

REMOVAL OF PERFLUORINATED COMPOUNDS FROM WATER: EXISTING AND POTENTIAL TECHNOLOGIES.

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Introduction

Perfluorinated compounds are used either for surface protection for example in the textile industry or as additive to lower the surface tension of aqueous based formulations like in paints, metal treatment or fire fighting foams. Perfluorinated chains are persistent in the environment and it is useful to find solutions to remove those compounds from water. In the present work we are describing a technique that has been developed at the lab scale and used with success in real scale. We also describe a new water treatment technique that is showing a good potential for the removal of perfluorinated compounds from water.

The treatment studied in the lab and used in real scale is based on activated carbon. At the lab scale we showed that a specific fluorinated surfactant be adsorbed onto activated carbon. The activated carbon can be in a cartridge or dispersed into the water to treat.

Cross filtration is also a promising technique because it can be optimised for the removal of very specific molecules.

Materials and Methods

The perfluoroalkyl carboxybetain was supplied by DuPont and used as received. The sodium octyl sulfate surfactant (Texapon1 842 from Henkel) and 2-(2-butoxyethoxy)ethanol from Aldrich were used as received.

Activated carbon with the commercial name Acticarbon[®] 25K, Acticarbon[®] ENO, all from CECA were used as received. Their characteristics are given in Table 1.

Adsorption of fluorinated surfactant on a powder of activated carbon

For those measurements, dispersions containing from 20 to 1000 mg/l of activated carbon and different concentrations in fluorinated surfactants were prepared. In order to reach the equilibrium, activated carbon and fluorinated surfactants remained in contact for 16 h before the centrifugation of the dispersions. Then, the concentration of fluorinated surfactant in the supernatant was measured by surface tension measurements.

Table 1. Characteristics of the two activated carbon used in this study

Commercial name	Specific surface (m ² . g ⁻¹)	Porosity (Å)
Acticarbon [®] 25K	1000	10-20
Acticarbon [®] ENO	1500	30-100

Concentration measurements (surface tension and mass spectroscopy)

For solutions containing only perfluoroalkyl carboxybetain, its concentration in water was evaluated by liquid surface tension measurement with a Lauda tensiometer. At first, the liquid surface tension was measured as a function of the perfluoroalkyl carboxybetain concentration at 25 °C. The results are presented in Fig. 1. The CMC of perfluoroalkyl carboxybetain was determined during the change of slope of the curve. The value obtained is 5.10⁻² g.L⁻¹ or 8.8.10⁻⁵ mol.L⁻¹. For water solutions of perfluoroalkyl carboxybetain having a liquid surface tension above 25 mN/m, the concentration was, then, directly obtained from the curve of Fig. 1 used as calibration curve. Solutions having a liquid surface tension below 25 mN/m were diluted 10 times in desionised water. With this dilution, a liquid surface tension above 25 mN/m is obtained and the calibration curve can be used.

Mass spectrometry coupled with high pressure liquid chromatography (HPLC) was used for treated solutions where perfluoroalkyl carboxybetain was mixed with Texapon1 842 and 2-(2-butoxyethoxy)ethanol. HPLC

apparatus was Hewett Packard Serie 1100 and the mass spectrometry apparatus was Fisons instruments VG Quatro II.

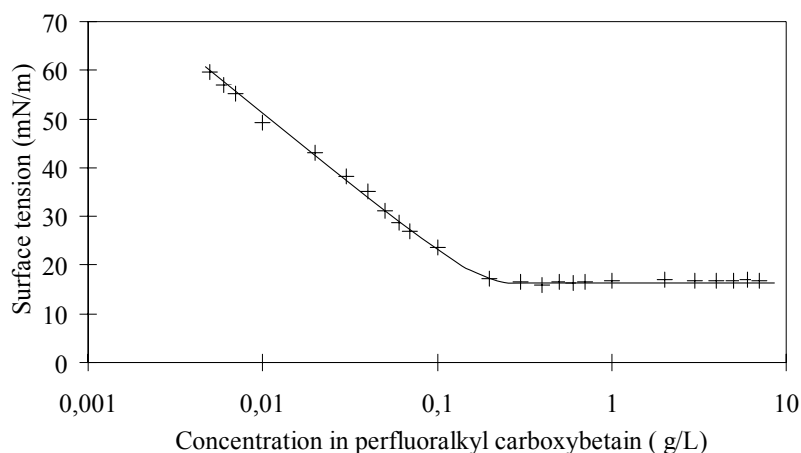


Figure 1: Surface tension as a function of the perfluoroalkyl carboxybetain concentration.

