



Use of strong anion exchange resins for the removal of perfluoroalkylated substances from contaminated drinking water in batch and continuous pilot plants



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ABSTRACT

In recent years abnormally high levels of perfluoroalkylated substances (PFAS) have been detected both in surface and underground water sampled in an area covering approximately 150 square kilometers in the Veneto region (Italy) indicating the presence of a pollution point source (fluorochemicals production plant). Adsorption on granular activated carbon is an emergency measure which is poorly effective requiring frequent replacement. This work focuses on the application of three strong anion exchange resins (Purolite® A520E, A600E and A532E) for the removal of traces of PFOA, PFOS, PFBA and PFBS (concentration of hundreds of ng L^{-1}) from drinking water. This technology is attractive for the possibility of reusing resins after an in-situ regeneration step.

A strong relationship between the hydrophobicity of the exchange functional group of the resin and its capacity in removing PFAS exists. A600E (non hydrophobic) and A520E (fairly hydrophobic) show a reduced sorption capacity compared to A532E (highly hydrophobic). While A600E and A520E can be regenerated with solvent-less dilute solutions of non-toxic NH_4Cl and NH_4OH , A532E requires concentrated solutions of methanol or ethanol and 1% NH_4Cl and for the sake of this work it was regarded as non-regenerable. The volume of regeneration effluents requiring incineration can be efficiently reduced by more than 96.5% by using reverse osmosis coupled with under-vacuum evaporation.

Transmission electron analysis on saturated resins showed that large molecular macro-aggregates of PFAS can form in the intraparticle pores of resin indicating that ion exchange is not the only mechanism involved in PFAS removal.

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1. Introduction

The term “PerFluoroAlkylated Substances” or PFAS indicates a broad group of anthropogenic compounds comprising a per-fluoroalkyl backbone and a terminal functional group.

In the last six decades these substances have been incorporated into a wide range of industrial and commercial products used in more than 200 applications: surfactants (Kissa, 2001), medical applications (Krafft and Reiss, 2007), surface protecting agents (Kostov et al., 2009), fire fighting foams (Magrabi, 2002), mist suppressor (Nishiyama and Ishikawa, 1979). Because of their past

and present widespread use, PFAS are ubiquitous micro pollutants found both in underground and surface water with concentration ranging from detection limits ($<1 \text{ ng L}^{-1}$) to several tens of ng L^{-1} .

Perfluoroalkylated substances have unique physico-chemical properties such as simultaneous hydro and oleophobicity, chemical, radiation and biological stability and extremely low surface tension.

All these properties are attributable to fluorine atoms which shield carbon–carbon bonds of the molecular backbone from physical and chemical attacks. Further, fluorination stiffens alkyl chains which self assemble at interface packing close together. This characteristic structure called “molecular-brush” forms a dense layer of trifluoromethyl groups which repels both water and oil. The number of completely fluorinated carbon atoms is the key factor in determining the degree of molecular packing: the longer the

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perfluoroalkyl chain the closer trifluoromethyl groups are packed at surface assuring better performances in term of hydro and oleophobicity (lower surface tension). Even if early studies reporting on detection of fluorinated compounds in humans date back to 1968 (Taves, 1968) and during the eighties and early nineties the evidences of possible adverse health effects increased markedly (Griffith and Long, 1980; Haughom and Spydevold, 1992) it is only in the late nineties that the availability of sophisticated routine analytical methods enabled analysis in the ppb range of PFAS and derivatives in various matrices. PFAS have been globally found in air, oceans, seas, lakes, rivers, human blood and serum (Gisey and Kannan, 2001; Kannan et al., 2001).

Because of the considerable concern aroused by the dissemination and the accumulation of PFOS and derivatives, 3M Company spontaneously decided to phase out their manufacturing since year 2000. This was the first step of a fifteen-years long process which has completely changed the scenario of perfluoroalkylated substances.

PFOS and related compounds were listed under Annex B of the Stockholm Convention on Persistent Organic Pollutants. PFOA and related compounds were included in the Candidate list of the Substances of Very High Concern (SVHC) published in accordance with Article 59(10) of the REACH Regulation.

In order to partially overcome environmental and health hazards associated with long chain PFAS manufacturers switched to short and ultra-short chain containing less than six fluorinated carbon atoms (and notably those based on a C₄ backbone such as perfluorobutanoic acid and perfluorobutansulfonic acid derivatives) which seem to have a most favorable eco-toxicological profile.

