Chemical Engineering Journal 328 (2017) 1153–1163

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Novel water-purification hybrid processes involving in-situ regenerated activated carbon, membrane separation and advanced oxidation

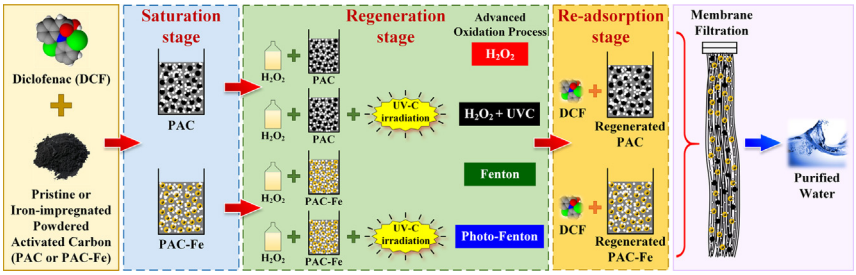
V.C. Sarasidis, K.V. Plakas, A.J. Karabelas *

Chemical Process and Energy Resources Institute, Centre for Research and Technology – Hellas (CERTH), 6th km Charilaou-Thermi Road, Thermi, Thessaloniki GR 57001, Greece

HIGHLIGHTS

- Novel water-purification hybrid processes combining PAC, UF, H_2O_2-based AOPs.
- Key novelty is the periodic *in-situ* PAC regeneration, in the main process equipment.
- Two adsorbents: Commercial PAC and special iron-impregnated PAC (PAC-Fe).
- Process alternatives: For each adsorbent, only H_2O_2 addition or H_2O_2 + UV-C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 February 2017
Received in revised form 21 June 2017
Accepted 14 July 2017
Available online 17 July 2017

Keywords:
Water purification
Hybrid PAC/UF/AOP processes
Pilot unit
(Photo)-Fenton oxidation
Diclofenac degradation

ABSTRACT

The reported pilot-scale development of hybrid process alternatives, combines *in-situ* regenerated powdered activated carbon (PAC), H_2O_2-based advanced oxidation techniques and membrane ultrafiltration (UF). Commercial PAC and special iron-impregnated PAC (PAC-Fe) were used as adsorbents, whereas diclofenac (DCF), a commonly detected pharmaceutical in water-sources, was employed as representative micro-pollutant. For PAC regeneration, modest on-line H_2O_2 dosage was adopted, alone or in combination with UV-C irradiation. Large DCF uptake was measured for both PAC (154.5 mg/g) and PAC-Fe (116.7 mg/g), while the regeneration efficiencies achieved with the photo-assisted H_2O_2 processes were much greater (122.2% and 131.6% for H_2O_2+UVC and photo-Fenton, respectively) than those obtained with H_2O_2 alone (70% and 77.6% for H_2O_2 and Fenton, respectively). For PAC-Fe, enhanced recovery of adsorption capacity suggests occurrence of heterogeneous Fenton-like reactions on iron-oxide particle surfaces leading to generation of $^{\cdot}OH$ and other reactive species by H_2O_2-decomposition.

The catalytic adsorbent (PAC-Fe) retained its stability and activity after three operating cycles, which would significantly reduce operating cost in practical applications. Considering the rather short regeneration-time of present tests (180 min) and the nearly basic pH of feed solutions, the novel processes investigated herein, involving PAC regeneration in *the same equipment* employed for water purification, hold distinct advantages over conventional methods.

1. Introduction

The rapid growth of human activities, such as agriculture and industrialization, together with the ever increasing urbanization, are the main causes of groundwater and surface water contamination by numerous toxic organic compounds and their derivatives at very low concentrations, i.e., in the range of ng/L to μg/L. Some of these compounds are regulated and included in routine monitoring programmes; i.e., pesticides, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Furthermore, other such compounds are defined as emerging contaminants as, for

* Corresponding author.
E-mail address: karabaj@cperi.certh.gr (A.J. Karabelas).

http://dx.doi.org/10.1016/j.cej.2017.07.084
1385-8947/

example, surfactants, pharmaceuticals and personal care products (PPCPs), gasoline additives, biocides, polar pesticides and various proven or suspected endocrine disrupting compounds (EDCs), as well as a huge number of transformation products (TPs) [1,2]. Owing mainly to their potential adverse effects on human health, reliable techniques with stable removal effectiveness are highly desirable.

Among the best available techniques proposed for the efficient elimination of organic micropollutants from water are ozonation, adsorption on powdered activated carbon (PAC) or filtration through granular activated carbon (GAC) [3]. In particular, PAC adsorption has been identified as an effective and easily adjustable technology to remove organic micropollutants [4,5]. Compared to GAC, PAC has better thermodynamic and kinetic characteristics [6]; however, its separation from the treated water is challenging and, after its saturation, it is typically incinerated or disposed of in landfills, whereas GAC (in form of fixed bed) can be regenerated [7].

The coupling of PAC adsorption with low-pressure membrane processes, such as microfiltration (PAC/MF) [6,8] or ultrafiltration (PAC/UF) [9–11] has resolved the separation and reuse issue of PAC, whereas the mixing of adsorbent into the membrane tank (in addition to micropollutants removal) has been shown to reduce the accumulation of fouling material on the membrane surface, preventing the reduction of permeate flux [12,13]. A number of full-scale PAC/UF plants operate worldwide. For example, the l' Apier Saint-Cassien and Vigneaux-sur-Seine plants in France use the PAC/UF process to cope with seasonal episodes of micropollutants (pesticides, taste and odors) and to reduce the content of natural organic matter (NOM) responsible for the formation of disinfection by-products (DBPs) [14,15].

