Removal of Diclofenac from Water using an Hybrid Process Combining Activated Carbon Adsorption and Ultrafiltration or Microfiltration

Hassan Abdi Bogoreh and Catherine Charcosset*

Laboratoire d'Automatique et de Génie des Procédés (LAGEP), Université Claude Bernard Lyon 1, 43 bd du 11 Novembre 1918, Bâtiment CPE, 69622 Villeurbanne Cedex, France

Abstract: Small amounts of pharmaceuticals are increasingly found in natural waters and wastewaters in treatment plants. Several processes are developed for their removal such as hybrid membrane processes. These techniques integrate membrane filtration (mainly ultrafiltration or microfiltration) to a physical technique (such as flocculation or sorption on activated carbon). In this study, we report results on a process with sorption on activated carbon and microfiltration or ultrafiltration using a ceramic membrane, with a specific attention to the influence of the membrane pore size. The membranes showed little fouling at the experimental conditions used (maximum 500 mg/L activated carbon), while an important increase in conductivity was observed in permeate samples due to the salting out of ions from the activated carbon particles. Besides, the removal of diclofenac and humic acid (both at 10 mg/L) was higher than 90 % during the treatment with both ultrafiltration and microfiltration, however microfiltration was preferred due to its higher flux. These results suggest that hybrid processes of activated carbon/ultrafiltration or microfiltration could be interesting alternatives for processing waters containing small amounts of pharmaceuticals.

Keywords: Activated carbon, Hybrid membrane process, Pharmaceutical, Diclofenac, Humic acid.

1. INTRODUCTION

Small amounts of pharmaceuticals are found in natural waters (lakes, rivers) and in waste waters in treatment plants as a consequence of their increasing consumption. These molecules are mainly non-steroidal anti-inflammatory drugs (ibuprofen, diclofenac), antiepileptic (carbamazepine), antibiotics (sulfamethoxazole, erythromycine, *etc*) and lipid regulators (propranolol, gemfibrozil). Even at very low concentration (some ng/L or mg/L), these molecules may have important negative effects on humans, animals and plants. For example, the feminization of fishes by ethinylestradiol contained in contraceptive pills has been reported. Also, the increasing use of antibiotics could be at the origin of bacterial resistance.

To eliminate pharmaceuticals in wastewater treatment plants, several methods have been proposed such as sand filtration [1], coagulation/floculation [2, 3], and chlorination [4]. Ultraviolet (UV) irradiation has also been tested and found to remove 50 to 80 % of seven common antibiotics: carbadox, sulfachlorpyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfathiazole, and trimethoprim [3]. However, because of the strong doses of UV needed, this technique may be not economically competitive with other treatments [5]. Also, advanced techniques such as ozonation, advanced oxidation processes (AOPs) and activated carbon are effective methods for removal of pharmaceuticals [1]. Besides, separation membrane processes such as reverse osmosis and nanofiltration were extensively investigated these last years and were shown to remove effectively pharmaceutical compounds [6-12].

Ultrafiltration and microfiltration were also tested as their permeate flux is much higher, however they reject very few small molecules like pharmaceuticals, and they have to be integrated to other techniques such as ozonation or adsorption on activated carbon to be effective. Indeed, to limit membrane fouling, ultrafiltration or microfiltration can be integrated to ozonation which is a high performance oxidation chemical treatment. For example, Ternes *et al*. [1] showed that 0.5 mg/L ozone removed more than 90 % of diclofenac and carbamazepine, while bezafibrate was eliminated by 50 % with a 1.5 mg/L dose. Oh *et al*. [13] measured the removal rates by microfiltration of several pharmaceuticals (ibuprofen, bezafibrate, amoxicilline and sulfamethoxazole). The pre-ozonation was able to reduce membrane fouling by eliminating pharmaceuticals in water before their accumulation on the membrane surface. The ozone/microfiltration hybrid process also decreased the transmembrane pressure (TMP): after 20 h of microfiltration with an ozone dose of 4.8 mg/L, the TMP was two-fold lower than the TMP obtained by microfiltration without addition of ozone. Mori *et al*. [14] also studied the effect of ozone on water

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*Address correspondence to this author at the Laboratoire d'Automatique et de Génie des Procédés (LAGEP), Université Claude Bernard Lyon 1, 43 bd du 11 Novembre 1918, Bâtiment CPE, 69622 Villeurbanne Cedex, France;
Tel: + 33 4 72 43 18 34; Fax: + 33 4 72 43 18 49;
E-mail: catherine.charcosset@univ-lyon1.fr

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treatment by microfiltration. These authors showed that ozone was able to decompose the organic gel formed on the membrane surface, thus reducing the membrane fouling and increasing the permeate flux.

