

Sorptive remediation of perfluorooctanoic acid (PFOA) using mixed mineral and graphene/carbon-based materials

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Environmental context. Per- and poly-fluoroalkyl substances (PFASs) are contaminants of emerging concern, creating a need to develop efficient multi-functional adsorbents for improved remediation performance. By exploiting the versatility of graphene technology, we demonstrate that combining mineral and carbonaceous phases greatly increases and strengthens PFAS-binding to the adsorbent. The study highlights the benefits and potential applications of mixed adsorbents in PFAS-remediation.

Abstract. As the degradation of perfluorooctanoic acid (PFOA) and related per- and poly-fluoroalkyl substances (PFASs) is energy-intensive, there is a need to develop in situ remediation strategies to manage PFAS-contamination. The sorption of PFOA by graphene oxide (GO), an iron-oxide-modified reduced-GO composite (FeG) and an activated-carbon(C)/clay/alumina-based adsorbent, RemBind™ (RemB), are evaluated. Sorption by FeG and RemB (>90 %) is much greater than GO (60 %). While an increase in pH hinders PFOA-sorption by GO, owing to the increased repulsion of anionic PFOA, variations in pH and ionic strength do not significantly influence PFOA-sorption by FeG and RemB, which indicates that binding is predominantly controlled by non-electrostatic forces. Hydrophobic interactions are assumed at the graphene or C-surface for all adsorbents, with added ligand-exchange mechanisms involving the associated Fe- and Al-minerals in FeG and RemB, respectively. Desorption of adsorbed PFOA is greatest in methanol, compared to water, toluene, or hexane, which provides estimates of the binding strength and reversibility from an environmental-partitioning perspective; i.e. risk of remobilisation of bound PFOA owing to rainfall events is low, but the presence of polar organic solvents may increase leaching risk. Iron-mineral-functionalisation of GO enhances the amount of PFOA adsorbed (by 30%) as well as the binding strength, which highlights the advantage of combining mineral and C-phases. Successful sorption of a range of PFASs from a contaminated-site water sample highlights the potential of using ‘mixed’ adsorbents like FeG and RemB in situ for PFAS-remediation, as they provide avenues for enhanced sorption through multiple mechanisms.

Additional keywords: PFASs, sorption.

Received 16 July 2018, accepted 25 September 2018, published online 31 October 2018

Introduction

Perfluorooctanoic acid (PFOA) is an anthropogenic fluorochemical belonging to the broader class of chemicals known as per- and poly-fluoroalkyl substances (PFASs). Owing to their unique physico-chemical properties, they have found use in a wide range of consumer and industrial applications, which include food packaging, stain and water-repellent fabrics and coatings, as well as fire-fighting foams (Renner 2001). However, owing to their bioaccumulation potential and persistence in the environment, PFOA and related PFASs have raised environmental and human health concerns over the last decade (Higgins et al. 2007; Moody and Field 2000; Sundström et al. 2011), with several cases of contamination reported worldwide (Lein et al. 2008; Washington et al. 2010). Concentrations of up to 4 µg L⁻¹ have been detected in drinking water supplies and surface environmental waters around the world (Rumsby et al. 2009), and up to 50 µg kg⁻¹ have been found in soils

(Zareitalabad et al. 2013). Point source concentrations (e.g. at a PFAS waste-storage pond) can reach up to the low mg L⁻¹ levels (Arias et al. 2015). Despite production largely being phased out, PFASs are ubiquitous in the environment owing to their persistence and mobility (Moody and Field 2000).

The strong carbon-fluorine (C–F) bonds of the structure make PFOA extremely resistant to chemical and biological degradation (O’Hagan 2008). While thermal decomposition of PFOA has been demonstrated at high temperatures of up to 1000 °C (Kucharzyk et al. 2017), this is very energy-intensive and often cannot be achieved in situ. Various physico-chemical techniques, like sonochemical degradation (Cheng et al. 2010) and advanced oxidation (Bruton and Sedlak 2017; Lee et al. 2013), have also been used to break down PFASs; however, complete mineralisation and de-fluorination are not always achieved, and sometimes toxic by-products may be formed (Kucharzyk et al. 2017).

As degradation of these chemicals is an energy-intensive process and presents challenges especially for use in situ, adsorption is a cost-effective strategy to manage PFOA contamination in situ by reducing contaminant mobility. Sorption of PFOA onto surfaces of carbonaceous materials (like chars, activated-C and nanotubes) (Deng et al. 2012; Wang et al. 2015) have been demonstrated, with granular activated-C used most commonly for the treatment of PFASs in ex situ filtration systems. These rely on hydrophobic interactions at the non-polar C-phase (Kucharzyk et al. 2017). Aluminium (Al) and iron (Fe)-based minerals (Feng et al. 2017; Gao and Chorover 2012; Hellsing et al. 2016; Wang et al. 2012), like alumina, hematite and goethite, have also been shown to bind PFASs through electrostatic or ligand-exchange mechanisms (Du et al. 2014). Graphene, composed of closely packed sp^2 hybridised C-atoms (Novoselov et al. 2012), the latest addition to the nanocarbon family, is an excellent candidate for use as an adsorbent, owing to its high surface area and versatile surface chemistry. Sorption of various organic contaminants (e.g. polycyclic aromatic hydrocarbons, dyes and pharmaceuticals) through hydrophobic interactions and π - π interactions with conjugated regions on the graphitic basal surface of graphene-based materials (GBMs) have been demonstrated (Fan et al. 2013; Ji et al. 2013). However, there is a lack of studies that investigate the use of GBMs for PFAS-sorption. One study has reported the use of graphene oxide (GO), the most common graphene-derivative, for sorption of perfluorooctanesulfonate (PFOS) in the presence of magnesium ions (Mg^{2+}), owing to the ability of Mg^{2+} to form a bridge between PFOS and GO (Zhao et al. 2016). Similar demonstrations for PFOA and other PFASs are not available.

Graphene oxide is known to have a highly negative surface charge owing to the presence of oxygen-functional groups, including epoxides, carboxyls and hydroxyls, on its surface (Dreyer et al. 2010; Marcano et al. 2010). The most common PFASs of concern, including PFOA and PFOS, exist as anions, which can be repelled by negatively-charged adsorbents. It is thus reasonable to assume that despite avenues for hydrophobic or bridging interactions (Zhao et al. 2016), GO is not the best candidate for PFAS sorption, and other GBMs may provide opportunities for superior binding. Graphene oxide is remarkably amenable to surface modifications, owing to its oxygen functionalities, and can be strategically functionalised for enhanced contaminant sorption. For instance, GO has been used widely for adsorption of organic dyes and heavy metals (Yusuf et al. 2015). However, functionalisation of GO with polydopamine further improved dye and metal adsorption, compared with pure GO, owing to additional surface active sites (Dong et al. 2014). We propose that the suitable functionalisation of GO could lead to the improved sorption of PFOA and other PFASs compared with GO. Given that Fe-based minerals have been shown to adsorb PFASs (Feng et al. 2017; Gao and Chorover 2012), an Fe-functionalisation was performed to prepare an Fe-oxide-modified reduced-GO composite (FeG) for testing. Given the separate successes of carbonaceous materials and minerals in PFAS-sorption, we propose that designing adsorbents composed of both carbon and mineral phases together may improve opportunities to explore a new generation of advanced 'mixed' adsorbents that provide multiple binding sites with high affinity for PFOA and other PFASs. This has not been explored before, particularly in the case of GBMs. To further support this, we also tested a non-graphene-based 'mixed' commercial adsorbent, RemBind™ (RemB; Ziltek Pty Ltd, Adelaide, South Australia,

Australia), which is composed of activated-C, kaolin, alumina and other proprietary additives.

