

# Adsorption and Desorption of Emerging Water Contaminants on Activated Carbon Fabrics

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**Abstract** –Nowadays, a wide variety of organic contaminants are present at trace concentrations in wastewater effluents. In order to face these pollution problems, the implementation of the REACH European regulation has defined lists of targeted pollutants to be eliminated selectively in water. It therefore implies the development of innovative and more efficient remediation techniques. In this sense, adsorption processes can be successfully used to achieve the removal of organic compounds in waste water treatment processes, especially at low pollutant concentration. Especially, activated carbons possessing a highly developed porosity demonstrate high adsorption capacities. More specifically, carbon cloths show high adsorption rates, an easily handling, a good mechanical integrity and regeneration potentialities. When loaded with pollutants, these materials can be indeed regenerated using an electrochemical polarization.

**Keywords:** Nanoporous carbons, activated carbon cloths, adsorption, micropollutants, emerging contaminants, regeneration, electrochemistry

## 1. Introduction

A wide variety of organic compounds that are used in domestic, agricultural and industrial applications are present at trace concentrations in wastewater effluents [1, 2, and 3]. These micropollutants include personal-care products, plasticizers, reproductive hormones, pesticides and pharmaceuticals. Adsorption properties of activated carbons offer great potentialities for water purification, particularly in the case of tertiary treatments as they appear as the most prevailing and competing adsorbents, especially at low pollutant concentration. However, the major encountered disadvantage is their short lifetime due to the low and expensive regeneration capacities. Generally, the loaded carbon adsorbent can be regenerated *ex-situ* through high energy-consuming processes, like thermal treatments or steaming.

Specifically, as compared to powder or granules, activated carbon cloths (ACC) show numerous advantages, regardless to their easily handling, high mechanical integrity and regeneration potentialities. Additionally, due to their microtexture and their small fiber diameters (around 10 micrometers), they are ideal candidates for an adsorption purpose as they show minimal diffusion limitation and greater adsorption rates towards noxious organic pollutants [4, 5].

In the present work, the adsorption properties of some micropollutants and emerging pollutants, especially pharmaceuticals residues, have been investigated using an activated carbon cloth. An electrochemical polarization has been applied to achieve the reversible desorption of adsorbed species and the regeneration of the adsorbent porosity [6, 7].

The involved mechanisms have been examined carefully and correlated to the nanoporous texture of the adsorbent by taking into account the adsorbate speciation and physico-chemical properties. It appears

that the reversible electrochemical desorption of the induced charged molecules offers great potentialities. Such systems could find a place of choice in industrial processes for tertiary treatment and for the treatment of hospital effluents, but also for underground water exploitation [7, 8].

## 2. Experimental

### A. Adsorbent

An activated carbon cloth possessing a highly developed surface area has been used (Table 1). Its porous network consists in large amount of micropores (0.7-2 nm) and ultramicropores (<0.7 nm). The pore size distribution is very narrow and centered at 1-1.2 nm

Table. 1. Microtextural Adsorbent Characteristics.

$S_{\text{bet}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{micro}}$ $\text{N}_2$ , DFT $\text{cm}^3/\text{g}$	$V_{\text{més}}$ $\text{N}_2$ , DFT $\text{cm}^3/\text{g}$	$V_{\text{micro}}$ $\text{N}_2$ , DR $\text{cm}^3/\text{g}$	$V_{\text{ultramicro}}$ $\text{CO}_2$ , DR $\text{cm}^3/\text{g}$	$V_{\text{total}}$ $\text{N}_2$ $\text{cm}^3/\text{g}$
1175	0.59	0.09	0.57	0.57	0.68

This material is rather hydrophobic and contains 95 % (mass%) of carbon and 1.2% of oxygen. It presents a basic zero charge pH (8.9) and a low amount of oxygenated surface groups (0.2 mmol/g). The diameters of the fibers are in the range of ten micrometers and micropores are directly accessible all along the fibers (Fig. 1).