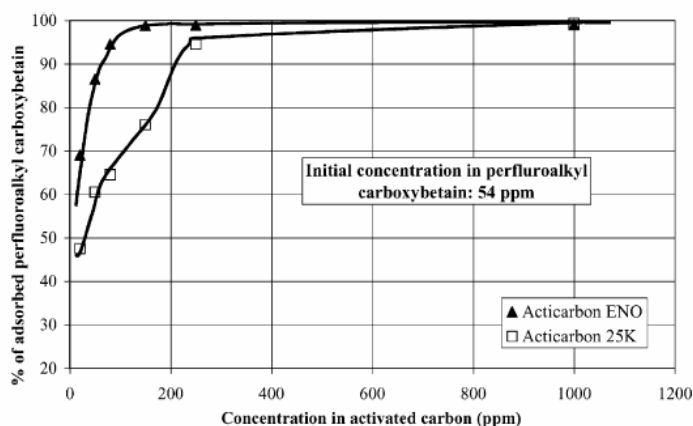
Results and discussion

Laboratory scale preliminary study¹

As fluorinated surfactants are not biodegradable and can persist in the environment, it is necessary to find a way of extracting them from water. Several techniques such as membranes², cationic polymers to precipitate anionic surfactants³ and activated carbon⁴ have been proposed and evaluated in the literature. However, the treatment of water containing aqueous film forming foam (AFFF) with activated carbon has not been studied in detail, according to our knowledge. In the case of pollution by pesticides, classical waste water stations producing drinkable water use activated carbon to remove these chemicals from water. The activated carbon is added to water at a concentration going from 20 to 50 mg/l. After the treatment, 95% of the activated carbon is recovered by decantation. The 5% remaining is eliminated by passing the water through sand filters. In the present study, the behaviour of a perfluoroalkyl carboxybetain surfactant face to this treatment was evaluated.

Then, in a second part of this preliminary study, the extraction of fluorinated surfactants from water is studied by building an activated carbon filter at the laboratory scale. Solutions containing either the perfluoroalkyl carboxybetain surfactant alone or mixed with sodium octyl sulfate (hydrocarbon surfactant) and 2-(2-butoxyethoxy)ethanol are treated. It has to be noticed that the blend containing the perfluoroalkyl carboxybetain surfactant, the sodium octyl sulfate and the 2-(2-butoxyethoxy)ethanol is used to simulate a fire fighting foam.

Adsorption of a fluorinated surfactant onto activated carbon powder



Two different activated carbons usually used in water treatment have been evaluated. The first one, Acticarbon[®] 25K, has a medium pore size ranging from 10 to 20 Å. As the perfluoroalkyl carboxybetain surfactant molecule has a length of 18 Å, this means that all the activated carbon pores are probably not accessible for this molecule. As a consequence, an other activated carbon is used with a medium pore size ranging from 30 to 100 Å (Acticarbon[®] ENO). Activated carbon rates vary over a broad range of concentration.

Figure 2: Adsorbed amount of perfluoroalkyl carboxybetain onto activated carbon as a function of concentration in activated carbon.

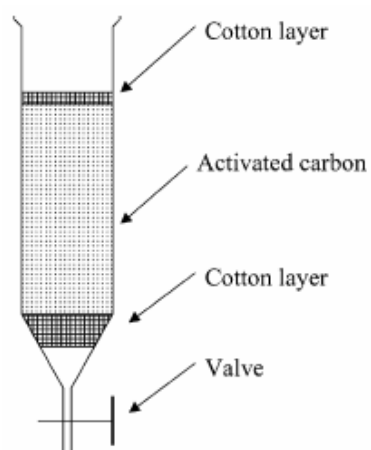
For perfluoroalkyl carboxybetain (54 ppm), the adsorbed percentage is measured as a function of the activated carbon concentration for both powders of activated carbon. Results are reported in Fig. 2. See Section Materials and Methods for details. Acticarbon® ENO gave better results than Acticarbon1 25K. With Acticarbon1 ENO, from a concentration of 250 mg/l more than 98% of the product was adsorbed.

This result can be explained by the fact that this activated carbon has a higher medium pore size than Acticarbon® 25K. With 1000 ppm of activated carbon, almost 100% of the surfactant was adsorbed. This means that the concentration in perfluoroalkyl carboxybetain in water after treatment was below 1.5 ppm. From this first set of experiment, we can conclude that this perfluoroalkyl compound has a very good affinity with activated carbon.

Water treatment with a cartridge containing activated carbon

In order to lower the required amount of activated carbon, a filtration system has been studied. The cartridge is a glass tube of 15 cm length with an interior diameter of 2.5 cm. As represented in Fig. 3, one end of this tube was fitted with cotton, completed with 1 g of activated carbon and then was also covered with a second cotton layer. The average flow rate through the cartridge was 250 ml of solution in one hour. The filtered solution was fractionated in samples of 150 ml whose concentration in perfluoroalkyl carboxybetain was measured.

The evolution of the adsorption rate as a function of elution volume for the perfluoroalkyl carboxybetain is plotted on Fig. 4. This Figure shows that after the filtration of 500 ml of solution, no fluorinated surfactant is detectable according to the surface tension measurement technique that we have used. This means that the concentration in perfluoroalkyl carboxybetain in the treated solution was below 1.5 ppm. With 1 g of activated carbon, it was possible to treat more than 1 l of solution (after the percolation of 1.35 l, the column was still not saturated).