In this study, we evaluated three adsorbents – GO, FeG and RemB – for PFOA-sorption, with potential for in situ remediation application. The carbonaceous nature of GO is in contrast to the 'mixed' mineral and C-based nature of the FeG composite (prepared from GO) and RemB. The influence of different pH conditions, ionic strength and PFOA concentrations were investigated using model PFOA solutions to evaluate the sorption efficiency under different environmental conditions. Subsequent desorption experiments were conducted to test the strength of PFOA-binding by the adsorbents, as well as to gain insight into the possible binding mechanisms involved. Finally, successful sorption of a variety of PFASs from a contaminated field water was demonstrated, which showed the practical application of the 'mixed' adsorbents for remediation of PFOA and related PFASs.

Materials and methods

Materials and chemicals

Natural graphite flakes were obtained from the Uley graphite mine (South Australia). All chemicals including potassium permanganate, sulfuric acid, phosphoric acid, 30% hydrogen peroxide, ferrous sulfate heptahydrate, hydrochloric acid (HCl), sodium hydroxide (NaOH), methanol, toluene and hexane were of analytical grade. Radiolabelled ^{14}C -PFOA (specific activity 2035 Bq $nmol^{-1}$) was purchased from American Radiolabelled Chemicals Inc. (St Louis, MO, USA). RemBind™ was sourced from an environmental remediation company in South Australia (Ziltek Pty Ltd).

Synthesis and characterisation of adsorbents

Two adsorbents were synthesised using the same base material, graphite. Briefly, strong oxidative exfoliation based on an improved Hummer's method (Marcano et al. 2010) was used to synthesise GO, which was then hydrothermally reduced in the presence of ferrous sulfate (Cong et al. 2012) to synthesise FeG. The morphology of the adsorbents was examined by transmission electron microscopy (TEM; Philips-CM100). An energy dispersive X-ray (EDX) detector coupled to a scanning electron microscope elucidated the elemental composition. X-ray diffraction (XRD; PANalytical X'Pert Pro MPD) and Fourier-transform infrared (FTIR; Nicolet 6700, Thermo Fisher) spectra were recorded for structural and functional characterisation. Surface area was determined by the methylene blue dye adsorption method using ultraviolet-visible spectroscopy (664 nm). Surface charge properties and point of zero charge (PZC) were determined by measuring the zeta potential across a pH gradient using dynamic light scattering (Malvern Zetasizer NanoZS). The complete synthesis and characterisation of these adsorbents have been published previously (Lath et al. 2018), and details are provided in the Supplementary Material.

Batch sorption studies

Radiolabelled ^{14}C -PFOA was used to prepare contaminated test solutions. A 10 mM $CaCl_2$ background electrolyte was used to minimise the effects of ionic strength variability, and the pH was maintained at pH 5.5. Batch sorption tests were carried out by mixing 5 mg of adsorbent with 10 mL of the test solutions, under constant agitation on an orbital shaker (100 rpm, 25 °C) to attain equilibrium. The equilibrium time for each adsorbent was determined by testing sorption for durations of 0 to 96 h.

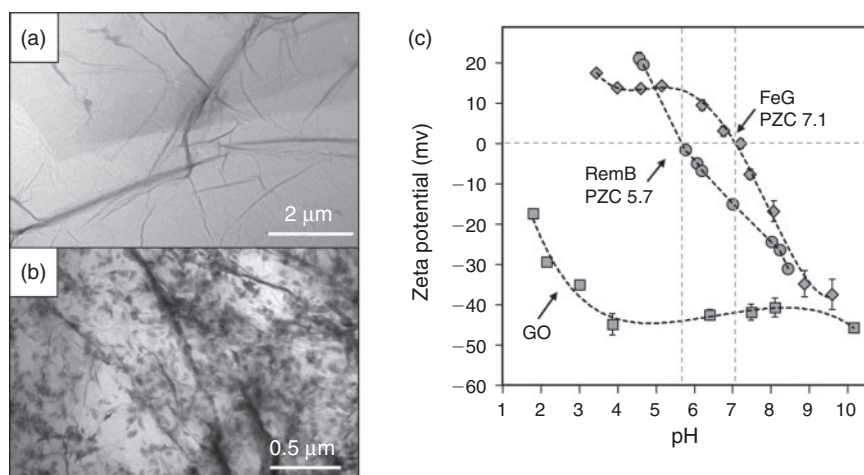


Fig. 1. Surface characterisation of adsorbents: (a) TEM image of graphene oxide (GO), (b) TEM image of an Fe-oxide-modified reduced-GO (FeG), where dark spots confirm the attachment of Fe-based nanoparticles (50–100 nm) and (c) surface zeta potential measurements of GO, FeG and a commercial adsorbent, RemBind™ (RemB) as a function of pH (25 °C).

Sorption was also investigated as a function of concentration by using initial PFOA concentrations in the range of 0–650 $\mu\text{g L}^{-1}$. The influence of pH was studied across a pH range of 3–9; minimal volumes (<100 μL) of 1 M HCl or 1 M NaOH were used to adjust the pH. By using background electrolyte solutions of different concentrations (0–100 mM CaCl_2), the effects of the ionic strength (salt effects) (0–17 dS m^{-1}) on sorption were also investigated. At the end of each sorption step, solutions were centrifuged (5500 g, 1 h) and 0.5 mL aliquots of the supernatants were analysed (see below).

Desorption of adsorbed PFOA from the adsorbents was also investigated. We used a 30 $\mu\text{g L}^{-1}$ PFOA solution, and mixed it with the adsorbents. The equilibrium solutions were then discarded and the remaining PFOA-loaded adsorbents were mixed with different solvents having increasing hydrophobicity and decreasing polarity (water, methanol, toluene and hexane). Amounts of PFOA desorbed from the adsorbents into the solvents were calculated as a percentage of the initial amounts adsorbed.

To assess the efficiency and potential of using GO, FeG and RemB in a field sample, sorption was also tested in a PFAS-contaminated water sample (pH 7.9) collected near a commercial airport in Australia.

