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Review

Advanced Oxidation/Reduction Processes treatment for aqueous perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) – A review of recent advances

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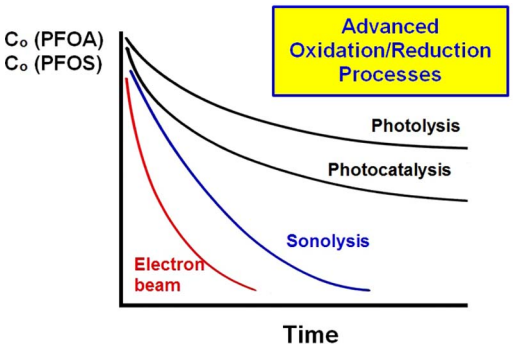
GRAPHICAL ABSTRACT



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ABSTRACT

Nowadays, an increasing emission of chemically resistant perfluorinated compounds (PFCs) to the natural environment, together with a global presence of those anthropogenic pollutants in both natural and treated waters and in both human and animal organisms, poses a great environmental challenge. A limited efficiency of their removal by commonly employed technologies prompts a search for more efficient and more cost-effective methods. Recent decades brought in water management an intense progress in Advance Oxidation Processes, based on decomposition of pollutants by free radicals, which can be produced in different ways. This review presents the recent advances in those methods for decomposition of the most commonly occurring PFCs in the natural environment – perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). For this purpose, there have been developed particular methods based on an oxidation and reduction of target pollutants, generally abbreviated as AO/RPs. The review, which was based on 180 cited references, includes photolytic and photocatalytic methods, electrochemical processes as well as sonolytic and radiolytic methods with the use of ionizing radiation, wet chemnical oxidation methods, ozonation and Fenton processes. Attempts on comparison of the developed methods, their applications to real samples and molecular mechanisms of occurring transformations are provided.

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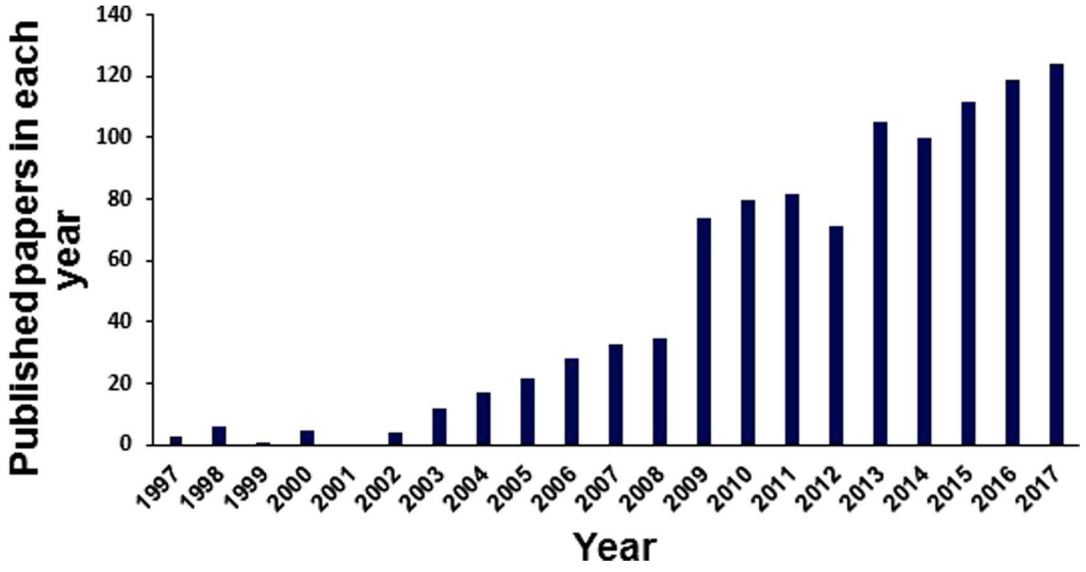

Fig. 1. Number of papers abstracted by data-base ISI Web of Science for topic keywords "perfluorinated" and "environmental" (23.10.2017).

