



Effects of different factors on photodefluorination of perfluorinated compounds by hydrated electrons in organo-montmorillonite system



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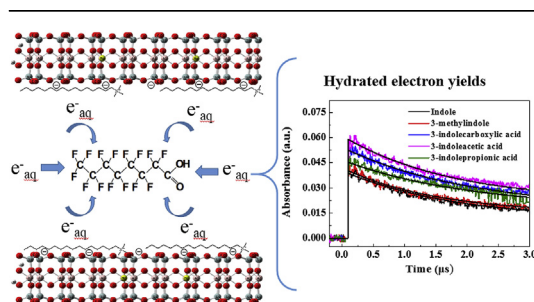
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HIGHLIGHTS

- Perfluorinated compounds can be effectively defluorinated under mild conditions.
- The concentration of hydrated electrons are detected by laser flash photolysis.
- Effect of different factors on the degradation of PFOA are accurately described.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 23 May 2017

Received in revised form

23 September 2017

Accepted 12 October 2017

Available online 13 October 2017

Handling Editor: Jun Huang

Keywords:

Hydrated electrons
Perfluorocarboxylic acids
Organo-montmorillonite
Photodefluorination
Indole derivatives
Laser flash photolysis

ABSTRACT

Perfluorinated compounds (PFCs) are considered as the most recalcitrant organic contaminants. Our previous research has shown that PFCs can be completely defluorinated in the UV/organoclay/3-indole acetic acid system, however, the factors that could affect the degradation of PFCs, are still not clear. In this study, we further investigated the effect of different indole derivatives and organo-modified montmorillonite on the degradation of perfluorooctanoic acid (PFOA). Based on multiple linear regression analysis, our results clearly indicate that hydrated electron yields of indole derivatives, adsorption of PFOA and indole derivatives on organo-montmorillonite contributed independently to the degradation of PFOA. In addition, the results also show that the presence of humic substance (even at 10 mg C L⁻¹) would not significantly suppress the degradation process due to the strong adsorption of humic substance on the organo-montmorillonite surface. This study would provide more information to design an efficient and environment-friendly system for degradation of PFCs, and this technique will have great potential for treatment of persistent contaminants under mild reaction conditions.

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1. Introduction

With the unique thermal and chemical stability and good

surface-active properties, perfluorinated compounds (PFCs) have a wide variety of industrial applications, e.g. emulsifying agents in polymer synthesis, water and stain proof coatings for paper and textiles, oxidative protective coatings on metals, and fire retardants (Renner, 2001; Moody and Field, 2000; Giesy and Kannan, 2002). Among these chemicals, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have drawn more attentions due to

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the large quantities of production, recent study also showed that both PFOA and PFOS could be transformed from other perfluorinated polymers (Houtz et al., 2013). Moreover, they are also the most frequently detected perfluorinated surfactants in different environmental matrices, biota, and serum of human beings (Li et al., 2017; Heydebreck et al., 2016; Woodruff et al., 2011; Pedersen et al., 2016). The concentration of PFOA in some natural water was reported up to ng L^{-1} level (Sun et al., 2011; Moody et al., 2002). Higher concentrations of PFOA or PFOS had been detected in groundwater (up to 6.6 mg L^{-1}) collected from the military bases where aqueous film forming foams were frequently used (Houtz et al., 2013). The concentrations of PFCs in wastewater from fluoropolymer manufacturing could even reach as high as 1387 mg L^{-1} (Key et al., 1997). Many studies have revealed that PFCs are persistent toxic pollutants and could accumulate in upper-trophic-level organisms through food chain, which might pose a significant risk to human health and ecosystem (Li et al., 2017; Pedersen et al., 2016). It was reported that PFOA and PFOS had been detected in almost all of biological tissue samples (99%) from U.S. pregnant women based on the 2003–2004 National Health and Nutritional Examination Survey (Woodruff et al., 2011). Therefore, it is greatly needed to develop an environmental-friendly and highly efficient technology to fully degrade PFCs into harmless species.

Due to the strong C–F bond, PFCs are considered as the most recalcitrant organic compounds (Sun et al., 2011). Many conventional treatments, such as advanced oxidation and biological techniques cannot effectively degrade PFCs (Vecitis et al., 2009; Dillert et al., 2007). Recent studies showed that PFCs could be degraded under photoreduction processes, in which SiC/Graphene was used as catalyst (Huang et al., 2016). The decomposition mechanism involves reductive cleavage of C–F bonds by the hydrodefluorination reaction via Si–H/C–F redistribution, indicating that reduction method is a promising strategy for decomposition of PFCs (Huang et al., 2017). The hydrated electron, which is a powerful reducing species with a standard reducing potential of -2.87 V (Bragg et al., 2004), has shown great potential for decomposition of PFCs (Park et al., 2009). Qu et al. (2010), and Song et al. (2013), investigated the hydrated electron induced photo-reductive defluorination of PFOA using KI and sulfite as a mediator, and about 98% and 89% defluorination could be achieved after 18 h and 24 h reaction period, respectively. However, due to the high reactivity of hydrated electron, the reaction must occur under anoxic and alkaline conditions to prevent the fast consumption of hydrated electrons by oxygen or protons (Qu et al., 2010; Song et al., 2013).