Quantitative analyses

All samples with ^{14}C -PFOA were subjected to radiochemical analysis. Aliquots of supernatants (0.5 mL) were collected and transferred into scintillation vials and topped up with 4 mL of scintillation cocktail. The activity of ^{14}C in the samples was measured by β -liquid scintillation counting (Tri-Carb 3110 RT; Perkin Elmer, Waltham, MA, USA). Concentrations of PFOA were calculated from the measured ^{14}C activity and the specific activity.

Analysis of a suite of PFASs from the contaminated field water samples (before and after remediation) were completed by a National Association of Testing Authorities (NATA)-accredited facility, National Measurement Institute (North Ryde, New South Wales, Australia), based on the USEPA 537 methodology using liquid chromatography-tandem mass spectrometry (LC-MS/MS) detection. Samples were extracted using

solid-phase extraction (weak anion exchange) and retained analytes were eluted with ammonia solution. High concentration samples were diluted before extraction. Quantitation was based on recoveries of isotopically labelled standards used as internal standards. Recoveries from laboratory control samples ranged from 90 % to 103 %. Reporting limits ranged from 0.01 $\mu\text{g L}^{-1}$ to 0.05 $\mu\text{g L}^{-1}$. Full names and abbreviations for PFASs measured in the field water sample are listed in Table S1 (Supplementary Material).

Data analyses

The amount of PFOA adsorbed was calculated as the difference between PFOA concentrations in solution before and after equilibration. The performance of each adsorbent was expressed either as a percentage, or as amount of PFOA adsorbed per gram of adsorbent ($\mu\text{g g}^{-1}$). All experiments were performed in triplicate. Losses of PFOA arising from sorption onto the polypropylene sorption tubes were observed; any such losses were corrected for in the calculations.

Results and discussion

Characterisation of prepared graphene-based adsorbents

The morphology of GO and FeG were examined using TEM imaging (Fig. 1). Oxidative exfoliation of graphite resulted in the formation of thin GO sheets (Fig. 1a). Hydrothermal reduction of GO with Fe^{2+} led to the formation of an Fe-oxide-modified, reduced-GO composite, FeG (Fig. 1b); the attached Fe-oxide-based nanoparticles were observed as dense spots (50–100 nm) distributed on the surface. EDX spectra (Table S2 and Fig. S1, Supplementary Material) confirmed the elemental composition of the adsorbents, all of which exhibited the presence of carbon and oxygen. FeG displayed an additional signal for Fe, and RemB displayed additional signals for Al and silicon (Si).

The mineralogical phase and crystal structure of the adsorbents were confirmed by XRD (Fig. S2, Supplementary Material). GO displayed an oriented ‘platy’ phase with a unit cell of 7.16 Å, which was consistent with monolayer spacings typically observed for GO (Marcano et al. 2010). Goethite mineral (α - FeOOH) was detected as the crystalline phase in FeG, which

confirmed the identity of the Fe-oxide nanoparticles. A dominant amorphous activated-C phase was detected in RemB, along with the aluminosilicate clays, kaolinite and muscovite. FTIR spectra (Fig. S3, Supplementary Material) revealed characteristic peaks of GO including the CO₂H stretching (1725 cm⁻¹) and COH bending vibrations (1220 cm⁻¹) (Marcano et al. 2010), which indicated the presence of carboxylic and alcohol groups. Appearance of additional peaks associated with Fe-OH bending (768 cm⁻¹ and 871 cm⁻¹), and Fe-O stretching vibrations (575 cm⁻¹) (Cong et al. 2012) on FeG confirmed the attachment of goethite.

The surface area and charge properties of a material play an important role in adsorbent-adsorbate interactions. The surface areas of GO, FeG and RemB, as determined by the methylene blue adsorption method (Fig. S4, Supplementary Material), were 434.6, 242.4 and 123.4 m² g⁻¹, respectively. The surface charge for FeG and RemB varied notably with pH (Fig. 1c). Their PZC (pH at which zeta potential is zero) were determined to be 7.1 and 5.7, respectively. Conversely, GO maintained a highly negative charge across the pH range investigated.

Batch sorption studies

Sorption by FeG and RemB took 3–4 h to attain equilibrium, whereas GO required at least 48 h to attain equilibrium (Fig. 2a). Using an initial PFOA concentration of 30 µg L⁻¹, FeG and RemB showed >90% sorption, while only up to 60% of the PFOA was adsorbed by GO; the incorporation of the goethite mineral phase onto the modified GO surface enhanced PFOA-sorption by 30%, which highlighted the advantage of combining mineral and C-phases. Considerable sorption, despite the highly negatively-charged surface of GO, suggested the role of non-electrostatic interactions with PFOA. Interestingly, the performance of the adsorbents in terms of amounts adsorbed (RemB = FeG > GO) was inverse to what would be expected from the measured surface areas of the adsorbents (GO > FeG > RemB).

By testing a range of initial PFOA concentrations (0–650 µg L⁻¹), the amounts of PFOA adsorbed per gram of adsorbent were plotted as a function of equilibrium solution concentration (Fig. 2b). In the range tested, sorption followed a linear trend, which indicated that the surface sorption sites were not fully saturated, with more active sites available for sorption. At higher concentrations, the so-called sorption plateau may be reached; a state in which the adsorbed amounts become independent of the concentration in solution. However, at the environmentally relevant concentrations used in our studies, sorption was not saturated. The sorption distribution coefficient, K_d , of a chemical is the ratio of the adsorbed concentration to the dissolved equilibrium concentration, and is a measure of the affinity of the chemical towards the adsorbent. The K_d values of PFOA onto GO, FeG and RemB, as determined from the adsorption isotherm, were 3732, 19288 and 26501 L kg⁻¹, respectively, which indicated a greater affinity for FeG and RemB. In a previous study quantifying PFOA sorption onto pure goethite (Li et al. 2012), the K_d for PFOA onto goethite was determined to be around 1 L kg⁻¹, which is several orders of magnitude lower than that observed for FeG (i.e. a goethite-modified graphene). This further demonstrates the benefit of ‘mixed’ phased adsorbents for improved binding properties.

The effect of solution chemistry, specifically pH and ionic strength, are illustrated in Fig. 3a and Fig. 3b, respectively. The acid dissociation constant, pK_a , of PFOA has been reported to be 2.8 (Moody and Field 2000). Hence, at the pH range investigated

