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Microwave discharge electrodeless lamps (MDELs). VI. Performance evaluation of a novel microwave discharge granulated electrodeless lamp (MDGEL)—Photoassisted defluorination of perfluoroalkoxy acids in aqueous media

Satoshi Horikoshi[a,b,*], Akihiro Tsuchida[c], Hideki Sakai[b,c], Masahiko Abe[b,c], Nick Serpone[d,**]

[a] Department of Material & Life Science, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyodaku, Tokyo 102-8554, Japan
[b] Research Institute for Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan
[c] Department of Pure and Applied Chemistry, Faculty of Science, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan
[d] Gruppo Fotochimico, Dipartimento di Chimica Organica, Universita di Pavia, Via Taramelli 10, Pavia 27100, Italy

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ABSTRACT

Novel microwave discharge granulated electrodeless lamps (MDGELs; 5 mm × 10 mm), fabricated using vacuum-UV (VUV) transparent quartz envelopes, have been examined for the treatment of model contaminated wastewaters. Evaluation of these MDGELs was performed through the self-ignition of the lamps at low microwave power levels and by the photoassisted decomposition and defluorination of trifluoroacetic acid (TFA), heptafluorobutyric acid (HFBA) and perfluorooctanoic acid (PFOA) in aqueous solutions in a flow-through microwave photoreactor (MW/Photo) containing 20 such MDGELs. A conventional single rod-shaped microwave discharge electrodeless lamp (MDEL) and a low-pressure electrode Hg lamp were also used to compare the performance of these novel MDGELs. The dominant performance of the MDGELs was established by the defluorination kinetics per surface area of the light source immersed in the solutions and by the applied electric power of the lamps. At pH 10, the kinetics correlated with the carbon chain length and with the number of C–F bonds in the three fluorinated acids. Microwave irradiation of the single rod-shaped MDEL device achieved a defluorination level of 51% (TFA), 67% (HFBA), and 37% (PFOA) for a 240-min VUV/UV irradiation of solutions at initial pHs = 4.7–5.2, whereas at pH = 10 defluorination of TFA and HFBA was 100% complete within 120–135 min of irradiation; defluorination of PFOA was ca. 80% complete after 200 min. With the 20 MDGEL system, 100% defluorination of TFA and HFBA was achieved after 105 min, whereas 100% defluorination of PFOA required ca. 400 min of irradiation. A decomposition/defluorination pathway is described for PFOA on the basis of intermediates identified by LC–MS techniques that involved initial VUV/UV irradiation (185 nm and 254 nm) of the PFOA contaminant followed by subsequent losses of CO_2 and $-CF_2$ units to complete defluorination and degradation.

1. Introduction

Microwave radiation is typically used as a heat source in the field of organic syntheses [1]. The important feature of microwave heating in these syntheses is manifested by prompt and selective heating since microwave radiation can heat very efficiently materials that possess high dielectric loss factors (ε''). In addition, sterilization and/or heat-treatment obtained upon converting microwave radiation to heat have also been examined in the purification of waters for the purpose of aquatic conservation. To the extent that the wavelength and the photon energy of commonly used 2.45-GHz microwaves are 12.24 cm and 1×10^{-5} eV, respectively, microwave energy is ca. five orders of magnitude smaller than the vibrational energy of typical molecules. Accordingly, the energy needed to cleave a chemical bond in an organic reaction is not directly available from the microwaves, and a direct reaction of organic substrates induced by microwave irradiation alone can be precluded.

In our long-standing strategy, the microwave energy is converted to another higher energy form, such as vacuum-UV (VUV) and UV radiations, through the use of microwave discharge electrodeless lamps (MDELs) [2]. Distinctive features that make MDEL

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* Corresponding author at: Department of Material & Life Science, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyodaku, Tokyo 102-8554, Japan.
** Corresponding author. Tel.: +39 0382 98 73 16; fax: +39 0382 98 73 23.
E-mail addresses: horikosi@sophia.ac.jp (S. Horikoshi), nickser@alcor.concordia.ca, nick.serpone@unipv.it (N. Serpone).

