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A Pilot Study of a Hybrid Process Involving In Situ Regenerated Activated Carbon, Membrane Separation and Advanced Oxidation for Water Pollution Abatement

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ABSTRACT

The assessment of a pilot-scale hybrid system coupling powdered activated carbon (PAC) adsorption with membrane ultrafiltration (UF), in respect of activated carbon regeneration and organic micropollutant removal, was investigated in this study. Field tests with two adsorbents (i.e. a commercial PAC and a PAC-Fe(II) composite), conducted in the premises of Thessaloniki Water Treatment Plant, demonstrated the high efficiency of the combined PAC/UF process. Regeneration efficiencies varying between approximately 95% and 110%, complete diclofenac (DCF) degradation and rather moderate mineralization (TOC removal) rates of up to 47%, can be achieved by UVC/H_2O_2 or photo-Fenton oxidation after 4 hours of treatment; this performance is attributed to the in situ generation of reactive oxidant species by photolysis of H_2O_2, which seems to enhance the process effectiveness. Among the two adsorbent materials tested, composite PAC-Fe(II) exhibited a higher DCF adsorption capacity than the original PAC, probably due to the improved chemisorption and/or the electrostatic attractive interactions between the negatively charged DCF molecules and the positively charged iron species, at neutral pH. Furthermore, a rather insignificant effect of PAC-Fe(II) loading on the regeneration efficiency was observed. The advantages of totally controlled H_2O_2 dosages and short operating times render the hybrid PAC/UF system a promising alternative to conventional and advanced drinking water purification methods.

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1. Introduction

On a global scale, pathogenic contamination of drinking water poses the most significant health risk to humans, and there have been countless disease outbreaks and poisonings throughout history resulting from exposure to untreated or poorly treated drinking water. However, significant risks to human health may also result from exposure to non-pathogenic, toxic contaminants that are often globally ubiquitous in the waters from which drinking water is derived. The number of substances that have been identified from surface waters and groundwater in Europe and globally [1, 2], is long and includes a wide variety of compounds such as personal care products (PCPs), pharmaceutically active compounds (PhACs), illicit drugs, flame retardants, industrial additives and reagents, artificial sweeteners, perfluorinated compounds, benzotriazoles, benzo-thiazoles, siloxanes, water disinfection by-products (DBPs), etc. The presence of this multitude of recalcitrant organic pollutants in freshwater and treated wastewater effluents, usually detected in a very low concentration range (from μg/L to ng/L), has alerted water and wastewater professionals. Indeed, many of these organic residuals are toxic and may pose a severe risk related to the consumption of drinking water (especially when the latter originates from surface water) and deterioration of the ecological status of the receiving waters [3, 4].

Among the different advanced treatment methods employed in the drinking water sector, for the effective removal of natural organic matter and organic contaminants of emerging concern, membrane filtration processes, including nanofiltration (NF) [5, 6] and ultrafiltration (UF) in combination with upstream powdered activated carbon (PAC) adsorption (PAC/UF) [7-11] are the most popular. Full-scale installations can be found in France (Méry-sur-Oise plant in the northern part of Paris) [12], Lausanne (Switzerland), Vigneux (France), Kopper (Slovenia) and San Antonio (Texas) [12, 13], where the main drivers for their adaptation have been the remediation of surface waters polluted with pesticides, taste and odours, as well as disinfection-by-products. In comparison to the tight membranes employed in NF and reverse osmosis (RO) processes, the combination of more porous membrane filtration processes (such as ultrafiltration) with upstream PAC adsorption is proven to have positive effects on the performance of the membrane-separation stage. The main reason for this trend is reported to be the adsorption of a certain fraction of the dissolved organic carbon upstream of the membrane to mitigate fouling [14-17]. Other advantages of PAC/UF over higher-pressure membrane processes include: [18] a) lower operating costs; b) process flexibility because the PAC type and doses can be quickly changed depending on the water quality; and c) unlike spiral-wound modules commonly used in NF and RO, UF hollow fiber modules can be backwashed, reducing the frequency of chemical cleaning, as some of them have a high tolerance to chlorine. In contrast to PAC conventional applications, the use of a UF membrane to retain PAC particles allows: a) higher disinfection capacity; b) the use of smaller PAC particles, with faster adsorption kinetics, but still with very efficient separation; c) the potential regeneration of PAC, considering that it may be isolated from other reagents; d) the recirculation of PAC during the filtration cycles, which enhances the carbon residence time and adsorption efficiency while minimizing the sludge production.

Although the general applicability of the PAC/UF process has been proven, significant challenges remain, particularly regarding the performance of the hybrid PAC/UF processes, in increased/rapid pollution episodes, and the need to reduce the PAC waste, in accordance with the principle of ‘zero waste discharge’. These challenges have been addressed in recent work by the authors [19], in which hybrid process alternatives have been investigated involving PAC/UF processes in conjunction with H_2O_2-based advanced oxidation processes (AOPs) for the combined removal of organic pollutants and the in situ regeneration of the powdered adsorbent, thus allowing efficient continuous operation with no polluting waste streams. The two AOPs tested were the UV light/hydrogen peroxide (UVC/H_2O_2) process and photo-Fenton (PF) reaction process, with the latter promoted by special iron oxide nanoparticles–PAC (PAC-Fe) composites as adsorbents. Similar advanced oxidation techniques were investigated by Horng *et al*. [20, 21] and Muranaka *et al*. [22, 23]. Both AOPs involve the generation of a very powerful oxidizing agent such as hydroxyl radical (•OH), and other reactive species by H_2O_2-decomposition in solution, in sufficient quantity to effectively regenerate the adsorbents, thus restoring their adsorption capacity. Motivated by the promising results of the research work carried out in a laboratory environment, new tests were performed in a relevant environment towards increasing the technology readiness level of the hybrid process (TRL 5-6). Specifically, the patented novel process [24] was validated in the Thessaloniki Water Treatment Plant (WTP), with the aid of a special PAC/UF pilot-scale experimental unit that was designed and constructed in-house by