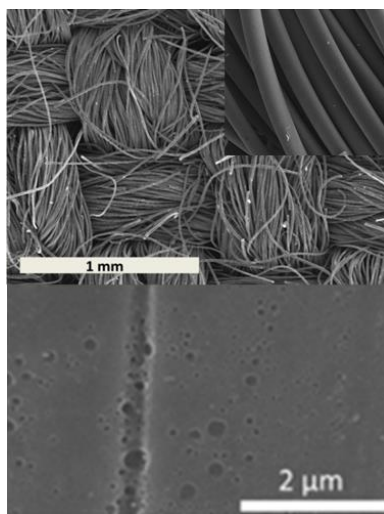


Fig. 1. SEM micrograph of activated carbon cloth.

### B. Targeted pollutants

Seven organic molecules, diclofenac (DCF), caffeine (CAF), acetaminophen (also called paracetamol POL), bisphenol A (BPA), carbamazepine (CBZ), pentachlorophenol (PCP) and ofloxacin (OFX) were selected (Fig. 2). These contaminants possess different physico-chemical properties (water solubility,  $pK_A$  values, hydrodynamic volumes).

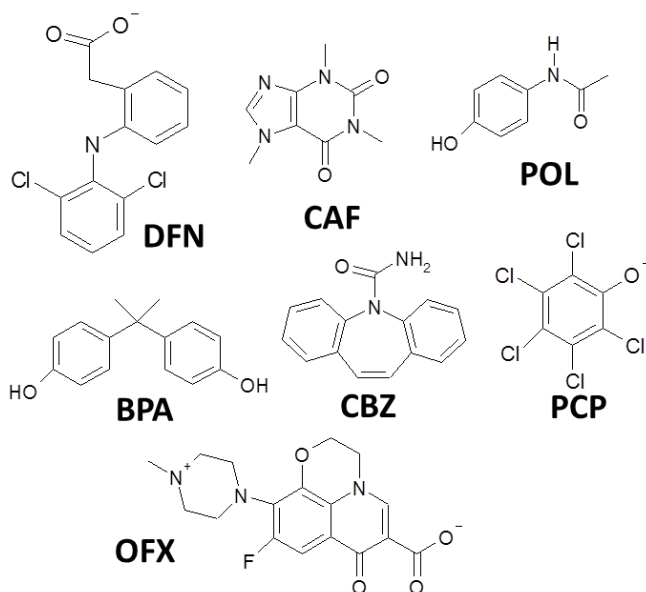


Fig. 2. Adsorbates formulas; and speciations at pH 7.5

### C. Analytical detection and quantification

Reverse phase HPLC measurements have been used to perform the detection and the quantification during adsorption kinetics, in binary or complex mixture and isotherm adsorption.

### D. Adsorption measurements

All the kinetics studies were conducted in a phosphate buffer at pH 7.5. In the case of binary mixtures, a total concentration of  $10^{-4}$  mol/L was set ( $5 \cdot 10^{-5}$  mol/L per each pollutant). For the complex mixture a total concentration of  $10^{-4}$  mol/L was set ( $1.43 \cdot 10^{-5}$  mol/L per each pollutant). The kinetics data were fitted with the pseudo second order model.

The adsorption isotherms were studied at 13, 25 and 40°C for DFN, CAF, CBZ, BPA and OFX. Experimentally, stoppered vials containing (12 mg disks) were placed in 50 mL pollutant solution at various concentrations (from about  $10^{-5}$  to  $10^{-3}$  mol/L) and stirred until equilibrium was reached. The solutions prepared at a given concentration were exactly the same for each three temperatures to get precise and comparable results. The solutions were filtrated on 0.45  $\mu$ m filter membranes prior to HPCL analysis.

### E. Regeneration under polarization

A free electrodes cell was used using Hg/H<sub>2</sub>SO<sub>4</sub> as reference electrode. Regeneration was performed in Na<sub>2</sub>SO<sub>4</sub> 0.01 mol/L as conducting electrolyte. Negative courants were applied to the carbon cloth electrode.

## 3. Results and Discussion

### A. Isotherm adsorption

Isotherms were studied at 3 different temperatures (not shown) in order to calculate the Gibbs free energy variation  $\Delta G^0$  at a maximum uptake for the adsorption of 5 molecules on the carbon fabric (Table 2).