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devices as attractive light sources are (a) the relatively long lifetime of the electrodeless lamp, (b) the absence of complications in lamp shape because the lamps are electrodeless, (c) the absence of variations in light intensity, (d) the observed ignition time to lighting the MDEL device is shorter than for a typical Hg electrode lamp, (e) the UV radiation can be supplied external to the reactor to avoid absorption of the microwave radiation by the reactor contents, (f) the facility of lamp replacement, and finally (g) both UV and MW radiations are simultaneously available to induce redox processes to destroy organic substrates and microorganisms using a microwave energy source alone. Moreover, an MDEL light source can be positioned in aqueous media because the "electric power" supplied by the microwave radiation to the MDEL device is wireless. Accordingly, the higher energy of the VUV radiation can be used to irradiate the wastewater immediately from the inner parts of the reactor without the microwaves being absorbed by air oxygen.

An MDEL device immersed in water also presents some problems in wastewater treatments, albeit non-insurmountable ones, with regard to the continuity of UV-light emission and most importantly self-ignition of the electrodeless lamp by the microwave radiation. This arises because when the MDEL is used in aqueous media having a high dielectric loss factor, most of the microwaves are absorbed by the dielectric medium. To compensate, the self-ignition of the MDEL device necessitates significantly higher applied microwave power levels. Nonetheless, there are methods by which the latter issue can be overcome. The first is to decrease the dielectric loss of the aqueous medium by heating this dielectric medium. For instance, the dielectric loss factor of water decreases by ca. 72% on increasing the temperature of the water from 22 °C to 99 °C [3]. Unfortunately, such a rise of temperature will be unsuitable for any scale-up methodology to treat large volumes of wastewaters. As such, in some of our studies we investigated several methods to achieve significant performance gain of the MDEL devices. The *first method* to overcome the high voltages needed to trigger the MDEL devices, when immersed in wastewaters, involves the use of a tungsten trigger connected to the MDEL devices. Self-ignition of such an MDEL system has been shown to be improved remarkably by the tungsten-trigger at relatively lower microwave power levels [4]. The *second method* involves a newly designed metallic condensing cone (equivalent to an optical lens) connected to the wave guide, which concentrates the microwave radiation onto the target medium [5].

Perfluoroalkylated pollutants have been detected globally in wildlife [6], including species in such remote areas as the Arctic [7]. Stable and chemically inert (C–F bond energy: 568 kJ mol^{-1} or 5.882 eV making it one of the thermodynamically strongest bond known), these perfluoroalkylated chemicals repel water and oil, reduce surface tension better than other surfactants, and work well under harsh conditions [8]. PFOA is used to make fluoropolymers that can release the precursor by transformation of some fluorinated telomers. In this regard, manufactured products may contain trace amounts of PFOA and other related perfluorinated chemicals as impurities [9]. PFOA exerts genotoxic effects on HepG2 cells, as a consequence of oxidative DNA damage induced by intracellular reactive oxygen species (ROS), especially hydrogen peroxide [10].

In 2006, eight major companies and EPA launched a stewardship program in which the industry was committed (i) to reduce global manufacturing emissions and product content of PFOA and related chemicals by 95% by 2010, and (ii) to work toward total elimination of emissions and product contents within the 2010–2015 period. PFOA does not degrade naturally, and even with the use of advanced oxidation processes, its decomposition is rather difficult; as well, pyrolysis of PFOA necessitates relatively high temperatures [11]. Accordingly, a methodology that operates under milder conditions would be desirable for the decomposition and defluorination of PFOA and other perfluoroalkyls. Germane to this effort, Hori and coworkers reported the photodegradation of PFOA in aqueous media with and without a photocatalytic heteropolyacid ($H_3PW_{12}O_{40}\cdot H_2O$) [12] or in the presence of persulfate ($S_2O_8{}^{2-}$) [13]. In addition, the photoassisted defluorination and degradation of PFOA in aqueous media can also occur by direct photolysis with 185-nm and/or 254-nm light from a low-pressure mercury lamp [14]. The extent of defluorination of PFOA achieved by the latter method was 17% with the 185-nm VUV light after a 2-h irradiation period.