Hybrid processes with activated carbon and ultrafiltration or microfiltration have also been investigated. In these hybrid processes, activated carbon particles bind low and high molecular compounds, while the membrane retains the active carbon particles and other large compounds. Several applications have been proposed such as removal of natural organic matter like humic acids [15-19], chemicals like bisphenol A [20], as well as pharmaceuticals and personal care products [21, 22]. The activated carbon has also the advantage to limit membrane fouling by scouring the membrane surface [17, 18]. However, it can also increase membrane fouling as the attachment of natural organic matter to the activated carbon particles can lead to an increase in cake layer resistance. Moreover, overdosing of activated carbon can cause fouling by blocking the membrane pores. For example, adsorption on activated carbon followed by ultrafiltration was used for removal of eleven emerging contaminants (acetaminophen, metoprolol, caffeine, antipyrine, sulfamethoxazole, flumequine, ketorolac, atrazine, isoproturon, 2-hydroxybiphenyl and diclofenac) [22]. Different concentrations of powered activated carbon (in the range 10–600 mg/L) were used by stirring during 24 h. Low activated carbon dose in the range 10–50 mg/L was enough in order to remove most of the contaminants.

In this study, we investigate a process integrating adsorption by activated carbon and ultrafiltration or microfiltration for removal of pharmaceuticals in water, especially the effect of membrane pores size on the rejection of model molecules and flux through the membrane. Diclofenac was chosen as the model pharmaceutical, and humic acid as the model organic molecule in solution. The hybrid process of adsorption by activated carbon and ultrafiltration or microfiltration was first tested with demineralized water, then for removal of diclofenac and humic acid.

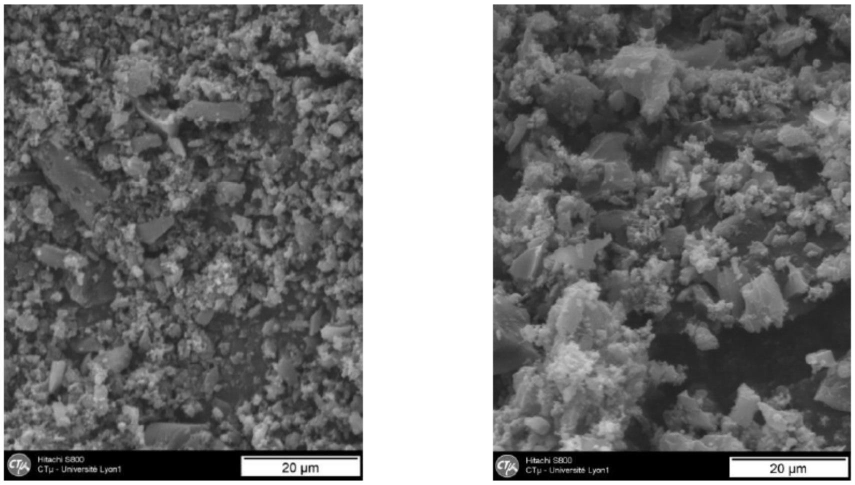
2. MATERIALS AND METHODS

2.1. Materials

Chemicals used in this work were sodium hydroxide (NaOH), acetic acid (CH_3COOH), diclofenac sodium salt and humic acid. They were supplied by Sigma Aldrich (France). The diclofenac sodium salt, $C_{14}H_{10}Cl_2NNaO_2$ is widely commercialized under various trade names. Its molecular weight is 318.13 g/mol (318.13 Da).

Humic acids are polymers with high molecular weight, negatively charged, with black or dark brown color. They are rich in carbon but less in oxygen. The molecular weight of humic acids may vary from 1 to 300 kDa.