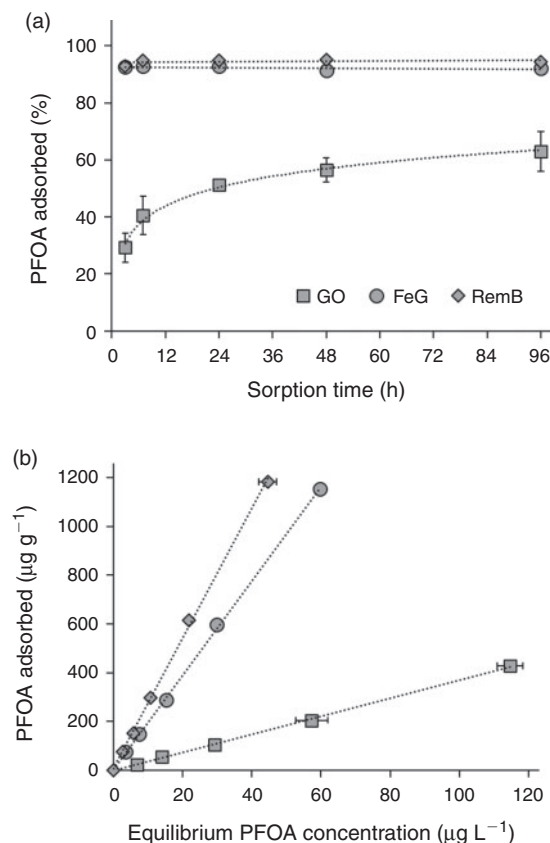


Fig. 2. Sorption curves showing (a) PFOA sorption equilibrium was attained in 48 h by graphene oxide (GO), and in 3–4 h by Fe-oxide-modified reduced-GO (FeG) and a commercial adsorbent, RemBind™ (RemB), at an initial PFOA concentration of 30 µg L⁻¹ in 10 mM CaCl₂ background at 25 °C, and (b) effect of increasing initial PFOA concentration in the range 0–650 µg L⁻¹, in 10 mM CaCl₂ background (pH 5.6, 25 °C, 48 h). Error bars represent standard deviation ($n = 3$). Error bars for FeG and RemB are small and hence not visible in the graphs.

in this study (pH 3–9), PFOA is expected to exist in its deprotonated anionic form. Despite GO having a high (net) negative charge (Fig. 1c), a considerable amount of sorption of the PFOA anion was observed, which overcame the anticipated repulsion between the adsorbate and adsorbent. This indicated the role of non-electrostatic sorptive mechanisms in binding. Given the carbonaceous nature of GBMs, these could be hydrophobic interactions between the graphene surface and the hydrophobic tails of the PFOA molecules (Zhi and Liu 2015). On increasing the pH from 3 to 9, a 20% reduction in the sorption of PFOA by GO was observed (Fig. 3a), likely to arise from an increased repulsion between GO and anionic PFOA, with GO acquiring a greater negative charge at higher pH (zeta potential of GO was –35 mV at pH 3, and –43 mV at pH 9; Fig. 1c). This increased repulsion reduced the likelihood of contact between GO and PFOA molecules, thus deterring the hydrophobic sorption interactions. Interestingly, variations in pH did not influence the sorption behaviour of FeG and RemB (Fig. 3a). Even above the PZC, where FeG and RemB have net negatively-charged surfaces, there was no significant reduction in PFOA-sorption, again suggesting the involvement of non-electrostatic forces in binding PFOA. A variety of results have been reported for the effect of pH on PFOA-sorption depending on the type of adsorbent. Sorption onto activated carbon fibres

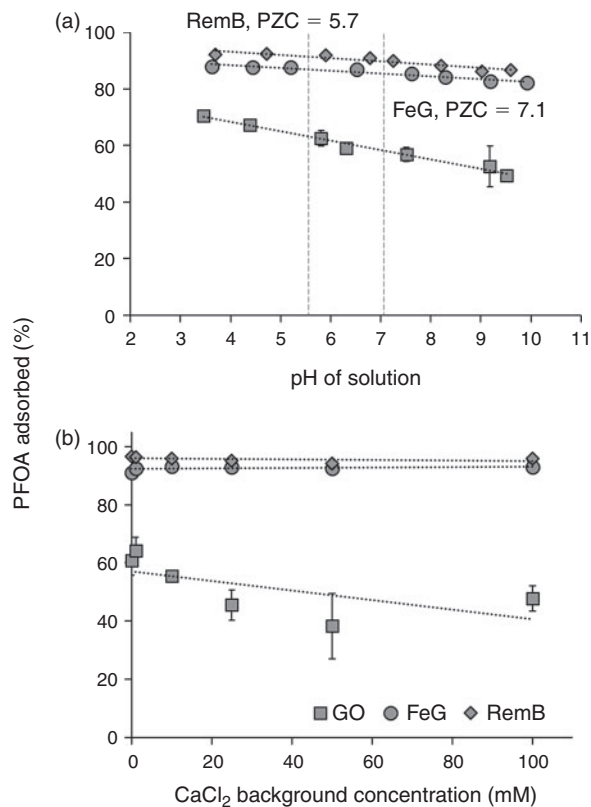


Fig. 3. (a) Effect of pH on PFOA-sorption by graphene oxide (GO), Fe-oxide-modified reduced-GO (FeG) and a commercial adsorbent, RemBind™ (RemB), at an initial PFOA concentration of $100 \mu\text{g L}^{-1}$ in 10 mM CaCl_2 background at 25°C , and (b) effect of ionic strength variability on sorption at initial PFOA concentration of $20 \mu\text{g L}^{-1}$ (pH 5.6, 25°C). Error bars represent standard deviation ($n = 3$). Error bars for FeG and RemB are small and hence not visible in the graphs.

and single-walled carbon nanotubes (CNTs) decreased by 12% and 32%, respectively (Deng et al. 2012; Wang et al. 2015), when the pH was increased from 3 to 9 (attributed to increased repulsion), whereas sorption onto powdered activated carbon was relatively unaffected (Deng et al. 2012), owing to a stable zeta potential in that pH range. A study comparing sorption of PFASs onto different types of CNTs found that pristine CNTs showed greater sorption compared with hydroxyl and carboxyl-functionalised CNTs (Deng et al. 2012), which demonstrated the role of hydrophobic interactions in PFAS-sorption by carbonaceous adsorbents.

Changes in ionic strength will usually affect the electrostatic nature of the surface of the adsorbents, and as a result, the interactions that occur at the surface. Ionic strength can also alter the activity or solubility of ionic species, and soil surface charge, hence influencing sorption. While a slight negative effect (20–25%) of increasing ionic strength on the sorption by GO was observed, it did not alter the PFOA-sorption by FeG and RemB (Fig. 3b), which gave further support to the hypothesis that binding may be non-electrostatic. It is important to note that in a sense, both FeG and RemB are ‘mixed’ adsorbents as they are comprised not only of a dominant carbonaceous phase, but also encompass mineral phases. Structural analysis using XRD revealed the presence of goethite mineral particles in FeG, and confirmed the presence of aluminosilicate clay minerals in RemB. It is thus possible that in addition to hydrophobic interactions with the carbonaceous phases of the adsorbents,

the Fe, Al and Si mineral phases are involved in strong ligand-exchange or inner-sphere complexation mechanisms with PFOA. Gao and Chorover (2012) suggested PFOA-sorption onto Fe-oxide surfaces was possible owing to ligand-exchange of the carboxylate functional group at surface hydroxy groups of the minerals. Similar mechanisms have also been observed at the surface hydroxy groups of an Al-based mineral, boehmite (AlOOH) (Du et al. 2014; Wang et al. 2012). In fact, some of these studies investigating PFOA-sorption by Fe- and Al-based minerals have indicated that sorption decreased considerably with an increase in ionic strength, owing to charge screening and diminished electrostatic interactions (Gao and Chorover 2012; Wang et al. 2012; Wang and Shih 2011). In these cases, the portion of sorption that was attributed to electrostatic interactions and outer-sphere complexation was thought to be influenced by variations in ionic strength, whereas sorption controlled by inner-sphere complexation was not considered to be affected (Gao and Chorover 2012). The proposed binding mechanisms involved in PFOA sorption by GO, FeG and RemB in this study are illustrated schematically in Fig. 4.

