentration of pollutant : 4000 ppm; temperature : 20 °C)

Table 3 : Comparison of adsorptive properties of carbons.

	q_{max} (g/g)	t_c (s)		q_c (g/g)	
		0.5 l/h	1.5 l/h	0.5 l/h	1.5 l/h
FC1201	0.489	2070	614	1.43	0.43
RS1301	0.577	1710	175	1.04	0.26
TE80	0.455	840	37	0.48	0.06

Conclusions

As evidenced by batch and in-line adsorption experiments, fabrics carbon show interesting performances for chlorophenol adsorption, especially the non woven one. The adsorption of 4-chlorophenol on active carbon has been modelised. The model describe well the breakthrough curves and thus allows for extrapolation from the laboratory scale to the pilot and industrial scale. However it has to be improved in order to allow for critical time prediction with a better precision.

References

1. Fouilloux P., de Bellefon C. and Felis V., WO 97/2617 to TREDI
2. Felis V., de Bellefon C., Fouilloux P. and Schweich D., Appl. Catal., 1999, 20:91-100.
3. Calleja G., Serna J. and Rodriguez J., Carbon, 1993; 31(5):691-697.
4. Villadsen J. V., Stewart W. E., Chem. Eng. Sci., 1967, 22: 1483-1501.