An article by Vecitis et al. [15] reviewed pre-2008 studies on degradation technologies of PFOA and related perfluorocarbons in terms of kinetics, mechanisms, energetic costs, and applicability; optimal PFOA treatment seems to depend on concentration, background organics and metal concentration, as well as the irradiation time. Since then, several recent studies [16–23] have taken up the degradation of PFOA, owing to its relevance as an important contaminant. For instance, Wang et al. [16] found that 47% of PFOA decomposed photochemically accompanied by 15% defluorination in the presence of Fe^{3+} after 4 h of 254-nm UV irradiation; the degradation and defluorination greatly increased to 80 and 48%, respectively, on increasing the Fe^{3+} concentration. Sonication-assisted photocatalysis with TiO_2 at near neutral pH and irradiation for 8 h with 254 nm UV light caused ca. 64% of PFOA to decompose; extent of defluorination was ca. 5%, somewhat lower than expected because of the likely adsorption of F^- ions onto the TiO_2 surface [17]. By contrast, using an Fe/Nb co-doped TiO_2 system, ca. 14% PFOA degraded in aqueous media at pH 4 after 3 h irradiation with 200–600 nm UV/visible light [19], whereas UV irradiation with 254 nm light of an anoxic (N_2 atmosphere) β-Ga_2O_3 dispersion for 3 h led to 37% of PFOA being photodegraded, accompanied by ca. 16% defluorination [18]. Cao et al. [20] used two Hg lamps, one emitting 254 nm radiation (UVC) and the other emitting both 254 and 185 nm light (VUV), to decompose an air-equilibrated solution of PFOA with the VUV radiation for 2 h (87% degradation and 25% defluorination) while it decomposed poorly under UVC light irradiation (9% and ca. 5%, respectively). Addition of $IO_4{}^-$ ions significantly increased the extent of decomposition and defluorination of PFOA when irradiated with UVC light for 2 h (ca. 70% and ~18%, respectively), whereas the presence of periodate decreased both processes under VUV irradiation to ca. 60% degradation and ~13% defluorination. A later study [23] showed that PFOA photolysis was slight with 254 nm light irradiation under anoxic conditions (N_2-purged), whereas significant decomposition of PFOA obtained on addition of $IO_4{}^-$; however, in the presence of O_2 the decomposition of PFOA decreased, whereas for the UV/TiO_2/$IO_4{}^-$ system, the extent of PFOA degradation was 54%, i.e. 15% lower than that observed for the UV/$IO_4{}^-$ system. Microwave-hydrothermal decomposition of perfluorooctanoic acid by persulfate oxidation activated by zero-valent iron at 90 °C for 2 h caused about 68% of PFOA to be decomposed and ca. 23% to be defluorinated [21]. Decomposition of perfluorooctanoic acid in aqueous phase in the presence of KI under anaerobic conditions with 254 nm irradiation at ambient temperature and pH 9 confirmed 98% defluorination after 14 h of UV irradiation of a PFOA/KI/N_2 system [22], whereas in the presence of oxygen (PFOA/KI/O_2 system) the extent of defluorination was only ca. 5%; no defluorination occurred in the irradiated PFOA/N_2 system, whereas in the presence of persulfate (PFOA/$S_2O_8{}^{2-}$) only ca. 20% of PFOA was defluorinated.

It is clear from the above that with substantive irradiation times and by proper irradiation methodologies, PFOA can be decomposed completely by VUV and UV irradiations. In the present study, we have improved the characteristic features of MDELs using 20 small grain-shaped MDELs, henceforth referred to as granulated MDELs (i.e. MDGELs) and have assessed their performance by examining the self-lighting efficiency and the extent and the dynamics of the photodecomposition/-defluorination of perfluorooctanoic