By varying the background electrolyte concentrations in this study (0, 1, 10, 25, 50 and 100 mM CaCl_2), the corresponding electrical conductivity conditions that the test solutions were exposed to were 0, 0.24, 2.11, 4.93, 9.24 and 17.11 dS m^{-1} , respectively. This covered a broad range of environmental conditions, and was particularly interesting from a practical perspective. For instance, soils with extracts of conductivities $>4 \text{ dS m}^{-1}$ are usually considered as saline. In landfills, leachates could be expected to have a conductivity of 5– 17 dS m^{-1} (Martinen et al. 2002). In addition to accepting PFAS-contaminated soils, landfills receive several other PFAS-containing commercial products that are discarded at the end of their functional life (Benskin et al. 2012). As a result, unlined landfills can act as a source of PFAS-release to groundwater (Lang et al. 2017). The resistance of FeG- and RemB-sorbed PFOA to desorption in such conditions suggests that the risk of diffusive transport of PFOA from landfills through leachates into the groundwater will be minimised, which makes these adsorbents highly favourable. Consequently, FeG and RemB could also potentially be laid down in landfill sites as a barrier-lining in multi-liner systems to mitigate the leakage or migration of landfill leachates into the water table. Previous research has demonstrated the applicability of GO for PFOS-sorption (Zhao et al. 2016). In this study, we prove that the performance of GO can be improved through strategic mineral-functionalisation, which makes FeG a better adsorbent (for a variety of PFASs, as shown in the section *Remediation of a contaminated-site water sample*). It is possible that with further optimisation, the performance of FeG may be further improved to surpass RemB. By increasing the Fe-loading during the synthesis procedure, the number of goethite nanoparticles on the FeG surface may be increased, which will provide additional active sites for greater PFOA-binding.

Desorption experiments

Like adsorption, desorption from a solid phase is another fundamental process controlling the fate and transport of soluble contaminants in the environment. To further test the strength of PFOA-binding and to gain insight into the possible binding mechanisms involved, we investigated the desorption of adsorbed PFOA into 4 solvents with different polarities, which were Milli-Q water, methanol, toluene and hexane. In the initial sorption step (before desorption) GO, FeG and RemB adsorbed

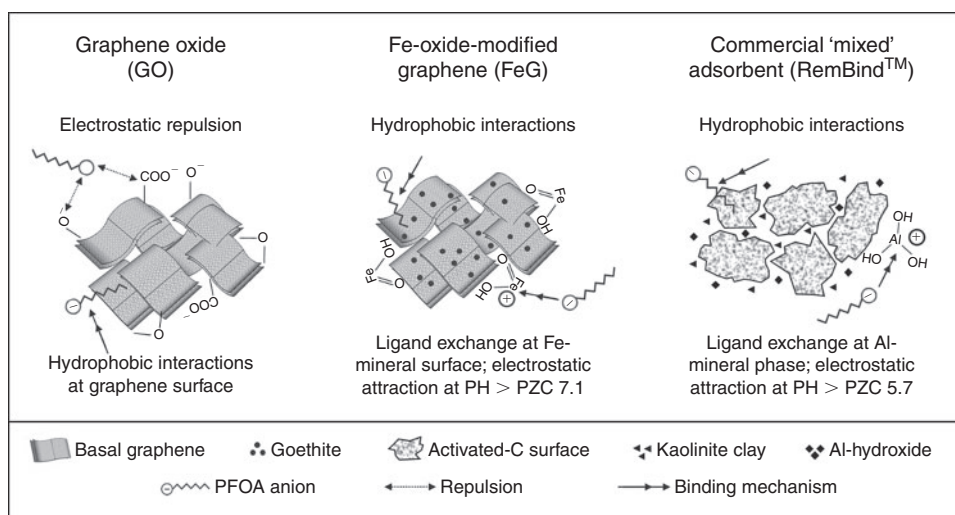


Fig. 4. Schematic illustration of the proposed binding mechanisms involved in PFOA sorption by graphene oxide (GO), Fe-oxide-modified reduced-GO (FeG) and a commercial adsorbent, RemBind™ (RemB).

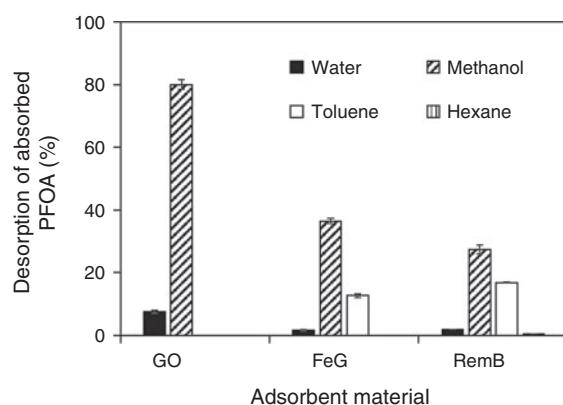


Fig. 5. Desorption of PFOA (expressed as a percentage of adsorbed amount) into Milli-Q water, methanol, toluene and hexane. Using an initial PFOA concentration of $30 \mu\text{g L}^{-1}$, amounts adsorbed by graphene oxide (GO), Fe-oxide-modified reduced-GO (FeG) and a commercial adsorbent, RemBind™ (RemB) were 16.3 , 26.7 and $25.8 \mu\text{g g}^{-1}$ PFOA, respectively.

16.3 , 26.7 and $25.8 \mu\text{g g}^{-1}$ of PFOA, respectively. The proportion of this adsorbed PFOA that was desorbed by the solvents is illustrated in Fig. 5. Overall, these results showed that methanol was the strongest desorbing solvent. This was not surprising given that methanol is known to impart PFOA with improved solubility (Kutsuna et al. 2012), and is the solvent of choice for extracting PFOA from various biological and environmental media (Du et al. 2014). The proportions of sorbed PFOA desorbed by methanol were 80 %, 37 % and 27 % for GO, FeG and RemB, respectively. In the case of FeG and RemB, where the binding appeared to be stronger than GO (as observed in Fig. 3a, b), toluene was able to desorb a small fraction of the adsorbed PFOA (13 % and 17 %, respectively). Only a small amount (8 %) of PFOA was desorbed by water from GO, whereas no desorption from FeG or RemB was observed in water. No PFOA was desorbed from either of the adsorbents by hexane.