Negative and small  $\Delta G^0$  show a spontaneous and physical adsorption process.  $\Delta G^0$  values are discussed in section III.B. Where thermodynamical process could overtake diffusion process for long adsorption time.

### B. Kinetics

In order to understand adsorption mechanisms and to determine the key parameters governing adsorption phenomenon, kinetics studies in binary or complex mixtures were performed. In some cases, competition effects are clearly visible as for example between DFN and CAF and between DFN and POL

(Fig. 2). Two regimes are detected: during the first five days the speciation of the adsorbates controls the adsorption kinetics, anionic adsorbates being adsorbed more slowly because of the electrostatic repulsions. In a second step for longer time, water solubility is then imposing the adsorption uptake, the less soluble DFN becoming easier to adsorb onto the hydrophobic carbon surface of the activated carbon cloth (Figs. 3 and 4).

Table. 2. Gibbs free energy For Different Micropollutants at a Maximum Uptake.

	<b>OFX</b>	<b>DFN</b>	<b>BPA</b>	<b>CBZ</b>	<b>CAF</b>
$\Delta G^0$ (kJ/mol)	-17.5	-14.6	-13.5	-10.2	-0.7

When time tends to equilibrium, the adsorption of DFN occurs in detriment of CAF or POL molecules thus demonstrating that these molecules are in competition for some adsorption sites and that when DFN enters in the porosity, POL or CAF gets out from the pores.

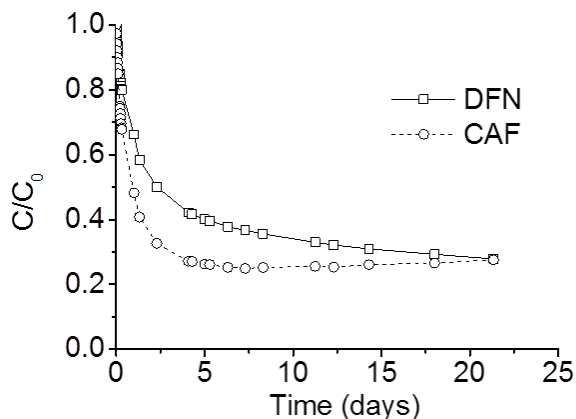


Fig. 3. Adsorption of DFN and CAF (kinetics data).

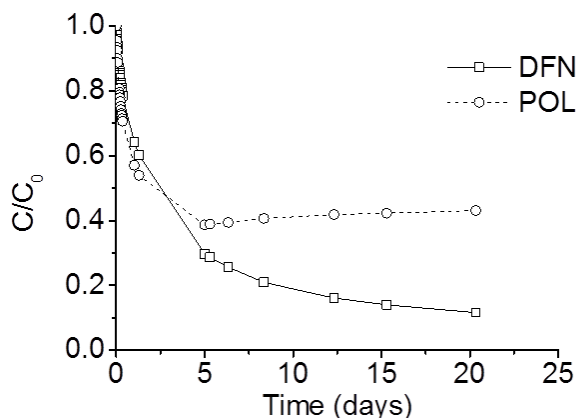


Fig. 4. Adsorption of DFN and POL (kinetics data).

If we examine the adsorption behavior of DFN in the different binary systems, it appears that its adsorption capacity and adsorption kinetic are affected in a different extent. Firstly, one must consider the large size of the DFN molecule, in the range of  $580\text{\AA}^3$ , as compared to the smaller molecules like POL,

PCP and CAF.

More precisely, adsorbed DFN uptake is lowered especially when DFN is co-adsorbed with species having high sizes like OFX and BPA (Fig. 5, table 3). For co-adsorbates having the smallest hydrodynamic volumes, like POL or CAF, the DFN adsorbed amounts are less affected and high adsorption uptake are measured.

These results show the major role of adsorbates size during adsorption processes. For two adsorbates having different volumes, each of them can easily find an adsorption site in the porosity. For molecules with a quite big size, as compared to the small size of the pores, it becomes more complicated, and adsorbates are in competition to reach the bigger micropores (Fig. 6).

