

NOVEL HYBRID 'POWDERED ACTIVATED CARBON – FENTON OXIDATION' PROCESSES FOR WATER TREATMENT

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ABSTRACT

This paper reports on the development of hybrid water treatment technologies that take advantage of the attributes of activated carbon adsorption and Fenton oxidation through the development of novel hybrid process schemes: i) a continuous Powdered Activated Carbon (PAC) – Fenton process using a dilute suspension of PAC in a well-mixed reactor vessel connected to a submerged ultrafiltration (UF) membrane module for the continuous production of purified water, with no reject stream, in combination with the in-situ electrosynthesis of hydrogen peroxide (PAC-EF-UF), ii) a PAC-EF-UF process coupled with ultraviolet light irradiation for treatment performance enhancement leading to the Photo-Electro-Fenton process (PAC-PEF-UF).

Preliminary results are presented herein of the PAC-Fenton process efficiency for degradation of diclofenac; the latter is a widely used non-steroidal anti-inflammatory drug and one of the most frequently detected pharmaceutically active compounds in surface waters (rivers, lakes). The adsorption characteristics of diclofenac and the regeneration capacity of PAC was investigated under homogeneous and heterogeneous Fenton reactions. Specifically, batch experiments were carried out using iron (II) sulfate heptahydrate as a precursor salt in the PAC solution (homogeneous system) and Fe-loaded PAC (heterogeneous system), both in combination with the external addition of H₂O₂. Emphasis was given on the optimization of the composite PAC/Fe material in terms of diclofenac adsorption and regeneration capability. In the case of the classic homogeneous Fenton treatment of PAC at acidic pH (~3), a significant loss of the adsorption capacity was observed (~60%), regardless the concentration of the Fenton reagent (H₂O₂/Fe salt) used. Diclofenac treatment with the optimum composite PAC/Fe adsorbent resulted to slight increase of solute adsorption (from 197.4 mg/g_{PAC} to 203 mg/g_{PAC/Fe}), and a smaller loss of the adsorption property (~25%) after the regeneration (heterogeneous Fenton) at neutral pH. Research is ongoing regarding the optimization of PAC regeneration through the synthesis of effective PAC/Fe materials for their subsequent testing in the novel PAC-(P)EF-UF system developed in the laboratory.

Keywords: powdered activated carbon adsorption, ultrafiltration, Fenton regeneration, diclofenac, water purification

1. Introduction

Activated carbon (AC) is an effective and widely used absorbent in drinking water treatment plants, in industrial wastewater reuse applications and in tertiary treatment of municipal wastewater effluents; however, AC regeneration entails significant cost and environmental burden. Therefore, considerable R&D activities are focused on the development of efficient and economically attractive technologies for regeneration of AC, saturated with organic pollutants. Concerns regarding the high energy/cost of the thermal, biological and chemical regeneration methods, that are currently employed, have prompted research into alternative regeneration treatments to reduce the cost and environmental impact of such processes. Advanced Oxidation Processes (AOP) have emerged as a promising technology for the in-situ regeneration of carbons saturated with non-polar (or very low polarity) organic compounds,

owing to their potency to degrade these species through the generation of very reactive and non-selective free hydroxyl radicals ($\cdot\text{OH}$) at ambient conditions (Zanella *et al.*, 2014). AOP possess significant advantages over other competing chemical and biological processes, including mild and environment-friendly process conditions, no side-streams requiring further processing and no “transfer” of pollutants from one environmental medium to another (as in chemical precipitation and volatilization). A common feature of all AOP studied so far for spent AC regeneration is the addition of H_2O_2 as an $\cdot\text{OH}$ oxidant source, with obvious drawbacks related to H_2O_2 production-cost and safety/handling issues (Bañuelos *et al.*, 2013). Moreover, they display relatively low efficiency due to the fact that pure activated carbon itself (with its chemical inertness) commonly exhibits low catalytic activity for advanced oxidation reactions. To improve the catalytic activity, external energy input is required, such as irradiation with ultraviolet light or increased temperature (150–180 °C) (Muranaka *et al.*, 2010) which incurs additional cost. For the commercial use of AOP for AC regeneration in full-scale treatment plants, the effective recovery and reuse of the regenerated carbon should be addressed to allow continuous water treatment.