Our previous research has demonstrated that hydrated electrons can be generated via UV irradiation of indole or its derivatives, and this process is significantly enhanced by the presence of natural montmorillonite clay mineral (Tian et al., 2015). Due to the unique structure of montmorillonite, the negatively-charged clay layer could provide a planar surface to stabilize the indole radical cation, consequently prolonging the lifetime of the radical and promoting the release of hydrated electron, finally facilitating the degradation of contaminants reduced by hydrated electron (Tian et al., 2015). On the other hand, for the surface reaction, clay mineral can also act as the geosorbent to concentrate both hydrated electron and organic contaminant in a constrained environment and increase their contact possibility (Tian et al., 2015). Our results further showed that when montmorillonite was modified with organic cationic surfactant, e.g., hexadecyltrimethylammonium (HDTMA), the hydrophobic phase in clay interlayer could not only significantly increase the adsorption of both PFCs and indole acetic acid, but also protect the generated hydrated electrons from quenching by oxygen and protons (Tian et al., 2016). In our system, PFCs can be completely defluorinated under ambient conditions,

and the final products are formic and acetic acids (Tian et al., 2016). Even our studies have indicated that PFCs could be effectively degraded in the UV/organoclay/3-indole acetic acid system, there is still lack of information about the factors that might significantly affect the degradation process, and this knowledge would be important to design a more efficient system for PFCs treatment.

The objective of this study was to investigate the effect of different indole derivatives and organo-modification on the degradation of PFCs. PFOA was used as the model compound. Multiple regression analysis was performed to evaluate the importance of different variables on the reaction process, the results showed that the hydrated electron yields of indole derivatives, adsorption of PFOA and indole derivatives on organoclay contributed independently to the degradation of PFOA. Furthermore, the effects of chain length of perfluorinated carboxylic acid (PCA) and the presence of humic substance were also studied. As both montmorillonite clay mineral and indole derivatives are natural substances, our reaction system might provide an environmental-friendly alternative for effective treatment of PFCs, one of the most persistent organic contaminants.

2. Materials and methods

2.1. Chemicals

Analytical grade (purity > 98%) indole and its derivatives, e.g., 3-methylindole, 3-indolecarboxyl acid, 3-indoleacetic acid, 3-indolepropionic acid were obtained from Sigma-Aldrich (St. Louis, MO). Perfluorooctanoic acid, perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), sodium acetate, sodium chloride, sodium carbonate, sodium bicarbonate, sodium hydroxide, hydrochloric acid, trimethylphenylammonium (TMPA) bromide, hexadecylpyridinium (HDPY) bromide, HDTMA bromide and dioctodecyltrimethylammonium (DODMA) bromide were also purchased from Sigma-Aldrich. Methanol and acetonitrile were of HPLC grade from Merck Inc. Suwannee River humic acid (SRHA) was used as the reference humic substance from International Humic Substances Society (IHSS). All the chemicals were used as received without any further purification.

2.2. Preparation of homoionic Na^+ - and organo-modified montmorillonites

Montmorillonite was obtained from Fenghong Inc. (Zhejiang Province, China) with measured cation exchange capacity (CEC) of 770 mmol kg^{-1} . To prepare Na^+ saturated clay mineral, nature montmorillonite was initially suspended in Milli-Q water, the clay-sized fraction ($<2 \mu\text{m}$) was collected by centrifugation for 10 min at 60 g. To remove carbonate impurities, clay suspension was titrated to pH 6.8 with 0.5 M sodium acetate buffer (pH = 5). After centrifugation, the clay particles were resuspended in 0.1 M NaCl solution for 12 h, then centrifuged at 3295 g for 25 min, and the supernatant liquid was discarded. This procedure was repeated six times to ensure that montmorillonite was fully saturated by Na^+ . Finally, after Na^+ -saturated montmorillonite (Na^+ -montmorillonite) was repeatedly washed using Milli-Q water until free of chloride as indicated by a negative test with AgNO_3 , the clay paste was freeze-dried and stored inside a desiccator. The organo-modified montmorillonite was prepared according to the method described by Boyd et al. (1988). Briefly, 50 g of the obtained Na^+ -montmorillonite was suspended in 500 mL water and stirred for 8 h. The solution with organic cationic surfactant was obtained by addition of predetermined amount (38.5 mmol) of HDTMA, DODMA, HDPY or TMPA into 1000 mL hot Milli-Q water (60°C). Aqueous solution

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