Two powered activated carbons were tested: SA SUPER with a mean particle size (D_{50}) of 15 μm and SA UF with a mean particle size (D_{50}) of 5 μm both provided by Norit (France). The two powers were observed by scanning electron microscopy (SEM) (Figure **1**) with a FEI Quanta 250 FEG microscope at the "Centre Technologique des Microstructures" (CTμ) from the University of Lyon 1 (Villeurbanne, France). A



(a) **(b)**

Figure 1: Activated carbon observed by scanning electron microscopy, (**a**) SA SUPER, and (**b**) SA UF.

small amount of activated carbon was deposited on a flat steel holder and coated under vacuum by cathodic sputtering with 10 nm of copper. The samples were then observed under an accelerating voltage of 15 kV. Figure **1** shows SEM pictures of the two activated carbons, which have a large distribution in size and shape.

2.2. Experimental Set-up

The experimental set-up is shown in Figure **2**. It included a Micro Kerasep® membrane device (Novasep, France). The activated carbon was added to a 5 L reactor containing 3 L of solution. The suspension was recirculated in a closed loop using a Quattro flow 1000S pump (Pall, France). Two pressure gauges were placed at the inlet and outlet of the module, and a valve at the outlet for increasing the TMP. A mechanic stirrer (RW 20, IKA-Werke, France) was used to stir continuously the suspension of activated carbon in the reactor (200 rpm).

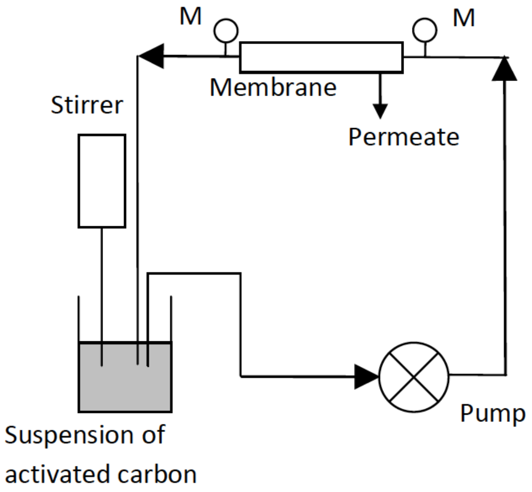


Figure 2: Experimental set-up of the hybrid membrane process of activated carbon/microfiltration.

The Kerasep® ceramic membrane is tubular, with an outside diameter of 10 mm, an inner diameter of 6 mm and a length of 40 cm; the active membrane area is therefore 0.0075 m^2. The active layer is made of ZrO_2/TiO_2 deposited on a monolithic TiO_2/Al_2O_3 support. Several membranes were tested with respectively 0.1 or 0.2 µm pore size (microfiltration), 50 kDa and 150 kDa cut-off (ultrafiltration). Table **1** summarizes the different properties of the membranes used.

2.3. Experimental Protocol

The feed flow rate was set to 5.45 L/min, corresponding to a mean tangential velocity of 3.2 m/s in the tubular membrane. The activated carbon was added to the reactor at a dosage in the range 100 - 500 mg/L as previously reported [*e.g.* 17, 22]. The initial feed volume was 3 L and the experiment was stopped when at least 1.5 L of permeate was recovered. The temperature of the suspension in the reactor was set to 20-22 °C. At regular time intervals, the permeate flow rate was measured. The permeate flux was obtained by dividing the flow rate by the membrane area. Permeate samples were collected at regular time intervals for analysis of conductivity, diclofenac or humic acid concentration.

Table 1: Membrane Characteristics

Membrane Support	Monolithic TiO_2/Al_2O_3
Layer	ZrO_2/TiO_2
Inner membrane diameter (m)	$6.0\ 10^{-3}$
Outer membrane diameter (m)	$1.0\ 10^{-2}$
Tube length (m)	0.4
Membrane area (m^2)	$7.5\ 10^{-3}$
Pore diameter or cut-off	0.1 µm, 0.2 µm, 50 kDa, 150 kDa

The initial concentrations in diclofenac and humic acid were 10 mg/L. Permeate samples were taken at regular intervals, and diclofenac and humic acid concentrations were measured by spectrophotometry (UV-Visible spectrophotometer Cary 50 Probe, Agilent Technologies, France). The absorbance was measured respectively at 276 and 254 nm for diclofenac and humic acid since these wavelengths correspond to the maximum absorbance in the UV spectrum. They also correspond to values reported for diclofenac by Sarasidis *et al*. [23] and humic acid by Rodrigues *et al*. [24]. Conductivity was measured using a CDM210 Conductivity Meter (Radiometer Analytical, France).