In view of the above technical challenges, alternative approaches are developed in the context of a joint R&D project between Greek and Israeli institutions which involve electrochemical AOP (EAOP) in conjunction (or not) with low pressure membrane processes. The most popular technique among EAOP is the electro-Fenton (EF) process, in which H_2O_2 is generated at a cathodic electrode through an oxygen-reduction reaction (with O_2 or air feeding) (Eq. 1) while an iron catalyst (Fe^{2+} , Fe^{3+} , or iron oxides) is either added to the contaminated water (homogeneous EF) or is embedded onto suitable materials (heterogeneous EF), in order to catalyze electrogenerated H_2O_2 to produce the oxidizing agent $\cdot\text{OH}$ via Fenton reactions (Eq. 2) (Brillas *et al.*, 2009). Compared with classical Fenton methods, the EF system can avoid the addition of expensive H_2O_2 and maintain an almost constant H_2O_2 concentration by electro-generation during the pollutant degradation process.



In the Natural Resources and Renewable Energies (NRRE) Laboratory at CPERI/CERTH the EF concept was implemented through the design and construction of a novel electro-Fenton device/“filter” in which hydroxyl radicals are produced in situ as a result of Fenton reactions involving electro-generated hydrogen peroxide and catalytic iron nanoparticles which are impregnated in porous cathodic electrodes (Plakas *et al.*, 2013, Sklari *et al.*, 2015); the attractive feature of in-situ H_2O_2 electro-generation should be noted here. As mentioned above the commercial use of AOP for AC regeneration in full-scale treatment plants is constrained by the effective recovery and reuse of the regenerated carbon. A promising approach for separation and reuse of AC is the utilization of low pressure membrane processes (ultrafiltration-UF, microfiltration-MF) for carbon separation from treated water (Stoquart *et al.*, 2012). In NRRE/CERTH this concept was already employed for catalyst separation in photocatalytic reactors (Photocatalytic Membrane Reactor-PMR) (Sarasidis *et al.*, 2014) and bioactive solids separation in membrane bioreactor (MBR) wastewater treatment (Patsios and Karabelas, 2011).

By taking advantage of the above expertise, NRRE/CERTH is currently working on the development of a novel hybrid PMR-EF process, combining the advantages of the two AOP, with applications in water treatment/purification and regeneration of activated carbon saturated/exhausted by organic pollutants. In this paper, the design characteristics of the hybrid water treatment technologies envisaged are briefly discussed, together with the preliminary results of the experimental work performed with a typical organic pollutant (diclofenac).

2. Experimental work

2.1. PAC-(P)EF-UF processes

Figure 1 shows a general configuration of the hybrid process(es) developed in the lab, involving a continuous PAC – Fenton system using a dilute suspension of PAC in a well-mixed reactor vessel (jacketed cylindrical vessel made of anodized aluminium) for the adsorption of pollutants (i.e. organic compounds) (PAC contactor), connected to a submerged ultrafiltration (UF) membrane module in a rectangular Plexiglas vessel for the continuous production of purified water, with no reject stream (PAC-EF-UF). The attributes of the electro-Fenton (EF) technology are assessed by applying suitable electrodes for the periodic in-situ electrogeneration of H_2O_2 in a specially designed permeate tank (PAC-EF-UF). The heterogeneous Fenton reactions are based on iron-impregnated PAC prepared by the authors according to a wet impregnation method. Further details on system characteristics are restricted as a patent application on this novel system is pending.