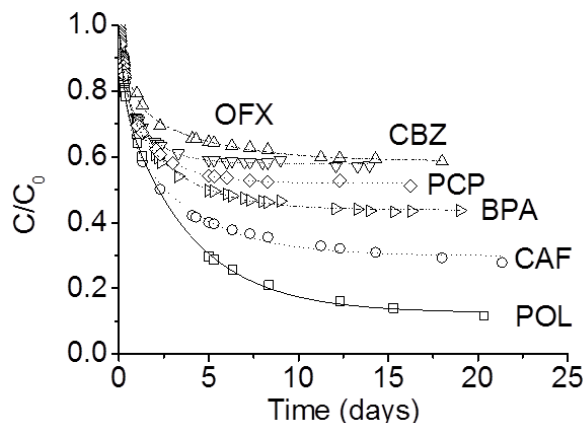


Fig. 5. Adsorption kinetics of DFN in binary systems depending on the co-adsorbate.

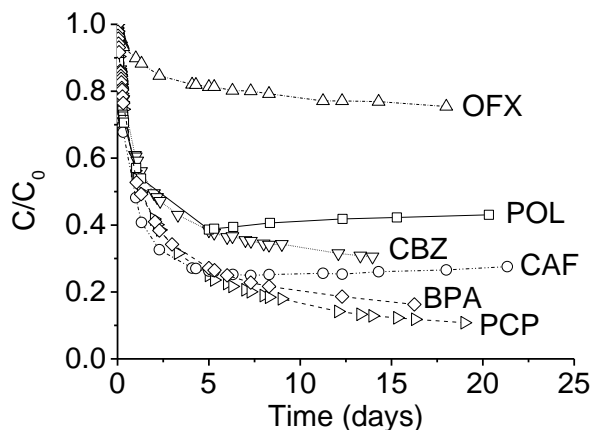


Fig. 6. Adsorption kinetics of the co-adsorbate in binary systems with DFN.

When the adsorption kinetics were studied in a complex mixture containing the seven adsorbates, the same tendency was observed. The adsorbate size appears to be the main parameter controlling the adsorption kinetics. The highest adsorption capacities are observed for the smallest organic molecules like PCP, and POL whereas OFX and DFN being neutral and having a large size show the slowest adsorption and smallest uptake (Fig. 7). The adsorption capacities can thus be directly correlated to the volume of the adsorbates.

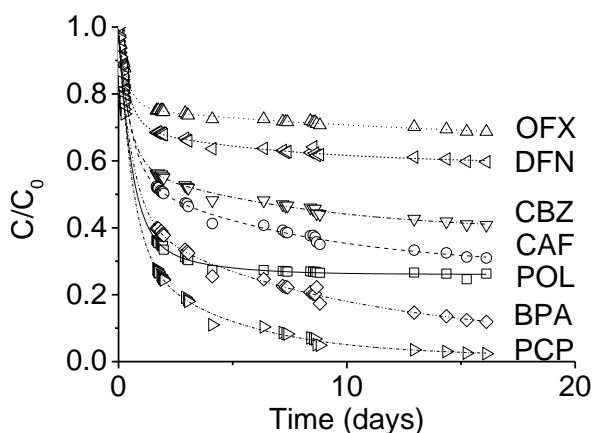


Fig. 7. Adsorption kinetics of each pollutant in the complex mixture

In order to complete the work, additional binary systems were studied with OFX in binary mixture and five co-adsorbates (PCP, BPA, DFN, CAF and CBZ).

As DFN, OFX is poorly adsorbed in the presence of PCP and BPA in the mixture (Fig 8.). OFX adsorption uptake at equilibrium is higher in the mixture with small size molecules such as CAF and CBZ. Moreover, CAF or CBZ single adsorption shows greater  $\Delta G^0$  than other molecules because of their small affinity with the carbon.