After each experiment, the activated carbon was removed by flushing the experimental set-up with water in an open loop configuration. The membrane and the experimental set-up were then cleaned by flushing successively with acid, water, base, water in a closed loop configuration while the permeate was removed. The protocol can be summarized as follows:

1) Open loop configuration (to remove activated carbon):
   - 2 L deionized water at T = 25°C

2) Closed loop configuration:

- 2 L 0.4% NaOH during 40 min at T=40° C, TMP = 1 bar
- 2 L deionized water
- 2 L 0.2 % acetic acid during 40 min at T=40°C, TMP = 1 bar
- 2 L deionized water

After each cleaning cycle, the membrane permeability was checked to be close to its initial value (more than 95%).

3. RESULTS

We present results obtained with activated carbon and ultrafiltration or microfiltration, first with demineralized water, then for the removal of humic acid and diclofenac.

3.1. Purified Water

We first studied the process using demineralized water (*i.e.* without diclofenac and humic acid) to see the effect of activated carbon on flux and membrane fouling. The change in activated carbon properties was recorded by measuring the conductivity of permeate samples.

The variation of flux and conductivity of permeate samples at regular time intervals is shown in Figures **3** and **4** for various concentrations of activated carbon SA UF and in Figures **5** and **6** for various concentrations of activated carbon SA SUPER. The ultrafiltration membrane is a ceramic membrane with 150 kDa cutoff. For the activated carbon SA UF at concentration of 100 and 500 mg/L, the flux remained constant during the experiment (1 h) while for the concentration of 300 mg/L the flux decreased slightly (Figure **3**). For the activated carbon SA SUPER, the flux was almost constant for the three concentrations (Figure **5**). These results indicated low membrane fouling. The activated carbon particles circulated tangentially to the membrane, without settling inside pores (internal fouling) or on the surface. Low fouling may be due to the large particles size, low particle concentrations, and low chemical interaction between the particles and the membrane. Besides, the fluxes obtained with both activated carbons were similar, being slightly higher for the activated carbon (SA UF), for which the average particles size is smaller.

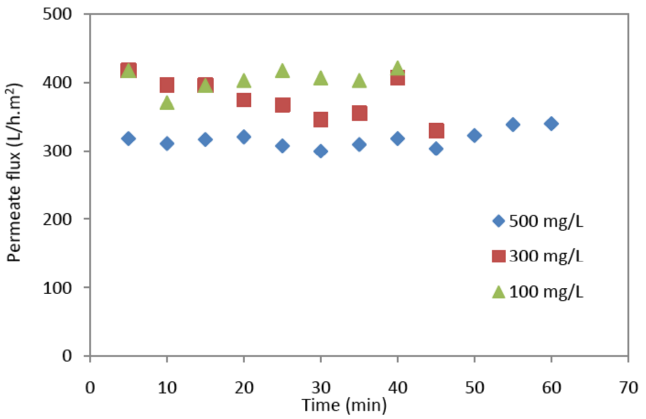


Figure 3: Variation of flux versus time for different concentrations of activated carbon SA UF (membrane UF 150 kDa).

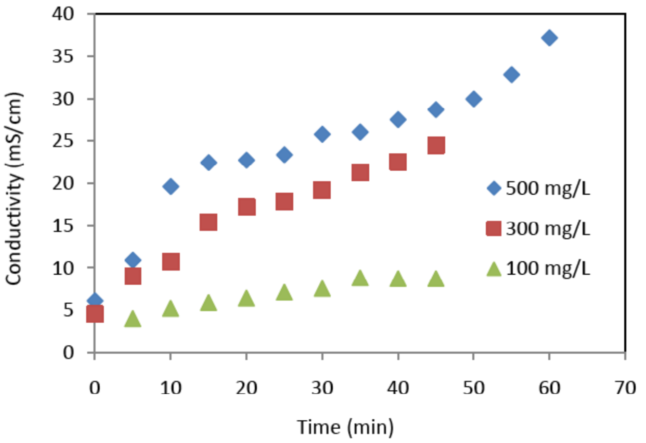


Figure 4: Variation of conductivity versus time for different concentrations of activated carbon SA UF (membrane UF 150 kDa).