PFOA is an anionic polar molecule with a long hydrophobic tail. Our results suggest that ionic PFOA molecules require polar

to moderately polar organic solvents (i.e. methanol and toluene) to solubilise or desorb PFOA, rather than non-polar solvents like hexane. The polarity of the solvents tested were in the order of water > methanol > toluene > hexane. Measures of desorption by these solvents could be considered as estimates of the strength of binding (Navarro et al. 2017) in the order opposite to that of polarity (toluene > methanol > water). Consequently, PFOA fractions desorbed by water were weakly bound, whereas fractions desorbed by methanol and toluene were bound much more strongly on the adsorbent surface. The PFOA molecules that were not desorbed could be regarded as bound irreversibly to the adsorbents (in the case of GO, FeG and RemB, these were 12 %, 49 % and 53 % of adsorbed PFOA, respectively). These desorption data are important from an environmental partitioning perspective, and can help us estimate the risks of remobilisation of adsorbent-bound PFOA, especially when used for in situ remediation of contaminated soils. For instance, it is reasonable to assume that precipitation from rainfall events is unlikely to desorb PFOA bound by FeG and RemB, hence any concerns for subsequent leaching into subsurface soils or groundwater can be discarded. Consequently, this would also suggest reduced bioavailability to plants and organisms exposed to the treated soil. However, at a waste disposal or landfill site, where PFASs may co-exist with organic solvent waste from accidental spills, increased PFOA mobility is likely. Considering the desorption behaviour of the two different GBMs tested here, FeG is expected to be a better adsorbent than GO for in situ remediation, given the potential for reduced leachability and reduced bioavailability of PFOA.

Remediation of a contaminated-site water sample

To demonstrate the efficiency of the adsorbents in a real environmental matrix, in the final experiment, we tested sorption of PFOA and other PFASs from a contaminated field water sample collected from a commercial airport site in Australia. The PFAS composition of the water sample is detailed in Table 1 (PFASs that were present at concentrations below the detection limits have been excluded); treatment efficiency is expressed as a percentage of removal of each PFAS.

Of the $30 \mu\text{g L}^{-1}$ of PFOA present in the sample, the 'mixed' adsorbents, FeG and RemB adsorbed 94 % and 95.7 % of the

Table 1. Treatment of PFAS-contaminated water by GO, FeG and RemB

PFASs detected in contaminated water sample	PFAS-concentrations in contaminated water ($\mu\text{g L}^{-1}$)	% Removal of PFASs		
		GO	FeG	RemB
Perfluoroalkyl carboxylates (increasing order of chain length)				
PFBuA	9.7	10.3	8.2	26.8
PFPeA	12	0	8.3	8.3
PFHxA	60	3.3	28.3	36.7
PFHpA	13	15.4	73.1	78.5
PFOA	30	3.3	94	95.7
PFNA	2.8	10.7	98.9	99.1
PFDA	1	5	98.0 (bdl) ^A	98.0 (bdl)
Perfluoroalkyl sulfonates (increasing order of chain length)				
PFBS	13	7.7	15.4	46.9
PFHxS	100	5	90.5	96
PFOS	600	-15	99.3	99.7
Fluorotelomers and perfluoroalkylsulfonamides				
6:2 FTS	2.6	98.1 (bdl)	96.3	98.1 (bdl)
8:2 FTS	6.1	99.2 (bdl)	99.2 (bdl)	99.2 (bdl)
PFOSA	2.3	43.5	99.1 (bdl)	99.1 (bdl)

^AWhere treated PFAS concentrations were below detection limits (bdl), the detection limit value (0.02 or $0.05 \mu\text{g L}^{-1}$, depending on the type of PFAS) was used to calculate percentage adsorbed.

PFOA, respectively. However, GO only adsorbed 3.3 % of the PFOA. This could occur due to the presence of several other competing ions as well as other PFAS species in the water sample. As has already been observed in the batch experiments, PFOA sorption onto GO could be compromised by high pH and also affected by ionic strength (Fig. 3a, b). The main component of the contaminated water sample was PFOS at $600 \mu\text{g L}^{-1}$, of which >99 % was removed by FeG and RemB. It has been observed in previous studies that for the same perfluorocarbon chain lengths, PFASs with sulfonate head groups exhibit greater sorption than those with carboxylate groups (Hellsing et al. 2016; Higgins and Luthy 2006; Wang and Shih 2011). Hence the extraordinary sorption of PFOS over PFOA can be attributed to the differences in functional groups. The removal rate of PFOS by GO was negative; that is, the amount of PFOS measured in the GO-treated sample was greater than that in the original field water sample. This could potentially be attributed to a variety of factors. The water samples were not subjected to any pretreatment or filtration before testing with the adsorbents. As PFOS can interact with natural organic matter and suspended particulate matter in water, any non-homogeneity in the samples could have led to differences in the PFOS distribution between samples. Moreover, owing to its highly surface-active nature, particularly at high concentrations, PFOS can preferentially accumulate at the interface of air-bubbles in an aqueous phase (Meng et al. 2014) – a property that can also be exploited for remediation by ‘fractionation’ (Ross et al. 2018). Differences in sample handling, such as greater agitation during subsampling, could lead to such a ‘foam fractionation’ effect, which would cause a non-homogenous PFOS distribution in the samples. Another possible explanation for increased PFOS concentrations could be attributed to the breakdown of certain PFOS-precursor compounds (Buck et al. 2011); however, these compounds were not tested as part of the analytical suite. As no PTFE-based apparatus were used during the experimental or analytical procedures, contamination of the dissolved phase was not expected to have occurred.

For the fluorotelomer sulfonates (6:2 FTS and 8:2 FTS), >96 % sorption was observed in the case of all adsorbents,

including GO. Fluorotelomers are only partially fluorinated, and comprise a $-\text{CH}_2-\text{CH}_2-$ spacer group occurring in between the fluorinated tail and the polar sulfonate head. The lower degree of fluorination may be the reason why GO was able to display enhanced sorption of these compounds compared with the fully fluorinated compounds. The presence of the $-\text{CH}_2-\text{CH}_2-$ group potentially allows interactions with the aliphatic regions (sp^3 hybridised carbon atoms) in the oxygenated GO structure (Dreyer et al. 2010).

Another important observation from the data is the apparent effect of chain length of the PFASs on sorption performance, specifically for FeG and RemB. For both perfluoroalkyl carboxylates as well as perfluoroalkyl sulfonates, greater sorption was detected as the chain length increased, which further substantiated the dominant role of hydrophobic interactions. This was consistent with what has been previously reported in the literature for sorption to other carbon-based remediation materials (Deng et al. 2012; Xiao et al. 2017). When keeping the functional group the same, increase in the C–F chain length decreases the solubility (Hellsing et al. 2016) and increases hydrophobicity of PFASs, which allows for stronger hydrophobic interactions with the adsorbents (Du et al. 2014).