NRRE/CPERI/CERTH expert staff [19]. Raw surface water obtained from Aliakmon River, Greece, subjected only to pH adjustment and coarse filtration, was treated by the PAC/UF unit, with the addition of diclofenac (DCF), a nonsteroidal, anti-inflammatory pharmaceutically active compound, frequently encountered in natural and surface waters in very low concentrations, affecting both human health and environment [25], as model organic micro-pollutant. The present work summarizes the results of the first series of field tests as well as the prospects of the proposed novel process for future large-scale applications.

2. Experimental

2.1. Materials and Reagents

A common commercial powdered activated carbon (DARCO® G60, Sigma-Aldrich) was chosen as the adsorbent material in this study. According to the manufacturer (Cabot, Norit NV) DARCO® G60 is high purity steam activated carbon, suitable for decolorizing and purifying pharmaceuticals, especially when high purity additives are used. Moreover, DARCO® G60 has a very high adsorptive capacity and excellent filtration characteristics that meet the requirements of the US Food Chemical Codex. The particle size of this charcoal-made PAC is 100 mesh, the BET surface area is 1052.9±3.34 m^2/g, the total pore volume is 0.93 cm^3/g, the average pore width is 3.0 nm, and the point of zero charge (pH_{pzc}) is 7.38 [26]. The material is characterized as mesoporous, as evidenced by the respective pore size distributions of DARCO®G60 that are readily available in the literature [27-29]. DARCO® G60, was also used for the preparation of PAC-Fe(II) composite, an iron-oxide impregnated PAC adsorbent, according to the procedure described elsewhere [26]. The main properties of PAC-Fe(II) are BET surface area 1037 m^2/g, total pore volume 0.91 cm^3/g average pore width 2.8 nm and point of zero charge (pH_{pzc}) ~7.56 [26]. Diclofenac sodium salt ($C_{14}H_{10}Cl_2NNaO_2$, Sigma-Aldrich) was selected as a representative toxic organic micro-pollutant and used without any pre-treatment. In all the experiments the DCF molecule is considered negatively charged due to the rather neutral pH conditions in conjunction with the acid dissociation constant (pKa) 4.15, related to the hydrophobicity of this compound ($\log K_{ow}$=4.51). A 30% w/w solution of hydrogen peroxide (H_2O_2, Chem-Lab NV) was used during the regeneration stage of the experimental protocol applied in this work (UVC/H_2O_2 or the heterogeneous PF oxidation). The PAC-Fe(II) composite adsorbent was prepared using iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, Merck). For H_2O_2 analysis, potassium hydrogen phthalate (KHP, Sigma-Aldrich), potassium iodide (KI, Sigma-Aldrich), ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, J.T Baker), sodium hydroxide (NaOH, Merck), and Milli-Q® water (Millipore, Milford, MA) with a resistivity of 18.2 MΩ · cm (at 25°C). All the above chemicals were of analytical or reagent grade. All the above chemicals were of analytical or reagent grade. The water matrix employed in this study was Surface Water (SW) obtained from Aliakmon River, Greece, which was subjected only to pH adjustment (from 8.3 to 7.5) and coarse filtration through ~30μm cartridge filter. Water quality parameters of SW are included in Table **1**. Four single-ended, germicidal low-pressure mercury vapor fluorescent lamps (PURO s.r.l.), suitable for disinfection and sterilization, with nominal power 39 W each, emitting at 253.7 nm, were used as a UVC light source of the system. 496 Ultrafiltration (UF) hollow fibers (PURON® PSH-31, Koch Membrane Systems), made of proprietary polyvinylidene fluoride (PVDF), with nominal pore size 30 nm and outer diameter 2.6 mm, were used to construct a membrane module of approx. 1 m length and of total surface area 4.19 m^2.

Table 1: Quality parameters of feed water.

Parameter	Annular Averaged Value
pH	7.5
Conductivity (μS/cm)	374
Turbidity (NTU)	3.0
Color Pt-Co (CU)	21
Total Organic Carbon (mg/L)	1.9
Suspended Solids (mg/L)	395

2.2. PAC/UF System

The pilot-scale PAC/UF system was designed and constructed in-house by NRRE/CPERI/CERTH expert staff. A schematic diagram and an image of the pilot system are shown in Figure **1**. The PAC/UF pilot is comprised mainly of a commercial UV sterilizer (4S, PURO s.r.l) and a membrane vessel. The UV sterilizer is a SS 316L closed cylindrical chamber of 15 L working volume. It is equipped with an advanced control panel for controlling and monitoring all operations of the UV system. Inside the chamber, there are four quartz glass sleeves placed vertically, where four UVC lamps are encased within. The membrane vessel is cylindrical, of 10 L volume, made of Plexiglass®, where a custom-made membrane module is submerged. The purified water (permeate) is collected in a 1 L backwash vessel, whereas the feed water (pretreated river water) is transferred to two tanks, one 200 L plastic tank, and a larger feed tank of 1500 L, made of fibreglass. The latter has been especially connected to serve the particular continuous pilot field tests in the premises of the Thessaloniki Water Treatment Plant (WTP), (Aliakmon water refinery). The PAC/UF system has 25 L total effective volume, 156 W total nominal power and approx. 1.2 m^3/d treatment capacity.