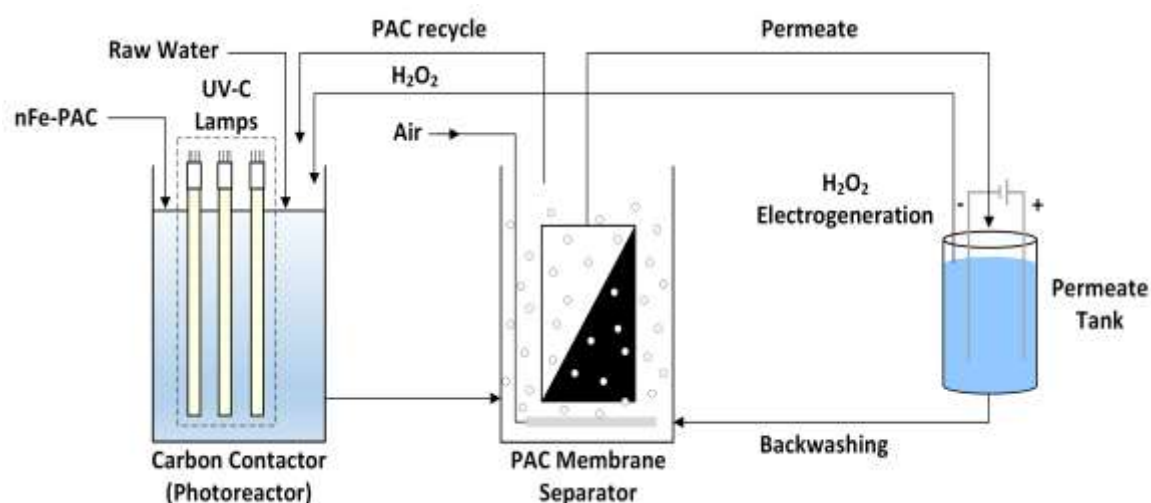


Figure 1: Schematic representation of the PAC-(P)EF-UF process(es) for water and wastewater treatment.

The efficacy of the PAC-EF-UF process to treat certain waste streams is a strong function of (i) the composition and pollutants concentration (load) of the stream in question and (ii) the treatment target itself. In fact, higher pollutants load and extent of pollution removal necessitate harsher treatment conditions to be applied. From this stand-point, treatment performance can be enhanced through coupling the PAC-EF-UF process with ultraviolet light irradiation which leads to the photo-electro-Fenton process (PAC-PEF-UF). To implement this scheme, one can utilize UV-A ($\lambda \sim 315-400$ nm), UV-B ($\lambda \sim 280-315$ nm), and UV-C ($\lambda < 280$ nm) irradiation. Since the dissociation of H_2O_2 into $\cdot OH$ is catalyzed at low UV wavelengths, UV-C light is generally favoured for this purpose. In this case, UV-C lamps are placed in special quartz sleeves and immersed vertically inside the PAC contactor (dash lines in Fig. 1).

2.2. Materials and methods

The chemicals were purchased from Aldrich or Merck and were used without any additional treatment. For the adsorption experiments, 5 mg of powdered activated carbon (DARCO® G60, Aldrich with BET surface area of 1052.9 ± 3.34 m²/g, total pore volume 0.93 cm³/g and average pore width 3.53 nm) were dissolved with 0.5 mg of diclofenac (2-[(2,6-dichlorophenyl) amino] benzeneacetic acid) in 1 L of table mineral water (Vikos water, pH 7.3, conductivity ~ 480 $\mu S/cm$). Simple homogeneous Fenton experiments were carried out with 0.5-5 mM of H_2O_2 (30%) and 1 mM of ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$). In all Fenton experiments the solution pH was adjusted to the desired value (~ 3) using dilute H_2SO_4 solution. During the experiments, samples of the reactant mixture were withdrawn at different reaction times, filtered through Millipore 0.45 μm cartridges and small portions of sodium metabisulfite were added in