It is generally agreed that PAC/UF presents several advantages compared with GAC columns, although the adsorption performance may be strongly deteriorated under increased concentration of target compounds. Such pollution episodes require the adjustment of main process parameters such as PAC dosage and/or the adaptation of additional treatment processes [11]. For this reason GAC systems are more popular, since operators do not have to determine dosages on a daily basis as influent conditions change. This is especially important if the source water comes from a highly traveled river where spills or contamination occur frequently. Moreover, the current trend toward zero waste discharge entails drastic reduction of PAC waste. An efficient regeneration of PAC could drastically reduce the quantity of PAC-sludge that requires disposal, thus, decreasing or even eliminating the toxicity of the exhausted PAC due to the adsorbed toxic compounds.

Numerous works have been published concerning regeneration of carbonaceous adsorbents; in a recent review by Salvador et al. [16] the developed regeneration methods have been classified into thermal, chemical, microbiological and vacuum. These techniques have certain advantages but are also associated with significant drawbacks, including non-destructive pollutants removal, significant chemicals consumption, relatively long treatment and generation of secondary waste streams. Recently, researchers have turned their attention to the so-called advanced oxidation processes (AOPs) for the regeneration of spent activated carbons. AOPs are based on the generation of highly reactive, and consequently short-lived, hydroxyl radicals (·OH) which degrade most organic pollutants rapidly and non-selectively. Homogeneous AOPs, such as hydrogen peroxide under ultraviolet irradiation (H_2O_2/UV) [17], ozonation under ultraviolet irradiation (O_3/UV) [18] and Fenton reagent (H_2O_2/Fe^{2+} or Fe^{3+}) [19–21] are promising methods because they are simple and easy to implement at large scale. The efficiency of these methods strongly depends on the catalytic activity of the carbon adsorbent, which may vary depending on its structure, porosity, surface area, as well as the iron content [21,22]. In order to increase the catalytic activity, several researchers have synthesized highly effective heterogeneous catalysts by supporting iron oxides (e.g. Fe_3O_4) [23,24] or semiconductors (e.g. TiO_2) on activated carbons [25,26] to promote high regeneration efficiencies, without significant loss of the carbon adsorption characteristics.

In the authors' Laboratory, the concept of continuous catalyst membrane-separation has been extensively investigated in photocatalytic membrane reactors (PMR) [27–29] and bioactive solids separation in membrane bioreactors (MBR) for wastewater treatment [30]. Moreover, iron oxide nanoparticles–PAC (PAC-Fe) composites have been successfully developed for water treatment and PAC regeneration by Fenton reactions [24]. By taking advantage of this expertise, alternative approaches have been investigated to enhance the effectiveness of water purification methods, which involve H_2O_2-based AOPs in conjunction with PAC/UF processes. The aim of this research was twofold: a) to increase the overall process performance (degradation of the 'free', non-adsorbed micropollutants) and b) to regenerate in-situ the carbon adsorbent, thus, prolonging its useful life time. To the best of the authors' knowledge, no well documented paper has been presented on the regeneration of spent PAC in PAC/UF systems by employing hybrid processes with different AOPs.

The present work is thus focused on the sequential adsorption and regeneration by H_2O_2-based AOPs of a commercial PAC and a composite PAC-Fe adsorbent saturated with diclofenac (DCF) as model organic pollutant, at pilot scale; DCF is a widely used non-steroidal anti-inflammatory drug and one of the most frequently detected pharmaceutically active compounds in water sources (e.g. groundwater, rivers, lakes, treated wastewater), in the range of ng/L to μg/L [31]. This investigation dealt with the adsorption kinetics and degradation degree of the particular processes as well as durability and reactivity of the PAC-Fe catalyst.

2. Experimental

2.1. Material and reagents

A commercial, charcoal made, powdered activated carbon (DARCO® G60), purchased from Sigma-Aldrich, was selected for this study, with particle size <149 nm (minus 100 mesh), BET surface area 1052.9 ± 3.34 m^2/g, total pore volume 0.93 cm^3/g, average pore width 3.0 nm and point of zero charge (pH_{pzc}) ~ 7.38 [24]. According to the manufacturer (Cabot, acquisition of Norit N.V.) DARCO® G60 is a steam activated carbon with a very high adsorptive capacity (e.g. Methylene Blue adsorption ≥15 g/100 g) and excellent filtration characteristics that meet the requirements of the US Food Chemical Codex. DARCO® G60, was also used for the preparation of a composite PAC adsorbent with impregnated iron-nanoparticles (PAC-Fe), according to the procedure described elsewhere [24]. Specifically, ferrihydrite-impregnated PAC with low iron content (~40.7 mgFe/gPAC) and high BET surface area (1037 m^2/g) was synthesized by mixing PAC with a $Fe(NO_3)_3{\cdot}9H_2O$ (0.1 M) solution for 1 h, after 2.0 M NaOH was added in a dropwise manner until the solution pH reached 7.0–8.0. PAC-Fe was separated through Millipore 0.45 μm filter and washed with deionized water to remove the salts. Finally, the composite adsorbent was dried overnight (~100 °C) and stored in a desiccator for further use. PAC-Fe was characterized by means of BET, XRD, SEM, EDS, and the results were presented in detail in a previous publication [24].

Diclofenac sodium salt of analytical grade (98.6% purity), purchased from Sigma-Aldrich (CAS Number 15307–79-6), was chosen as a model toxic organic pollutant and used as received. DCF is considered as hydrophobic ionic compound ($logK_{ow}$ = 4.51), with