Two gear pumps are used for permeate suction operation, and for supplying solution from the feed tank into the system, operating at approx. 60 L/h and 50 L/h, respectively. A centrifugal pump is used for the recirculation of feed solution-activated carbon mixture, between the UV sterilizer and the membrane vessel, at a rate of approx. 1.3 m^3/h. An air compressor provides sufficient air at the bottom of the membrane vessel, through a porous diffuser, at a rate of approx. 90-130 L/h. A touch-screen/panel PC, an appropriate data logging system with a memory card and various sensors serve for the monitoring and the recording of experimental data including transmembrane pressure (TMP), permeate flux, airflow, pH, electrical conductivity and temperature. A periodic backwashing protocol is implemented; i.e., 1 min backwash with the collected permeate after 9 min suction operation, as it was shown to be satisfactory in similar water treatment applications in NRRE laboratory [30-32]. This novel PAC/UF pilot system is fully automated and can run either unattended for a long time period or remotely monitored. Further details on the construction, characteristics, automations, innovative features and distinct advantages of the pilot system can be found elsewhere [33].

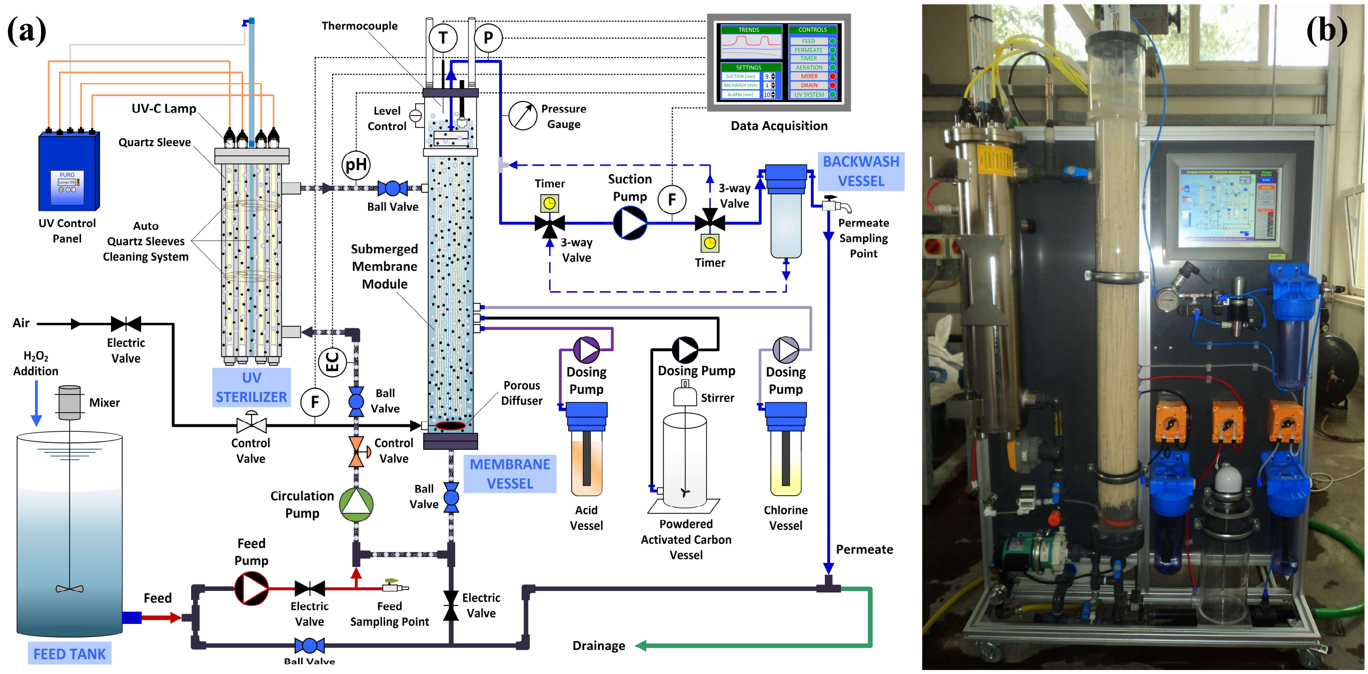

Figure 1: (a) Schematic diagram and **(b)** front view of the PAC/UF pilot system.

2.3. Experimental Procedures

All pilot experiments were performed in the premises of Thessaloniki WTP, where the PAC/UF pilot system was installed temporarily, so as to assess and validate the hybrid process in a relevant environment (TRL 5). It is noted that Thessaloniki WTP treats surface water using cutting edge methods including ozonation, ozonation coupled with hydrogen peroxide (O_3/H_2O_2) and activated carbon filtration, which render the water clean and safe for drinking purposes. The facility is characterized at present by a daily treatment capacity of 150,000 m^3.