In order to simulate the behaviour of this type of cartridge face to an fire fighting foam, a mixture of the perfluoroalkyl carboxybetain, sodium octyl sulfate and 2-(2-butoxyethoxy)ethanol was treated. Mass spectrometry coupled to high liquid pressure chromatography was used to characterize the filtrated solution. Results are reported in Table 2 where the initial concentrations correspond to a 3% fire fighting foam diluted into water. Concentrations in the treated solution (results reported in Table 2) are reduced by a factor higher than 10 compared to the initial solution, this is a very interesting result. From those results, the system has been tested in a much larger scale.

Figure 3: Schematic representation of the activated carbon cartridge used in this study.

Table 2: Aqueous solution composition before and after treatment on the activated carbon cartridge (in the treated solution, concentrations are below the detection limit of each component).

	Concentrations in the initial solution (ppm)	Concentrations in the treated solution
Sodium octyl sulfate	564	<0.025 ppm
Perfluoroalkyl carboxybetain	54	<0.175 ppm
2-(2-Butoxyethoxy)ethanol	400	<0.180 ppm

Activated carbon used at real scale⁵.

In Jan 2005 a fire of hydrocarbons occurred in Missouri. The extinction of this fire generate 4.2.10⁶ L of effluent. This effluent was mainly made of water but was also containing a significant amount hydrocarbons and components of fire fighting foams. After a preliminary trial, this effluent has been treated with two cartridges containing a total weight of 4500 Kg of granular activated carbon. After several days of filtration, the “discharge

was in compliance with the effluent limitations specified in the Department of Natural Resources permit". Once fluorinated components are adsorbed onto the activated carbon, this activated carbon can be incinerated in a special incinerator that is able to capture the decomposition products of perfluorinated compounds.

It is important to remind that if the effluent cannot be pumped, activated carbon as a powder can be used like the treatment of drinkable water against pesticides (as mentioned above).

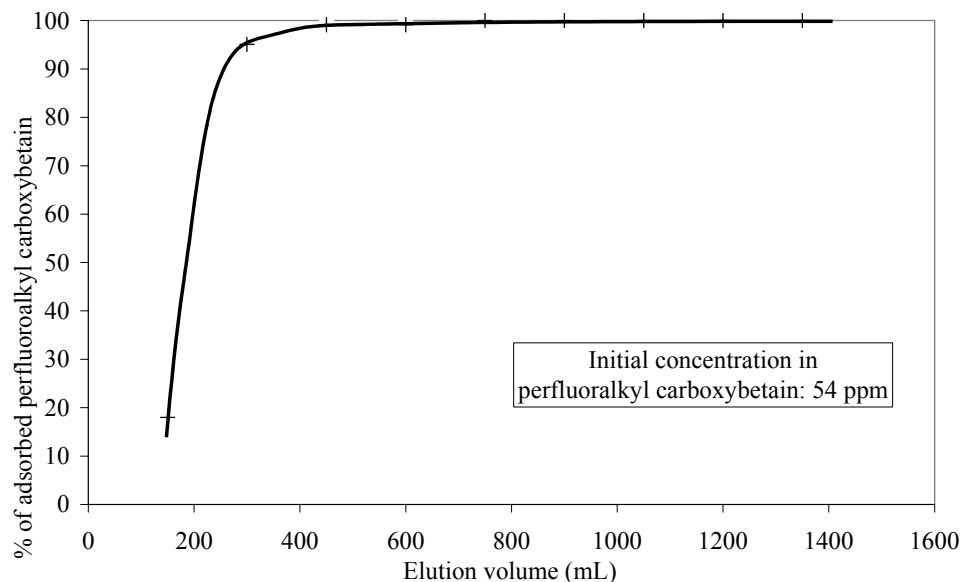


Figure 4: Evolution of the adsorbed rate as a function of the elution volume for the perfluoroalkyl carboxybetain.

Cross filtration.

As an alternative to activated carbon, cross filtration techniques can be evaluated. This technique consists in using a diafiltration membrane above which the fluid to be purified circulates in parallel to the membrane's surface. This system avoids the accumulation of large molecules on one side of the membrane. Such systems already proved their efficiency to remove mercury from water^{6, 7}. In that case, mercury is complexed with a cationic polymer. Water passes through a membrane and the polymer/mercury complex remain on one side of the membrane. A similar system could be applied to fluorinated compounds because cationic polymers that are able to interact with them are already well known. This work represents a very good opportunity for the development of a new technique for the removal of fluorinated compounds from water.

Conclusion

In the present work we show that the removal of fluorinated compounds from water is possible with existing technologies.

One of the presented possibilities has already been applied in real scale. Even if the example presented here deals with a fire fighting effluent, the discussed technologies can be tested in other domains as long as a fluorinated compound has to be removed from water.

References

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