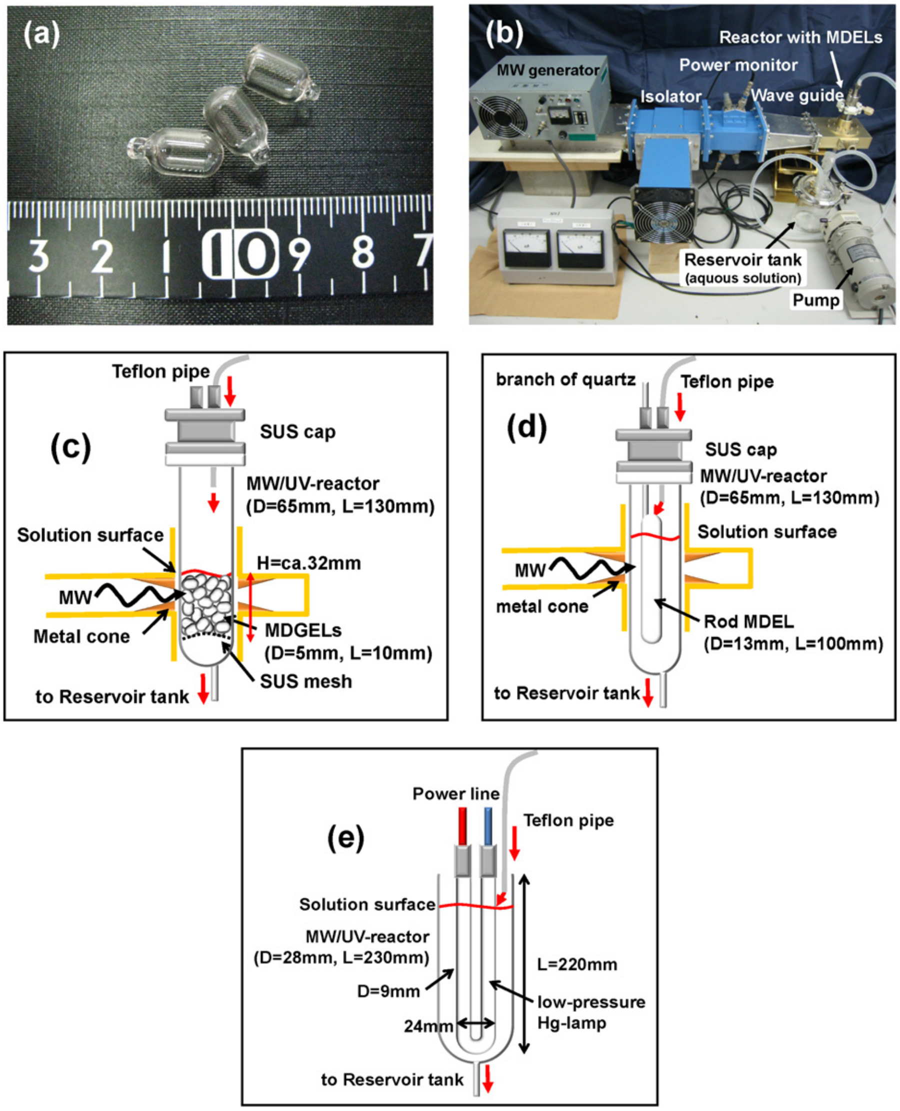


Fig. 1. (a) Photograph of the MDGELs and (b) the global experimental setup showing the MDEL device placed in a single mode microwave apparatus. Sketch of the location of the (c) MDGELs setup and (d) rod-shaped MDEL setup inside the MW/Photo reactor and the waveguide with the metallic condensing cone to concentrate the microwaves; (e) sketch of the location of the U-shaped 24-W low-pressure Hg lamp in the photoreactor.

acid (PFOA), heptafluorobutyric acid (HFBA) and trifluoroacetic acid (TFA), which we used to represent perfluoroalkylated contaminants in aqueous media, i.e. as model contaminated wastewaters. Major attention was expended on the perfluorooctanoic acid, as the other two substrates were intermediates during the degradation of PFOA.

2. Experimental setup

2.1. Chemical reagents and analytical procedures

Purity grade trifluoroacetic acid (TFA; CF_3COOH; Wako Pure Chemicals Industries, Ltd.), heptafluorobutyric acid (HFBA; C_3F_7COOH; Aldrich Chemical Co.) and perfluorooctanoic acid (PFOA; $C_7F_{15}COOH$; Wako Pure Chemicals Industries, Ltd.) were used as received and as the perfluoroalkylated contaminants of our model wastewaters.