A DCF stock solution of approx. 80 mg/L was prepared under stirring at 250 rpm for approx. 2 h. In parallel, an activated carbon suspension was prepared by dispersing a specific amount of powder in deionized water and magnetically stirred for 30 min. The feed tank was initially filled with SW, which was subjected to coarse filtration through a ~30 μm cartridge filter. Next, the DCF solution was diluted with SW in the feed tank, up to a total final volume of 800-1500 L, to achieve the desirable concentration of approx. 50 μg/L (similar to the concentration level of micropollutants in raw surface waters). The feed solution was continuously stirred in the feed tank, with the aid of a mechanical mixer.

The experimental protocol from this point consists of three sequential stages, i.e., saturation stage, regeneration stage and re-adsorption stage.

- At the first stage (duration 20 h), the adsorption of DCF on the dispersed adsorbent particles is pursued, till saturation. Initially, the system was fed with fresh PAC or PAC-Fe(II) suspension, diluted to a volume of 25 L. The DCF-PAC mixture was recirculated between the photoreactor and the membrane vessel under aeration for about 20 min, a time period sufficient to achieve uniformity of the adsorbent concentration and homogenization of the mixture. During this stage, the system operated in a batch mode and the permeate was recirculated from the membrane vessel back to the feed tank.
- At the second stage (duration 4 h), the regeneration of the saturated with DCF PAC or PAC-Fe(II) is investigated with the addition of hydrogen peroxide and simultaneous UVC irradiation. During this stage, a specific volume of 30% w/w H_2O_2 solution was added to the feed tank, obtaining the desirable concentration, and at the same time, the four UVC lamps were turned on. The system operated in a continuous mode and the permeate stream was rejected. *The photo-assisted H_2O_2 regeneration of the pure PAC is designated hereafter as UVC/H_2O_2 and that of the PAC-Fe(II) as photo-Fenton (PF).*
- The third stage (duration 4 h), includes the re-adsorption of DCF on the regenerated PAC and PAC-Fe(II) adsorbents. In this stage, a new DCF feed solution of the same concentration (50 μg/L) was added to the feed tank. The system operated in a batch mode and the permeate was recirculated, similarly to the first stage, from the membrane vessel back to the feed tank.

The total duration of all pilot runs (saturation, regeneration and re-adsorption stages) was 28 h. Feed and permeate samples were collected at specific time intervals and analyzed for their DCF and TOC concentrations. At the end of each test, the whole pilot system (tanks, vessels, UV chamber, cartridge filter etc.) was cleaned meticulously and the UF membrane module was rinsed well with fresh tap water prior to the implementation of the next experiment.

2.4. Analytical Methods and Measurements

The Total Organic Carbon (TOC) concentration was measured immediately after the sample collection by a TOC analyser (TOC-5000A, Shimadzu Co.) Variations of DCF concentration were determined by reversed-phase High-Performance Liquid Chromatography (HPLC). A liquid chromatography (LC-10AD VP, Shimadzu) fitted with a column (Discovery® HS C18 Supelco, Sigma-Aldrich), 5 μm, 150 mm x 4.6 mm (i.d.) at 30°C, and coupled with a diode array detector (DAD SPD-M20A, Shimadzu) set at 268 nm was used. The mobile phase of the applied isocratic elution consisted of 70% CH_3CN and 30% 0.025 M phosphate buffer solution (pH 3) at a flow rate of 1.0 mL/min. The injection volume of the samples was 20 μL. For DCF determination at concentrations of a few micrograms per litre (detection limit 11 μg/L), a pre-concentration by Solid-Phase Extraction (SPE) was followed and the percentage recovery of DCF was assessed with the aid of an internal standard (Sulfamethoxazole-SMX). Details about DCF extraction can be found elsewhere [31]. The achieved recoveries varied between 86 and 103%. The H_2O_2 concentration was determined spectrophotometrically (UV-1700 Pharmaspec, Shimadzu) by the iodide method, with a detection limit of 20 μg/L H_2O_2. Two calibration curves were prepared for low (0-180 μg/L quartz cells of 10 cm) and high (200-3400 μg/L quartz cells of 1 cm) H_2O_2 concentrations. Aliquots (3 mL) of samples were diluted to 50 ml by using Milli-Q® water. Then, this solution was mixed with 3 mL of 0.1 M potassium hydrogen phthalate and 3 mL of iodine reagent (0.4 M potassium iodide, 0.06 M NaOH, ~10^{-4} M ammonium molybdate). The obtained mixture was transferred to the appropriate quartz cuvette and finally, the absorbance of the formed I_3^- in the solution was measured with the spectrophotometer at 351 nm [33-35].

3. Results and Discussion

Table **2** summarizes the experimental conditions of the four preliminary pilot tests carried out in this study. A fairly realistic DCF feed concentration, a constant UVC radiant power per unit volume (P_R) and a rather narrow range of H_2O_2 doses were employed; i.e., approx. 50 μg/L, 2.1 W/L and 130-180 mg/L, respectively. In addition, two different adsorbents (PAC and PAC-Fe(II)) and two adsorbent loadings (5.2 and 20.4 mg/L) were examined.

It is noted that Exp. No 1 was conducted in a single stage (saturation stage) as a reference experiment, with the aim to examine the DCF adsorption on system components. On the contrary, Exp. No 2-4 were performed according to the aforementioned experimental protocol, in three sequential stages; i.e., saturation, regeneration and re-adsorption.

Table 2: Summary of experimental conditions.