1. Introduction

The presence of fluorinated organic compounds in human serum was discovered in the late 1960s [1]. They have been produced for numerous industrial applications since 1940s as refrigerants, polymers, pharmaceuticals, adhesives, insecticides and fire retardants [2]. A particular interest in poly- and perfluorinated compounds (PFCs) erupted at the end of 1990s when a common global presence of those anthropogenic compounds was found in human serum [3], in groundwater [4] and in the tissues of wildlife including fish, birds and marine mammals [5]. This initiated, beginning in the early 2000s, a very intense development of analytical methodologies for their determination (see example reviews [6–8]), toxicological studies [9–11] and broad investigations of their sources, transport in environment and chemical transformations [12–14]. The essential increase of interest in the role of perfluorinated compounds in the natural environment can be illustrated by the number of papers published in the last two decades provided by ISI Web of Science data-base (Fig. 1).

Basic structural elements of anthropogenic PFCs are: a partially or fully fluorinated alkyl chain (a hydrophobic part) and a terminated functional group (carboxylates, sulfonates, sulfonamides, phosphonates), which constitutes a hydrophilic part of a molecule. Due to the presence of both hydrophobic and hydrophilic parts, PFCs exhibit surfactant properties, reducing surface tension stronger than other major classes of surfactants. Because of a high electronegativity and a small size of the fluorine atom, the carbon-fluorine bonds are the strongest bonds in organic chemistry [14a]. PFCs are nonflammable and resistant towards acids, bases, the majority of oxidants and reductants [15]. Those physicochemical properties are utilized for numerous applications of PFCs, including fire-fighting foams, coating of clothing fabrics, leather and paper products used for food packing. Such a broad scope of applications results in their global distribution to the natural environment, wildlife and human organisms. The consequence of this is their presence in food, which significantly contributes to human exposure to those compounds [16,17].

The most commonly encountered and investigated PFCs in the environment, food and biological samples are perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonates and sulfonamides, fluorotelomer alcohols, acids, olefins and sulfonates. Over the past few years more than 100 papers devoted to different environmental aspects of those compounds have been published every year. Due to the most frequent occurrence in both natural environment and living organisms, the closest research attention was given to perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) – see their structures below.

Perfluorooctanoic acid (PFOA)

Perfluorooctanesulfonic acid (PFOS)

Numerous different processes are indicated as the sources of PFOA in the natural environment [13]. They include a direct production process (mostly in fabrication of ammonium perfluorooctanoate, APFO) by electrochemical fluorination, which has been used since 1950s to produce fluoropolymers. As shown in the diagram in Fig. 2A the other main sources of estimated total global historical PFCAs emissions, besides fluoropolymer manufacture from APFO, are also the use of fire-fighting foams as well as consumer and industrial products. The indirect sources of PFCAs contribute much less to total emission to the environment (about 5% according to [13]). The main indirect source is degradation of semi-volatile fluorotelomer alcohols (FTOHs) in atmosphere to yield a homologous series of PFCAs, which is an especially important source of PFCA pollution in the remote areas [12]. FTOHs are linear PFCs manufactured by telomerization process containing even-numbered alkyl carbon chains with a different number of fluorinated and two hydrogenated carbons. They are raw materials used in the manufacture of surfactants and polymeric products. They are present in these materials at low levels of unreacted residues [18], being precursors to the formation of PFCAs, and they can be also found in surface water, *e.g.* at 0.1–0.25 μg/L level even far from the location of manufacturing plants [19]. Modeling global-scale fate and transportation of PFOA emitted solely from direct sources compares favorably to observed concentration in the world's oceans [20]. The occurrence in aquatic environment and health effects of PFOA have been reviewed in recent years by several authors [21–23].

As far as the occurrence of PFOS in the environment is concerned, it also comes from manufacture releases when employed in specialized industrial processes (semiconductor, medical devices, aviation, metal plating). It is also a component of aqueous film forming foams and an impregnation agent. In an indirect way, it comes from the manufacture of perfluorooctane sulfonyl fluoride (POSF) and the breakdown of POSF-derivatives in the environment [24]. An estimated release of POSF from various sources is shown in Fig. 2B. As can be seen in the