Moreover, Figure **4** shows the variation of conductivity at different concentrations of activated carbon SA UF for the ultrafiltration 150 kDa membrane. The conductivity increased versus time, whatever the activated carbon concentration and type. Besides, at higher activated carbon concentration, the conductivity of the permeate was higher. The same trends were observed for the activated carbon SA SUPER (Figure **6**). The increase in conductivity of permeate samples is due to the increasing amount of ions. Indeed, in a previous study on the relation between chemical and physical properties of activated carbon, Julien *et al*. [25] measured the various ions concentrations released after agitation during 24h. Mineral components liberated in water by activated carbon were measured by conductivity showing that large quantities of mineral ions, mostly calcium were released.

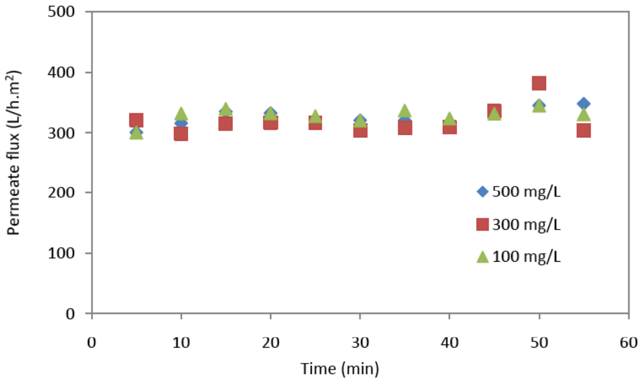


Figure 5: Variation of flux versus time for different concentrations of activated carbon SA SUPER (membrane UF 150 kDa).

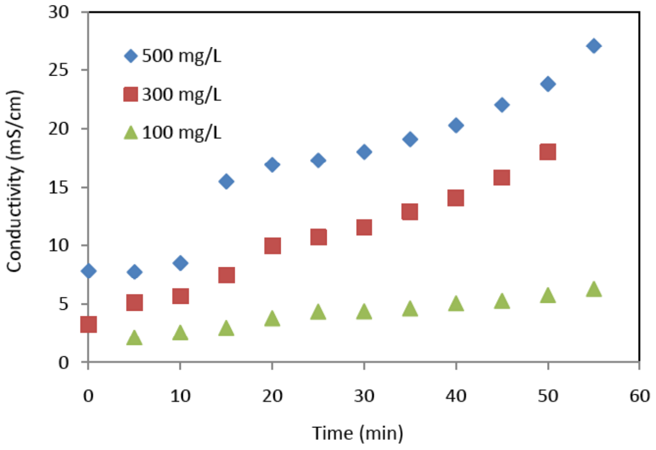


Figure 6: Variation of conductivity versus time for different concentrations of activated carbon SA SUPER (membrane UF 150 kDa).

In addition, various membranes were tested: 50 kDa and 150 kDa ultrafiltration membranes (TMP=2 bar) and 0.1 µm microfiltration membranes (TMP= 1 bar) to see the effect of membrane pore size on the hybrid sorption/filtration process. Figures **7** and **8** show the variation of permeate flux and conductivity for the three membranes. As expected, the flux was much higher for the microfiltration 0.1 µm membrane (3.5 times the value obtained with the ultrafiltration membranes). The time needed to obtain the same volume of permeate was then much lower (around 10 min) with the microfiltration membrane than with the ultrafiltration membrane (50 min). The fluxes of the two ultrafiltration membranes were nearly the same despite different cut-offs, which can be explained by the high surface heterogeneity of these ceramic membranes. Besides, the conductivity was higher for the 0.1 µm microfiltration membrane, than with the ultrafiltration membrane. In the following experiments, only results obtained with the activated carbon SA UF are reported.

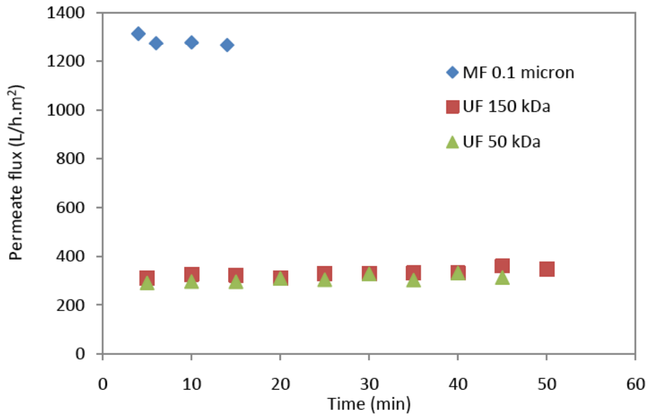


Figure 7: Variation of permeate flux versus time for different membranes (activated carbon SA UF = 300 mg/L).