Parameter	Experiment No			
	1	2	3	4
DCF feed concentration (μg/L)	50	51	52	59
PAC concentration (mg/L)	No	5.2	No	No
PAC-Fe(II) concentration (mg/L)	No	No	5.2	20.4
H_2O_2 concentration (mg/L)	No	129	177	150
Radiant power per unit volume (W/L)	No	2.1	2.1	2.1
Total Volume (L)	800	1364	1500	900
Temperature (°C)	22.6	25.4	24.5	22.7
pH	8.3	8.1	8.1	8.1
Electrical Conductivity (μS/cm)	395	390	382	385
Backwashing mode (min)	1/9	1/9	1/9	1/9
Hydraulic Residence Time (min)	59.3	32.4	32.4	32.4
Permeate Flux (L/(m²·h))	7.5	13.8	13.8	13.8
Air Flow (L/min)	2.2	2.0	1.5	1.5
Transmembrane pressure (mbar)* **(median values)*	-82.7	-303.3	-321.5	-296.4

3.1. Adsorption on PAC/UF System

An adsorption test was carried out without UVC irradiation (in the dark) and in the absence of PAC to evaluate the possible adsorption of DCF on the pilot system (tank, vessels, hollow fibers, UV chamber, tubes, etc.). The initial DCF feed concentration was 50 μg/L and the feed solution was recirculated into the system for about 20 h. The Hydraulic Residence Time (HRT) of the process was 60 min, corresponding to a permeate flux of 7.5 L/m²·h, while the periodic backwashing protocol was set to the '1/9' mode. As shown in Figure **2**, DCF feed concentration decreases with time until the system reaches an equilibrium, where DCF feed concentration is stabilized and equals the DCF concentration in the permeate stream. Thus, DCF feed concentration after the recirculation in the dark was slightly decreased to 46-48.5 μg/L, corresponding to an insignificant DCF loss of approximately 3-8%, indicating that adsorption of DCF on the system can be neglected. In other words, DCF shows almost no tendency for adsorption on the PAC/UF system, and the system begins to operate under constant conditions rather soon; i.e., in the first 3-5 hours.

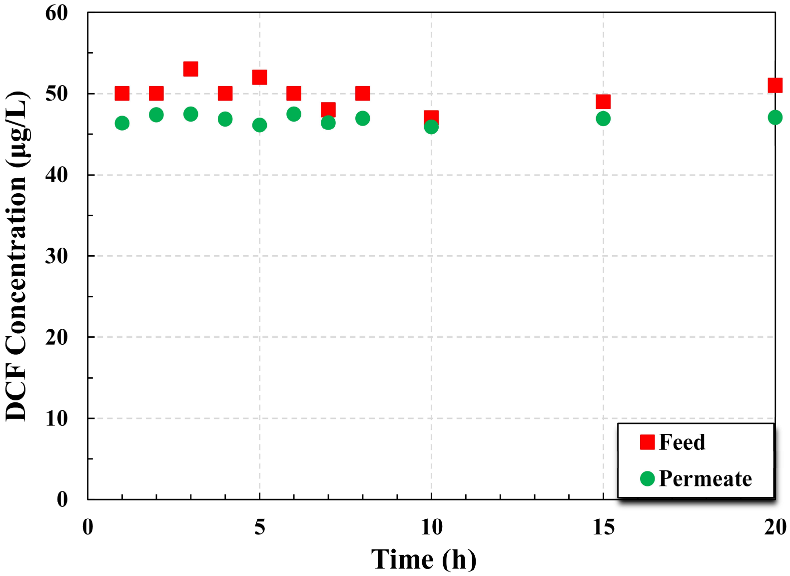

Figure 2: DCF concentration in feed and permeate stream vs operating time during adsorption on PAC/UF system (Exp. No 1).

3.2. Adsorption Capacity and Regeneration Efficiency

The amount of DCF mass adsorbed on the two different PAC materials was calculated from mass balances following the termination of the saturation stage of each pilot run, during which the system was operated in batch mode for 20 h reaching an equilibrium. The DCF uptake in equilibrium was denoted as the adsorption capacity of the specific pollutant on PAC or PAC-Fe(II) and is depicted in Figure **3**. For the same adsorbent loading (5.2 mg/L), the DCF adsorption capacity of PAC-Fe(II) is significantly higher than that of PAC, i.e., 150.1 mg DCF/g PAC-Fe(II) and 121.2 mg DCF/g PAC). This is in agreement with a previous work of the authors, and is attributed to the enhanced adsorption mechanisms of DCF on the composite PAC; e.g., monolayer instead of multilayer adsorption, chemisorption interactions with the impregnated iron oxides, greater electrostatic attractive forces [19, 26]. The effect of PAC-Fe(II) loading on DCF uptake was also investigated with the repetition of two identical experiments with different PAC-Fe(II) concentrations. Specifically, the increase of PAC-Fe(II) dosage from 5.2 to 20.4 mg/L, which corresponds to an increase of the PAC-Fe(II)/DCF mass concentration ratio from 100/1 to 400/1, resulted in a significant decrease of DCF adsorption capacity; i.e., from 150.1 to 77.7 mg DCF/g PAC-Fe(II). This is probably the result of the stronger competition with the natural organic matter substances present in the feed surface water for adsorption sites on the active PAC-Fe(II) surface sites, at higher PAC-Fe(II) loadings. Therefore, higher PAC-Fe(II) dosages are not necessarily favorable for practical applications.