Conclusions

Overall, the ‘mixed’ mineral and C-based adsorbents, FeG and RemB, showed excellent potential for PFOA-sorption, when compared with GO. While variations in pH and ionic strength conditions hindered PFOA-sorption by GO, they did not compromise the performance of FeG. Results from our desorption study demonstrate that the binding of PFOA by FeG is strong in aqueous as well as ionic media (CaCl_2) and the risk of contaminant remobilisation through rainfall events, solubilisation, desorption, or leachability is minimal, unless polar organic solvents, like methanol and toluene, co-exist at the contaminated sites. Such resistance to changes in environmental solution chemistry and strength of binding make FeG and RemB favourable in situ adsorbents for PFASs, with added potential for use as barriers to line landfills that accept PFAS-waste, to mitigate the migration of the leachate. Finally, successful

sorption of a range of PFASs from a contaminated field water sample by FeG and RemB demonstrates the potential application of these ‘mixed’ adsorbents for PFAS-remediation. Owing to the versatile surface functionality of GBMs, further modifications and optimisation of the FeG surface (e.g. increased loading of Fe-minerals during synthesis) could be performed to achieve a greater amount of sorption. This is the first study to highlight the advantages of using mixed mineral and C-based materials for enhanced PFAS-sorption, and demonstrates the potential of novel graphene technology for this purpose.

Supplementary material

Synthesis of graphene oxide (GO) and Fe-oxide-modified reduced GO composite (FeG); sample preparation for characterisation of adsorbents; full names and abbreviations for the suite of PFASs measured in the field water sample; elemental composition of adsorbents GO, FeG and RemBind™ (RemB); EDX spectra of adsorbents; XRD spectra of adsorbents; FTIR spectra of adsorbents; and Methylene Blue standard calibration curve for measurement of surface areas of adsorbents are available on the Journal’s website.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

We would like to thank Dr Mark Raven (CSIRO) for performing XRD analyses, as well as Adelaide and Waite Microscopy for access to TEM and SEM-EDX facilities. Financial support from Australian Research Council Discovery Grant DP150101760 is gratefully acknowledged. We would also like to thank Ziltek Pty Ltd for their financial support and provision of RemBind™.

References

- Arias EVA, Mallavarapu M, Naidu R (2015). Identification of the source of PFOS and PFOA contamination at a military air base site. *Environmental Monitoring and Assessment* **187**, 4111. doi:10.1007/S10661-014-4111-0
- Benskin JP, Li B, Ikononou MG, Grace JR, Li LY (2012). Per- and polyfluoroalkyl substances in landfill leachate: patterns, time trends, and sources. *Environmental Science & Technology* **46**, 11532–11540. doi:10.1021/ES302471N
- Bruton TA, Sedlak DL (2017). Treatment of aqueous film-forming foam by heat-activated persulfate under conditions representative of in situ chemical oxidation. *Environmental Science & Technology* **51**, 13878–13885. doi:10.1021/ACS.EST.7B03969
- Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, de Voogt P, Jensen AA, Kannan K, Mabury SA, van Leeuwen SPJ (2011). Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management* **7**, 513–541. doi:10.1002/IEAM.258
- Cheng J, Vecitis CD, Park H, Mader BT, Hoffmann MR (2010). Sonochemical degradation of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in groundwater: kinetic effects of matrix inorganics. *Environmental Science & Technology* **44**, 445–450. doi:10.1021/ES902651G
- Cong H-P, Ren X-C, Wang P, Yu S-H (2012). Macroscopic multifunctional graphene-based hydrogels and aerogels by a metal ion induced self-assembly process. *ACS Nano* **6**, 2693–2703. doi:10.1021/NN300082K
- Deng S, Zhang Q, Nie Y, Wei H, Wang B, Huang J, Yu G, Xing B (2012). Sorption mechanisms of perfluorinated compounds on carbon nanotubes. *Environmental Pollution* **168**, 138–144. doi:10.1016/J.ENVPOL.2012.03.048
- Dong Z, Wang D, Liu X, Pei X, Chen L, Jin J (2014). Biol.-inspired surface-functionalization of graphene oxide for the adsorption of organic dyes and heavy metal ions with a superhigh capacity. *Journal of Materials Chemistry A: Materials for Energy and Sustainability* **2**, 5034–5040. doi:10.1039/C3TA14751G
- Dreyer DR, Park S, Bielawski CW, Ruoff RS (2010). The chemistry of graphene oxide. *Chemical Society Reviews* **39**, 228–240. doi:10.1039/B917103G
- Du Z, Deng S, Bei Y, Huang Q, Wang B, Huang J, Yu G (2014). Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents – A review. *Journal of Hazardous Materials* **274**, 443–454. doi:10.1016/J.JHAZMAT.2014.04.038
- Fan L, Luo C, Sun M, Qiu H, Li X (2013). Synthesis of magnetic β -cyclodextrin–chitosan/graphene oxide as nanoadsorbent and its application in dye adsorption and removal. *Colloids and Surfaces B: Biointerfaces* **103**, 601–607. doi:10.1016/J.COLSURFB.2012.11.023
- Feng H, Lin Y, Sun Y, Cao H, Fu J, Gao K, Zhang A (2017). In silico approach to investigating the adsorption mechanisms of short chain perfluorinated sulfonic acids and perfluorooctane sulfonic acid on hydrated hematite surface. *Water Research* **114**, 144–150. doi:10.1016/J.WATRES.2017.02.024
- Gao X, Chorover J (2012). Adsorption of perfluorooctanoic acid and perfluorooctanesulfonic acid to iron oxide surfaces as studied by flow-through ATR-FTIR spectroscopy. *Environmental Chemistry* **9**, 148–157. doi:10.1071/EN11119
- Hellsing MS, Josefsson S, Hughes AV, Ahrens L (2016). Sorption of perfluoroalkyl substances to two types of minerals. *Chemosphere* **159**, 385–391. doi:10.1016/J.CHEMOSPHERE.2016.06.016
- Higgins CP, Luthy RG (2006). Sorption of perfluorinated surfactants on sediments. *Environmental Science & Technology* **40**, 7251–7256. doi:10.1021/ES061000N
- Higgins CP, McLeod PB, MacManus-Spencer LA, Luthy RG (2007). Bioaccumulation of perfluorochemicals in sediments by the aquatic oligochaete *Lumbriculus variegatus*. *Environmental Science & Technology* **41**, 4600–4606. doi:10.1021/ES062792O
- Ji L, Chen W, Xu Z, Zheng S, Zhu D (2013). Graphene nanosheets and graphite oxide as promising adsorbents for removal of organic contaminants from aqueous solution. *Journal of Environmental Quality* **42**, 191–198. doi:10.2134/JEQ2012.0172
- Kucharzyk KH, Darlington R, Benotti M, Deeb R, Hawley E (2017). Novel treatment technologies for PFAS compounds: A critical review. *Journal of Environmental Management* **204**, 757–764. doi:10.1016/J.JENVMAN.2017.08.016
- Kutsuna S, Hori H, Sonoda T, Iwakami T, Wakisaka A (2012). Preferential solvation of perfluorooctanoic acid (PFOA) by methanol in methanol–water mixtures: A potential overestimation of the dissociation constant of PFOA using a Yasuda–Shedlovsky plot. *Atmospheric Environment* **49**, 411–414. doi:10.1016/J.ATMOSENV.2011.12.009
- Lang JR, Allred BM, Field JA, Levis JW, Barlaz MA (2017). National estimate of per- and polyfluoroalkyl substance (PFAS) release to U.S. municipal landfill leachate. *Environmental Science & Technology* **51**, 2197–2205. doi:10.1021/ACS.EST.6B05005
- Lath S, Navarro D, Tran D, Kumar A, Losic D, McLaughlin MJ (2018). Mixed-mode remediation of cadmium and arsenate ions using graphene-based materials. *CLEAN – Soil, Air, Water* **46**, 1800073. doi:10.1002/CLEN.201800073
- Lee YC, Lo SL, Kuo J, Huang CP (2013). Promoted degradation of perfluorooctanoic acid by persulfate when adding activated carbon. *Journal of Hazardous Materials* **261**, 463–469. doi:10.1016/J.JHAZMAT.2013.07.054
- Lein NPH, Fujii S, Tanaka S, Nozoe M, Tanaka H (2008). Contamination of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in surface water of the Yodo River basin (Japan). *Desalination* **226**, 338–347. doi:10.1016/J.DESAL.2007.01.247
- Li C, Ji R, Schaffer A, Sequaris J-M, Amelung W, Vereecken H, Klumpp E (2012). Sorption of a branched nonylphenol and perfluorooctanoic acid on Yangtze River sediments and their model components. *Journal of Environmental Monitoring* **14**, 2653–2658. doi:10.1039/C2EM30394A
- Marcano DC, Kosynkin DV, Berlin JM, Sinitskii A, Sun Z, Slesarev A, Alemany LB, Lu W, Tour JM (2010). Improved synthesis of graphene oxide. *ACS Nano* **4**, 4806–4814. doi:10.1021/NN1006368
- Marttinen SK, Kettunen RH, Sormunen KM, Soimasuo RM, Rintala JA (2002). Screening of physical–chemical methods for removal of organic