the filtrate to stop the reaction. For the preparation of iron-impregnated PAC adsorbent, PAC (1.0 g) was dissolved in an Erlenmeyer flask with 100 mL $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution (0.018 M). After 2 h of stirring at 200 rpm, 25 °C, the PAC/Fe was collected and 1.0 M NaOH was added in a dropwise manner until the solution pH reached 7.0–8.0. The iron-impregnated PAC was collected (filtration through 0.45 μm) and washed with deionized water to remove the salts. Finally, it was dried overnight in the oven (~105 °C) and stored at room temperature before use. The final iron load was estimated to be 40.7 mgFe/gPAC (mass balance of iron in collected solutions measured photometrically according to APHA3500-FeB). N_2 adsorption-desorption (BET) measurements showed that the surface area and pore volume values of PAC/Fe were slightly decreased in comparison to the pure PAC adsorbent ($1037.1 \pm 3.40 \text{ m}^2/\text{g}$ and $0.87 \text{ cm}^3/\text{g}$, respectively). The variation of diclofenac concentration was followed by HPLC/DAD according to the method described elsewhere (Sklari *et al.*, 2015). The concentration of hydrogen peroxide consumed during the experiments was determined photometrically by the iodide method.

3. Results & discussion

The adsorption of diclofenac (DCF) before and after the regeneration of PAC and PAC/Fe through Fenton reactions is shown in Figure 2. The values reported correspond to the equilibrium reached after approximately 180 min. The regeneration of saturated PAC with the single addition of H_2O_2 ($\text{PAC}_{\text{reg},4}$) was followed by a decreased DCF re-adsorption, implying that the specific PAC does not favour the catalytic decomposition of H_2O_2 into $\cdot\text{OH}$. In the case of the homogeneous Fenton regeneration, the best results were obtained for low concentrations of dissolved iron catalyst and H_2O_2 in the PAC solution ($\text{PAC}_{\text{reg},1}$), with the respective loss in DCF adsorption capacity reaching ~60%. The recovery of the adsorption capacity was found significantly higher in the case of the composite PAC/Fe adsorbent. The latter implies that the presence of iron catalysts on the PAC surface is beneficial for achieving a higher regeneration efficiency by heterogeneous Fenton reactions, even at neutral pH. The enhanced efficiency observed at lower H_2O_2 initial concentrations ($\text{PAC/Fe}_{\text{reg},2}$) is probably due to the surface properties of the composite material, which can be altered significantly at harsher environments (higher H_2O_2 concentrations). It is noted that an excellent stability of PAC/Fe was observed during the regeneration, as evidenced by the negligible leaching of iron.

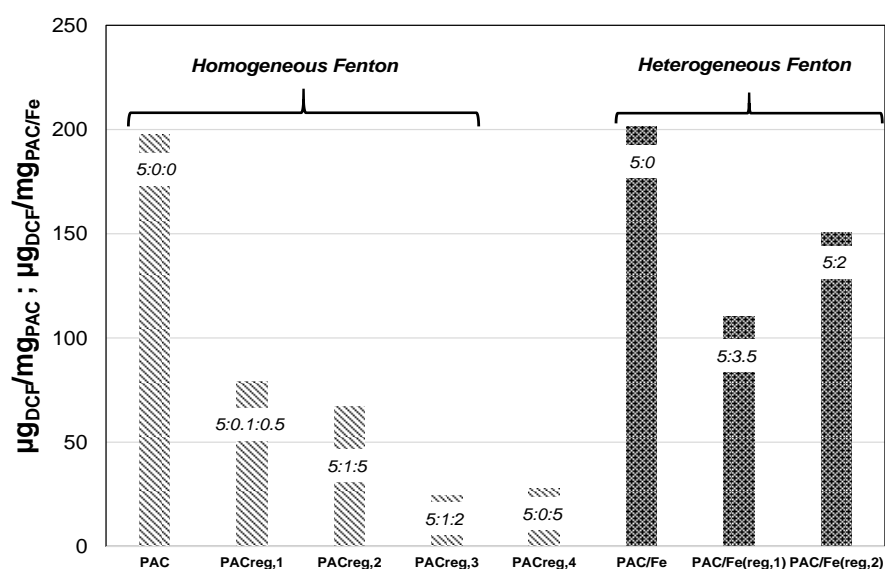


Figure 2: Amount of DCF adsorbed per unit mass of PAC or PAC/Fe before and after their Fenton regeneration. The numbers on the bars correspond to the concentrations of the materials used (homogeneous Fenton, PAC: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}:\text{H}_2\text{O}_2$ in mg/L:mM:mM; heterogeneous Fenton, PAC/Fe: H_2O_2 in mg/L:mM).

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