The role of the H_2O_2-AOP based regeneration process on the overall PAC/UF system performance can be assessed by the regeneration efficiency (RE) of the oxidation process, which can be calculated from the ratio of the re-adsorbed DCF mass on the adsorbent after the regeneration to the saturated DCF mass prior the regeneration [36]. Thus, the RE percentage is given as follows:

$$\text{RE}(\%) = [\text{AC}]_R / [\text{AC}]_S \cdot 100 \qquad (1)$$

where $[\text{AC}]_R$ and $[\text{AC}]_S$ are the adsorption capacities (in mg DCF/g PAC or PAC-Fe(II)) in the re-adsorption and saturation stage, respectively.

It is obvious from Figure **3** that the UVC/H_2O_2 oxidation process not only exhibits complete regeneration of PAC but in addition considerably enhances the adsorption capacity (RE>100%) over the tested pollutant, a phenomenon that in some cases is also observed in the literature [37, 38]. Almost complete regeneration of PAC-

Fe(II) by PF oxidation can be achieved. Specifically, a DCF uptake increase of approx. 10% after PAC regeneration was achieved, while negligible effect (<2%) of adsorbent loading on RE was recorded; i.e. 94.7% for 5.2 mg/L PAC-Fe(II) and 95.8% for 20.4 mg/L PAC-Fe(II), respectively. Although the almost complete regeneration of PAC-Fe(II) confirms the excellent stability of the composite material, the regeneration efficiency of the PAC remains higher than that of the PAC-Fe(II) (by approx. 16%). These improved and/or maintained adsorption characteristics of both PACs were expected considering the catalytic effect of the high energy UVC irradiation on a) the successful H_2O_2 photolysis towards the generation of •OH or other reactive species, b) the promotion of heterogeneous Fenton-like reactions on the iron oxide nanoparticles' surfaces [39] and c) the appropriate H_2O_2 dose that is responsible for kinetic reactions acceleration [19].

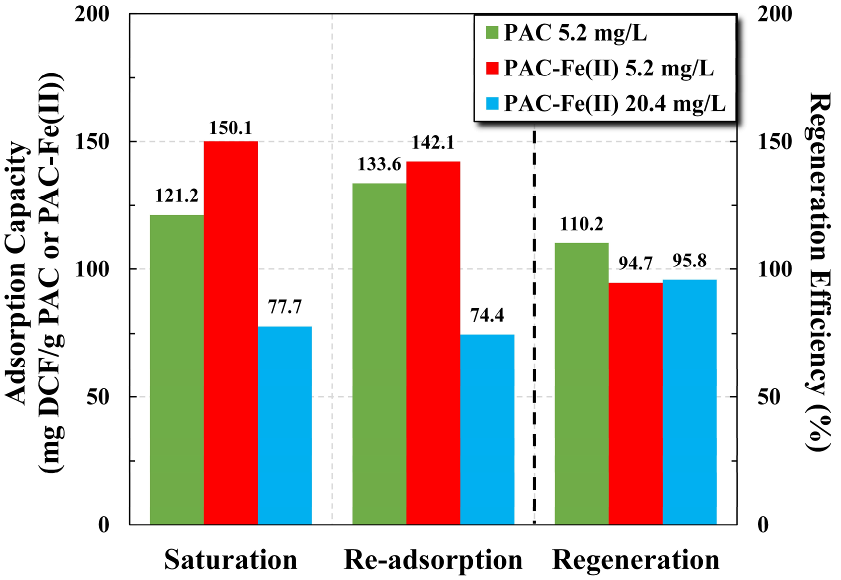

Figure 3: Adsorption capacity during saturation and re-adsorption stage and regeneration efficiency of PAC and PAC-Fe(II) (Exp. No 2-4).

3.3. DCF and TOC Removal

Degradation and mineralization rates attained during regeneration of PAC adsorbents by the UVC/H_2O_2 process, are represented in Figure **4** and expressed as DCF and TOC removal percentages, respectively. It is observed that almost complete (97.2-99.8%) DCF degradation is achieved with the addition of 129-177 mg/L H_2O_2 and the application of 2.1 W/L UVC irradiation for 4 h, regardless of the material involved. This was expected since the photolysis of H_2O_2 by high energy UVC light favors the production of powerful oxidants (•OH) leading to complete decomposition of DCF molecules [40]. Similar results in terms of total degradation of other organic substances by the PAC/UF process have been reported in the literature [41-43]. On the other hand, the degradation of DCF molecules results in the formation of intermediate organic by-products, which can be more recalcitrant to mineralization. Fragments and transformation products of DCF decomposition have been studied and identified in previous work by this research group [31, 33]. Thus, taking also into consideration the existence of background organic load, originating from several non-biodegradable contaminants present in the water matrix, the lower TOC removal rates in comparison with DCF rates can be explained. As previously stated, the raw river water consisted of a heterogeneous mixture of organic compounds, mainly humic substances and was subjected only to pH adjustment and coarse filtration through a cartridge filter, rendering its treatment demanding. Furthermore, the composite PAC-Fe(II) showed slightly higher TOC removal (approx. 17%) than the original PAC; i.e. 46% for PAC-Fe(II) and 39.4% for PAC, when the same loading of adsorbent (5.2 mg/L) was used. This trend is attributed to the well-known Fenton oxidation mechanism which leads to effective decomposition of the adsorbed DCF and humic molecules to CO_2, H_2O and inorganic ions [44]. The increase of PAC-Fe(II) loading from 5.2 to 20.4 mg/L appeared to have a negligible effect on the mineralization rate under the specific experimental conditions.