- material, nitrogen and toxicity from low strength landfill leachates. *Chemosphere* **46**, 851–858. doi:10.1016/S0045-6535(01)00150-3
- Meng P, Deng S, Lu X, Du Z, Wang B, Huang J, Wang Y, Yu G, Xing B (2014). Role of air bubbles overlooked in the adsorption of perfluorooctanesulfonate on hydrophobic carbonaceous adsorbents. *Environmental Science & Technology* **48**, 13785–13792. doi:10.1021/ES504108U
- Moody CA, Field JA (2000). Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams. *Environmental Science & Technology* **34**, 3864–3870. doi:10.1021/ES991359U
- Navarro DA, Kookana RS, McLaughlin MJ, Kirby JK (2017). Fate of radiolabeled C60 fullerenes in aged soils. *Environmental Pollution* **221**, 293–300. doi:10.1016/J.ENVPOL.2016.11.077
- Novoselov KS, Falko VI, Colombo L, Gellert PR, Schwab MG, Kim K (2012). A roadmap for graphene. *Nature* **490**, 192–200. doi:10.1038/NATURE11458
- O'Hagan D (2008). Understanding organofluorine chemistry. An introduction to the C–F bond. *Chemical Society Reviews* **37**, 308–319. doi:10.1039/B711844A
- Renner R (2001). Growing concern over perfluorinated chemicals. *Environmental Science & Technology* **35**, 154A–160A. doi:10.1021/ES012317K
- Ross I, McDonough J, Miles J, Storch P, Thelakkat Kochunarayanan P, Kalve E, Hurst J, Dasgupta SS, Burdick J (2018). A review of emerging technologies for remediation of PFASs. *Remediation Journal* **28**, 101–126. doi:10.1002/REM.21553
- Rumsby PC, McLaughlin CL, Hall T (2009). Perfluorooctane sulphonate and perfluorooctanoic acid in drinking and environmental waters. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **367**, 4119–4136. doi:10.1098/RSTA.2009.0109
- Sundström M, Ehresman DJ, Bignert A, Butenhoff JL, Olsen GW, Chang S-C, Bergman A (2011). A temporal trend study (1972–2008) of perfluorooctanesulfonate, perfluorohexanesulfonate, and perfluorooctanoate in pooled human milk samples from Stockholm, Sweden. *Environment International* **37**, 178–183. doi:10.1016/J.ENVINT.2010.08.014
- Wang F, Shih K (2011). Adsorption of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) on alumina: Influence of solution pH and cations. *Water Research* **45**, 2925–2930. doi:10.1016/J.WATRES.2011.03.007
- Wang F, Liu C, Shih K (2012). Adsorption behavior of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) on boehmite. *Chemosphere* **89**, 1009–1014. doi:10.1016/J.CHEMOSPHERE.2012.06.071
- Wang Y, Niu J, Li Y, Zheng T, Xu Y, Liu Y (2015). Performance and mechanisms for removal of perfluorooctanoate (PFOA) from aqueous solution by activated carbon fiber. *RSC Advances* **5**, 86927–86933. doi:10.1039/C5RA15853B
- Washington JW, Yoo H, Ellington JJ, Jenkins TM, Libelo EL (2010). Concentrations, distribution, and persistence of perfluoroalkylates in sludge-applied soils near Decatur, Alabama, USA. *Environmental Science & Technology* **44**, 8390–8396. doi:10.1021/ES1003846
- Xiao X, Ulrich BA, Chen B, Higgins CP (2017). Sorption of poly- and perfluoroalkyl substances (PFASs) relevant to aqueous film-forming foam (AFFF)-impacted groundwater by biochars and activated carbon. *Environmental Science & Technology* **51**, 6342–6351. doi:10.1021/ACS.EST.7B00970
- Yusuf M, Elfghi FM, Zaidi SA, Abdullah EC, Khan MA (2015). Applications of graphene and its derivatives as an adsorbent for heavy metal and dye removal: a systematic and comprehensive overview. *RSC Advances* **5**, 50392–50420. doi:10.1039/C5RA07223A
- Zareitalabad P, Siemens J, Hamer M, Amelung W (2013). Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater—A review on concentrations and distribution coefficients. *Chemosphere* **91**, 725–732. doi:10.1016/J.CHEMOSPHERE.2013.02.024
- Zhao C, Fan J, Chen D, Xu Y, Wang T (2016). Microfluidics-generated graphene oxide microspheres and their application to removal of perfluorooctane sulfonate from polluted water. *Nano Research* **9**, 866–875. doi:10.1007/S12274-015-0968-7
- Zhi Y, Liu J (2015). Adsorption of perfluoroalkyl acids by carbonaceous adsorbents: Effect of carbon surface chemistry. *Environmental Pollution* **202**, 168–176. doi:10.1016/J.ENVPOL.2015.03.019

Handling Editor: Kevin Wilkinson