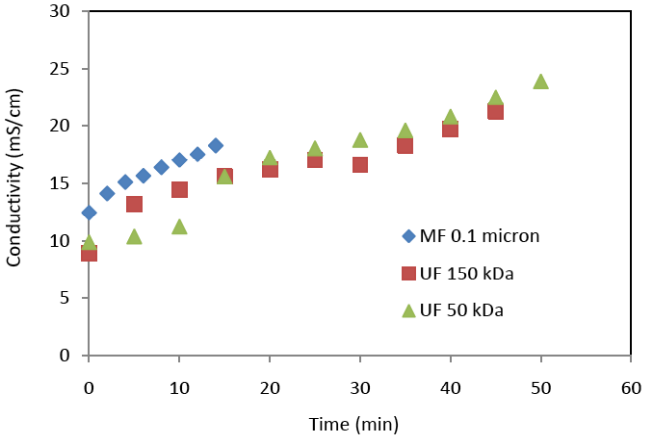


Figure 8: Variation of conductivity versus time for different membranes (activated carbon SA UF = 300 mg/L).

3.2. Removal of Humic Acid

Natural waters (rivers, lakes) and effluents from wastewater treatments plants often contain organic matter in suspension. Humic acid is often used a model molecule of organic matter.

The effect of the membrane type has been studied for acid humic removal by activated carbon and ultrafiltration or microfiltration. Figure **9** shows the variation of flux versus time for the different membranes during removal of humic acid. For the two ultrafiltration membranes, the flux was around 310 L/h.m^2 and was constant during the treatment. For the 0.2 µm microfiltration membranes, the flux was 6 times higher. The removal of humic acid by activated carbon followed by ultrafiltration has been previously investigated (*e.g.* 15, 19). These studies show the effect of the membrane chemistry on membrane fouling, due to interactions between humic acid molecules, activated carbon particles and the membrane. At our experimental conditions (around 1.5

L of permeate was recovered), the ceramic membrane did not show fouling, but this has to be further tested with larger volumes.

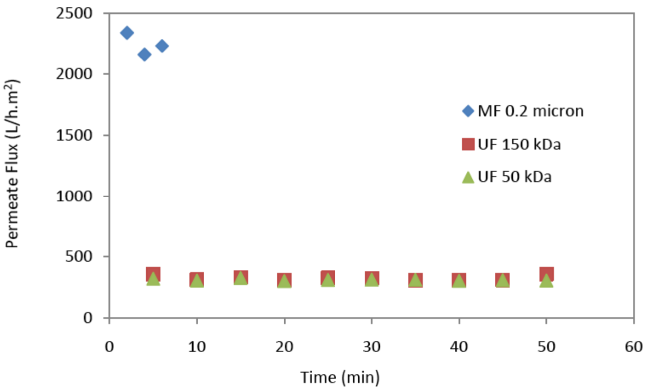


Figure 9: Variation of flux versus time for different membranes during humic acid removal ([humic acid]$_0$ = 10 mg/L, activated carbon SA UF = 300 mg/L).

Figure **10** shows the variation of humic acid removal rate for different membranes. Around 90-95 % of humic acid was removed by activated carbon combined to ultrafiltration or microfiltration. High removal rate was obtained by Lee *et al*. [19] with activated carbon and ultrafiltration in a dead-end system, although high fouling was reported. Mozia *et al*. [15] used activated carbon and ultrafiltration, and also observed fouling by humic acid which depends strongly on the membrane material used. Our results show that microfiltration was able to removed humic acid at similar rate as ultrafiltration, but with a much higher flux.

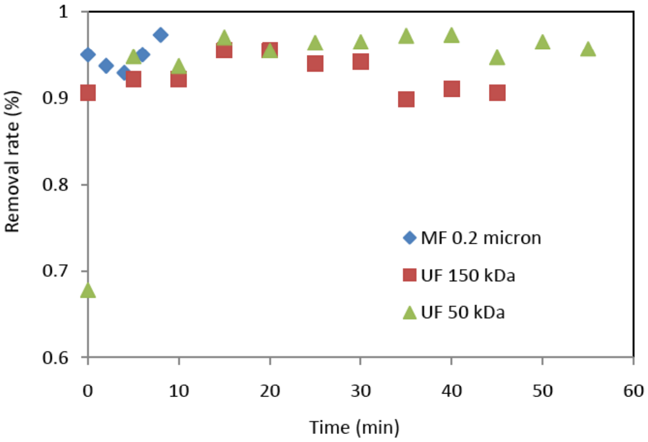


Figure 10: Variation of humic acid concentration in the permeate versus time for different membranes during humic acid removal ([humic acid]$_0$ = 10 mg/L, activated carbon SA UF = 300 mg/L).