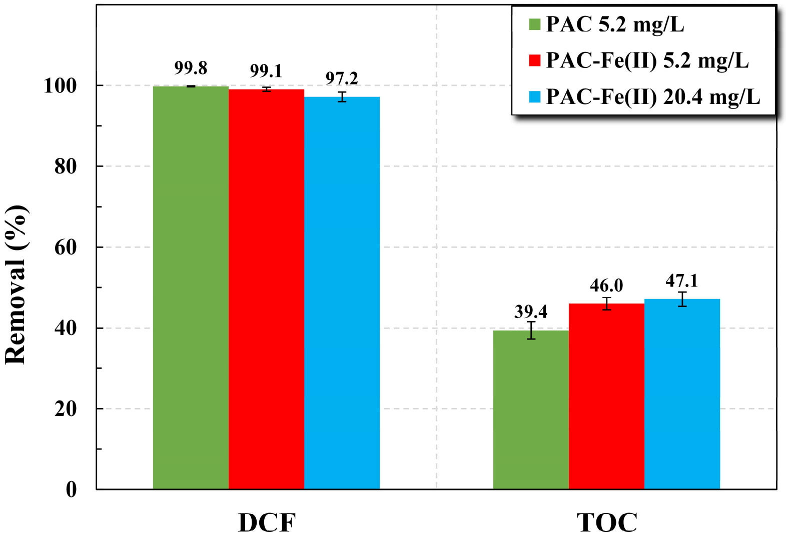

Figure 4: DCF and TOC percentage removal during regeneration stage of PAC and PAC-Fe(II) (Exp. No 2-4).

3.4. H_2O_2 Consumption

The H_2O_2 percentage consumption during the regeneration of the two adsorbents was estimated on the basis of the H_2O_2 concentration in the permeate stream at different time intervals as follows:

$$H_2O_2 \text{ consumption } (\%) = ([H_2O_2]_{feed} - [H_2O_2]_{perm}) / [H_2O_2]_{feed} \cdot 100 \quad (2)$$

where $[H_2O_2]_{feed}$ is the initial H_2O_2 concentration in the feed tank and $[H_2O_2]_{perm}$ is the H_2O_2 concentration in the permeate stream at a specific time.

H_2O_2 percentage consumption is shown in Figure **5**. High values were achieved for both adsorbents; i.e., 85% for the pure PAC and 83.5% for the composite PAC-Fe(II), in Exp. No 2 and 4, respectively, resulted in satisfactory TOC percentage removals up to 47%. Slightly lower H_2O_2 consumption was obtained in Exp. No 3; i.e., 69.3%, probably due to the higher concentration of H_2O_2 employed in the specific test; such concentrations may degrade the system performance due to the reaction of the excess H_2O_2 with the strong oxidants (e.g., •OH), resulting in reactive species production of lesser oxidation potential. Nevertheless, H_2O_2 percentage consumption correlates well with the TOC percentage removal (Figure **4**). Consequently, although a lower H_2O_2 concentration is initially

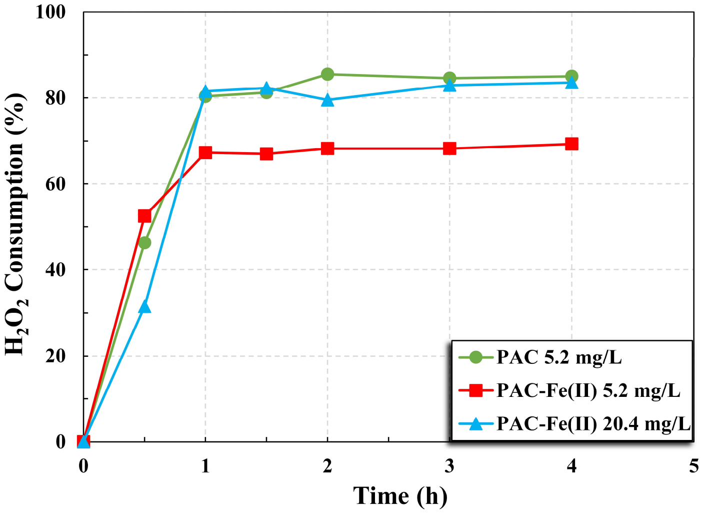

Figure 5: Temporal variation of H_2O_2 consumption during regeneration of PAC and PAC-Fe(II) (Exp. No 2-4).

employed in the system in Exp. No 4, higher consumption is obtained, corresponding to a greater generation of hydroxyl radicals (•OH), leading finally to a slightly higher TOC removal compared to Exp. No 3. On the other hand, a similar decline of concentration profile was observed in all tests, regardless of the experimental conditions. The H_2O_2 consumption occurred rapidly, in the first 30-60 min and reached a steady-state after this time period till the end of the regeneration stage. This can be an indicator of the reaction kinetic mechanism of the process, meaning that the H_2O_2 photolysis by UVC irradiation is more intensive at the beginning of the experiment, during which rapid photolysis occurs.