Although short and ultra-short chain PFAS are potentially less bioaccumulative compared to long chain ones they are still environmentally persistent as recently underlined by the Madrid statement on Poly- and Perfluoroalkyl substances (Blum et al., 2015) which suggests that a switching to short-chain and other fluorinated alternatives would not reduce the total amount of PFAS in the environment.

This issue is of the utmost importance because in the near future the removal of short chain PFAS such as PFBA and PFBS would become predominant and adequate removal technologies (notably from drinking and discharge water) must be developed.

1.1. PFAS in the Veneto region (Italy)

In recent years abnormally high levels (from several tens to over five thousand ng L⁻¹) of PFAS were detected both in surface and underground waters sampled in an area covering approximately 150 square kilometers in the Veneto region (Italy) indicating the presence of a pollution point source (fluorochemicals production plant).

Adsorption of PFAS on granular activated carbon (GAC) was adopted as an emergency measure in many drinking water treatment plants to meet the performance limits set by the Italian Ministry of Health for drinking water (30 ng L⁻¹ for PFOS, 500 ng L⁻¹ for PFOA and 500 ng L⁻¹ for the sum of all other PFAS).

Many authors have reported the application of GAC for PFAS removal both on bench and full scale applications (Carter and Farrell, 2010; Flores et al., 2013; Thompson et al., 2011; Appleman et al., 2013). All the findings reported were in general agreement indicating that GAC is effective in removing PFOA and PFOS and only poorly effective for PFBA which completely saturated sorption beds in short time.

Data collected in 5 full scale drinking water treatment plants operating in the polluted area show that fresh GAC is effective in removing PFAS but its efficiency dramatically drops with time

proving to be a strong function of the length of the fluorinated chain and the nature of the functional group of PFAS. In the case of PFOA the time required for reaching breakthrough is 10–12 months but this value drops to only 1–3 months for PFBA which was detected in the effluent water only after few weeks requiring the frequent replacement of carbon in order to fulfill limits set by health authorities. Further, replacement of exhausted adsorbing beds should be performed quickly because it was noted that soon after reaching of the saturation point for PFBA the concentration in the outlet water suddenly overcome the inlet concentration indicating a certain desorption of the adsorbate confirming data previously reported by Gellrich (Gellrich and Knepper, 2011).

A significant reduction in the service life of filters operating without a pre-filtration stage was also observed. This effect is attributable to natural organic matter (NOM) preloading as previously noticed by Eschauzier (Eschauzier et al., 2011). Data reported by Takagi (Takagi et al., 2011) on PFAS removal by GAC in five water treatment plants in Osaka (Japan) showed a limited efficiency in removing long chain PFAS but no mention was made to shorter ones. Further, the authors reported a negative removal ratio for PFOA and PFOS once reached saturation indicating a possible desorption.

Appleman (Appleman et al., 2014) reported that in full-scale water treatment systems the removal efficiency of activated carbon depends on PFAS functional group and on the length of the fluorinated chain: short chain perfluorocarboxylic acids present very early breakthrough.

In light of these data the removal of short chain PFAS (and notably PFBA and PFBS) appears an even more challenging task compared to PFOA and PFOS.

1.2. Objectives of the study

In this research three types of Purolite® commercial strong anion exchange resins (A600E, A520E and A532E) were tested both in batch laboratory-scale and in continuous pilot-scale plants for determining their ability in removing traces of complex mixtures of PFOA, PFOS, PFBA and PFBS from groundwater intended for drinking use. Although some data on the application of strong anion resins for PFAS removal are available in the literature they focus mainly on long chain PFOA and PFOS especially from concentrated solutions (from tens to hundred mg L⁻¹) (Deng et al., 2010; Senevirathna et al., 2010; Lampert et al., 2007).

The role of the hydrophobic sorbate-sorbed interactions on selectivity and exchange capacity of resins for PFAS was investigated. The contribution of resin in modulating the strength of hydrophobic interactions was studied by varying the structure of exchange functional groups. The role of the structure of PFAS molecules was outlined by tracking exchange capacities of a specific resin as a function of chain length and strength of the acid functional group (carboxylic and sulfonic).

As a further element of novelty the formation of molecular macro-aggregates of PFAS in intraparticle pores of resin was investigated by transmission electron microscopy (TEM).

Data obtained for resins were compared with those collected by three water companies for 5 full-scale GAC filters operating with the same groundwater in order to obtain a reliable estimate of differences in term of PFAS selectivity and removal efficiency. Finally the possibility of regenerating *in situ* spent resins with minimization of eluates requiring special disposal or incineration was investigated.

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