3.3. Removal of Diclofenac

The effect of the membrane type (ultrafiltration or microfiltration) on diclofenac removal was studied. Figure **11** and **12** show the flux variation and diclofenac concentration versus time, respectively. As for humic acid, the membrane flux was much higher with the 0.2 µm membrane, than the ultrafiltration membrane. For the ultrafiltration membrane, the flux was almost constant during 50 min of filtration, which suggests low fouling. However, higher volumes would have to be treated to investigate fouling in more severe conditions.

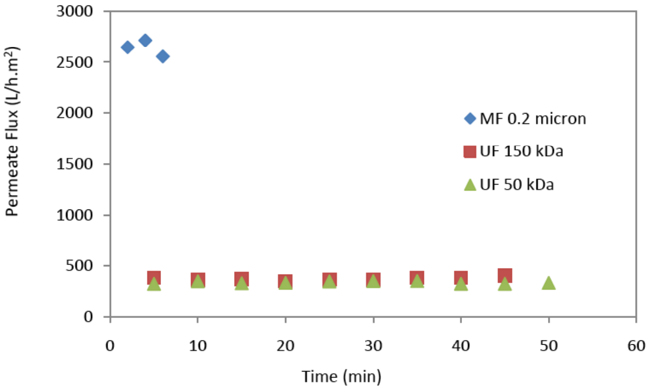


Figure 11: Variation of flux versus time for different membranes during the removal of diclofenac ([diclofenac]$_0$= 10 mg/L, activated carbon SA UF = 300 mg/L).

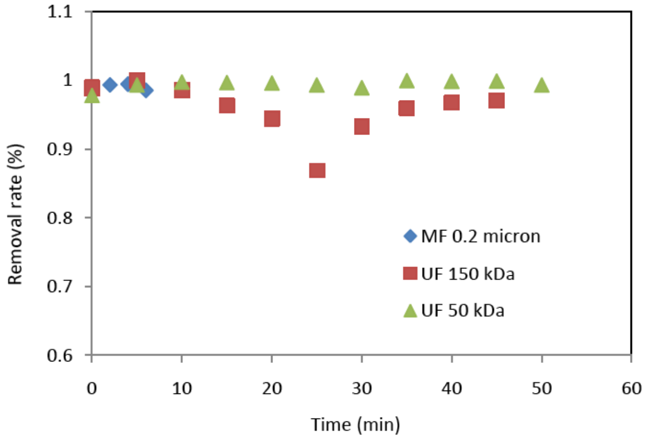


Figure 12: Variation of diclofenac concentration versus time for different membranes during the removal of diclofenac ([diclofenac]$_0$ = 10 mg/L, activated carbon SA UF = 300 mg/L).

Figure **12** shows the variation of diclofenac removal rate in the permeate for the different membranes. Like for humic acid, 90-95 % diclofenac was retained by the activated carbon and ultrafiltration or microfiltration membrane. The diclofenac molecule has a low molecular weight (236.15 Da) compared to the membrane cut-off of the ultrafiltration membranes (50 and 150 kDa). This suggests that diclofenac removal occurs mainly by sorption on the activated carbon particles, and not by steric rejection by the membrane, as it could happen for humic acid. Using activated carbon as a pretreatment before ultrafiltration, Acero *et al*. [22] obtained around 100 % of diclofenac removal rate, mainly due the initial sorption by activated carbon.

CONCLUSION

In this study, results were obtained using a hybrid process of sorption by activated carbon and ultrafiltration or microfiltration. Sorption was achieved simultaneously to filtration as the membrane retains the activated carbon particles in suspension. The process was shown to remove 90-95 % of diclofenac and humic acid at the experimental conditions tested (maximum 500 mg/L activated carbon). Microfiltration was preferred to ultrafiltration because of similar removal rates by much higher fluxes. In the future, a process with continuous addition of water containing pharmaceuticals and larger volumes will be investigated.

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