3.5. Membrane Filtration Performance

The UF hollow fibers showed excellent behavior during the PAC/UF process. Not only completely rejected (>98% based on turbidity measurements, data not shown here) the adsorbent particles but also contributed to the overall satisfactory performance of the hybrid system. TMP temporal variation and details of TMP profile during four sequential filtration cycles for two different experiments are depicted in Figure **6**. It is noted that the negative values correspond to the suction operation, whereas the positive values designate the backwashing operation. No indication of irreversible fouling was observed in any of the tests carried out. This trend is reflected in the recorded transmembrane pressure values. In particular, TMP remained constant with insignificant (~9%) variations; i.e. 282-308 mbar in Exp. No 4 and 307-335 mbar in Exp. No 3, during system operation regardless of the PAC material used. Therefore, the well functioning of the applied automatic periodic backwashing protocol is essentially pointed out. However, this stability is expected due to the employed moderate permeate flux (approx. 14 L/m^2/h).

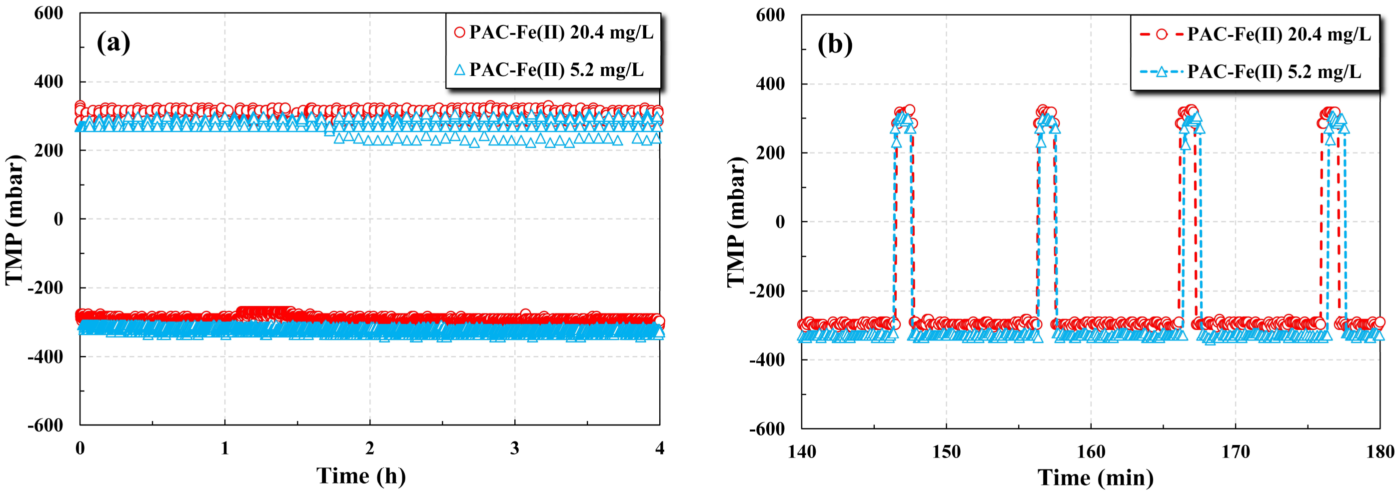

Figure 6: **(a)** Temporal variation of TMP during continuous system operation (regeneration stage) and **(b)** details of TMP profile for four filtration cycles (Exp. No 3 and 4).

4. Conclusions

In this work, encouraging results are presented from the operation of a novel hybrid PAC/UF pilot system involving both removal of organic pollutants and in situ regeneration of the adsorbent materials by H_2O_2-based AOP, treating real surface water (river water) under real operating conditions. Tests with diclofenac (DCF), a model organic pollutant at low concentrations (that simulate those identified in real water matrices) confirmed the importance of the adsorbent material type, the concentration of the H_2O_2 and the UVC light irradiation dose on process efficiency. The latter is assessed on the basis of the improved effectiveness of adsorption and regeneration of the system via photolysis and generation of strong oxidants (e.g., hydroxyl radicals) from H_2O_2-decomposition. The use of composite PAC materials with impregnated iron-nanoparticles (PAC-Fe(II)) in conjunction with hydrogen peroxide and UVC irradiation, resulted in improved adsorption performance and regeneration efficiency. Indeed, strong/effective degradation of the organics was due to the heterogeneous (photo) Fenton-like (PF) oxidation reactions on the surfaces of the iron oxide particles, even at nearly basic pH, towards the generation of •OH and other reactive species by H_2O_2 decomposition. Almost complete DCF removal (>97%) and rather sufficient mineralization rates (approx. 39-47%) were observed during the regeneration of the tested adsorbents by UVC/H_2O_2 or PF processes. Moreover, the coupling of PAC/UF with H_2O_2-based AOPs (that tend to degrade organic compounds/foulants) mitigated drastically the decline of membrane permeate flux, for prolonged operation, which is commonly caused by membrane fouling. Finally, noteworthy is the synergistic role of ultrafiltration membranes that contributed to the overall good performance of the PAC/UF hybrid system, since almost complete retention (>98%) of the adsorbent particles and TMP stability were observed, during a 24 h operation of the system.

In conclusion, the advanced hybrid PAC/UF/H_2O_2-AOP pilot system described herein is capable of a) successfully treating polluted aqueous matrices (e.g., surface and ground waters) under various pollution episodes/conditions and b) drastically reducing PAC waste in the spirit of ‘zero waste discharge’ goal. These attributes greatly contribute to rendering the process sustainable in terms of cost-effectiveness and overall satisfactory environmental performance. However, further research is needed for an improved understanding of various simultaneous reaction mechanisms and synergistic phenomena, which will enable the optimization of key operating parameters. A patent application has been filed regarding the PAC/UF hybrid process proposed and demonstrated in this research.

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