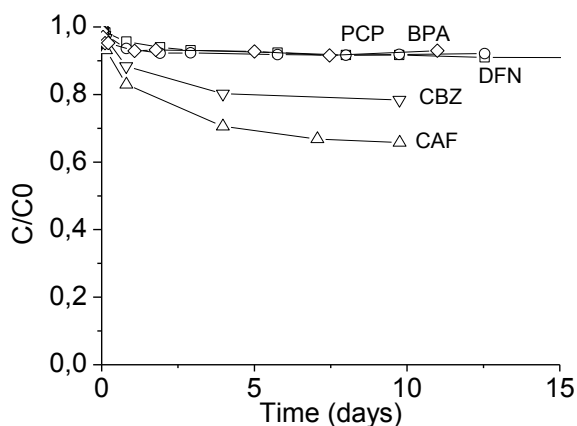


Fig. 8. Adsorption kinetics of OFX in binary systems depending on the co-adsorbate.

Size effect was confirmed to be a key parameter driving the adsorption process in a binary system. Large size molecules such as DFN and BPA diffuse slowly into the pores because of steric hindrance whereas small molecules such as PCP and CAF diffuse quicker and deeper inside the pores (Fig 9).

### C. Regeneration under polarization

After loading activated carbon cloths with organic contaminants, a tempted regeneration was conducted under cathodic polarization of the carbon cloth.

Depending on the nature on the adsorbate, it was possible to perform the reversible desorption of the adsorbed species. A complete regeneration is observed in the case of POL whereas for BPA or DFN desorption is more difficult (Fig.8). We suppose that the desorption is performed through electrostatic repulsions occurring between the negatively charged carbon surface and dissociated organic molecules, reinforced by the presence of the electrical field.

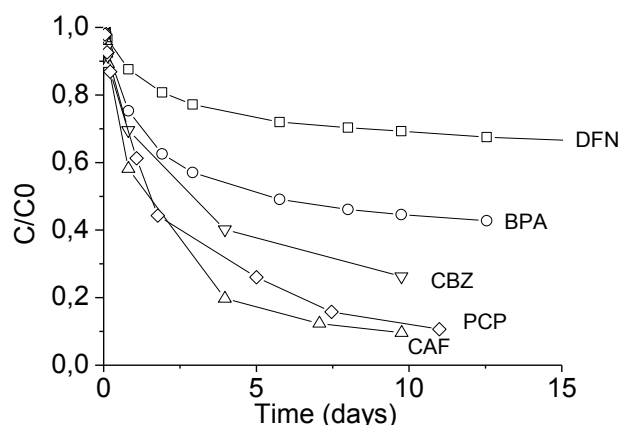


Fig. 9. Adsorption kinetics of the co-adsorbates in binary systems with OFX.

One can assume that for adsorbates possessing high hydrodynamic volumes the reversible desorption become more difficult probably because of steric hindrance within the porosity.

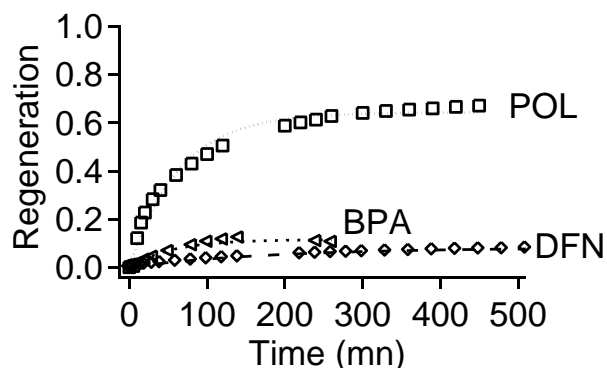


Fig. 10. Regeneration percentages (%) as a function of polarization time for POL, BPA and DFN.

#### 4. Conclusion

Activated carbon cloths are one of the most prevailing adsorbents able to trap emerging water contaminants in water.

The small and neutral molecules show the best adsorption capacities. The knowledge of the thermodynamic parameters such as  $\Delta G^0$  reveals itself to be a useful tool to assess in which extent a molecule would be well adsorbed in a binary mixture at equilibrium. The adsorbent can be partially regenerated through a cathodic polarization.

#### Acknowledgment

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