The concentration of F^- ions from the photoassisted defluorination of the fluorinated substrates was assayed with a JASCO ion chromatograph equipped with a CD-5 conductivity detector and with a I-524 anion column using a mixed solution of phthalic acid (2.5 mM) and tris-(hydroxymethyl)aminomethane (2.3 mM) as the eluent (adjusted to pH 4). The intermediates were identified by direct injection into the mass spectral detector of an Agilent Technologies 1100 LC-MSD (electrospray ionization: API-ESI) system operated in the negative ion mode; capillary voltage was 2800 V. The eluent was a solution of acetonitrile/water (1:1 ratio, v/v). Note that the LC column was not used in this study. The flow rate of the sheath of heated dry nitrogen gas (heater temperature, 300 °C) was maintained at 10 L min^{-1}; gas pressure was 40 psi. The spectrometer was scanned from $m/z = 50$ to 800 at 0.3 mL min^{-1} for recording the mass spectra.

2.2. Preparation of the MDEL photolytic system

The microwave discharge granulated electrodeless lamps (MDGELs) were fabricated using vacuum-UV transparent synthetic quartz as the envelope and a mixture of Hg and Ar as the gas-fills. Dimensions of the devices were 10 mm (length) by 5 mm (external diameter) (see Fig. 1a). Subsequent to evacuating the MDEL quartz envelope to 133×10^{-7} Pa, the system was purged with argon gas (133×10^{-3} Pa) after which a small quantity of liquid mercury was added.

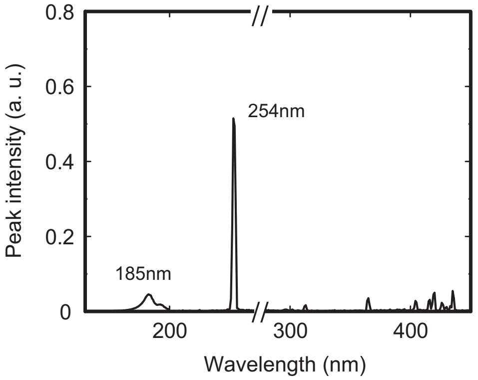


Fig. 2. Vacuum-UV, UV, and visible wavelengths emitted by the granulated MDGELs under microwave irradiation (near-IR wavelengths not shown).

Continuous microwave irradiation was obtained using a Hitachi Kyowa Engineering System microwave generator (frequency, 2.45 GHz; maximal power, 800 W), an isolator, a power monitor and a short-circuit plunger (Fig. 1b). The 300-mL air-equilibrated aqueous solutions of TFA, HFBA and PFOA (0.10 mM) were circulated with a peristaltic pump through the multipass MW/Photo reactor containing the MDGELs (20 pieces) at a flow rate of 600 mL min^{-1} (Fig. 1c). The MW/Photo reactor was sealed using a stainless used steel (SUS) cap with a silicone O-ring. The silicone tubing (internal diameter, 5 mm) was connected to the MW/Photo reactor and to the reservoir tank containing the aqueous perfluoroalkyl contaminated solutions. The Teflon pipe (internal diameter, 2 mm) was fixed to the SUS cap of the MW/Photo reactor. The circulated solution was cooled in the reservoir tank by an ice bath. The concentrated microwaves emanating from the wave guide and the condensing metallic cone were used to irradiate the MW/Photo reactor. The optimal setup of metallic cones in the wave guide has been reported in an earlier study [5]. The SUS mesh was positioned at the bottom of the MW/Photo reactor so as to prevent the MDGELs from blocking the flow of the solution. A rod-shaped MDEL was used as the conventional MDEL to compare the MDGEL system (Fig. 1d); its dimensions were 130 mm (length) × 65 mm (external diameter) and enclosed a gas-fill mixture identical to the gas-fill used in the MDGELs. The rod-shaped MDEL was connected with a quartz branch to the SUS cap [5]. A U-shaped low-pressure electrode mercury lamp (24 W; Wako Rika Co. Ltd.; 220 mm (length) × 9 mm (external diameter)) was also used to compare the photoassisted defluorination of the PFOA contaminant to the defluorination occurring with the MDGEL system. The Hg lamp was positioned in the photoreactor as illustrated in Fig. 1e; the light wavelengths emitted by the lamp were 185 nm and 254 nm (intensity ratio, 1:9) according to the data sheet reported by the manufacturer.

3. Results and discussion

3.1. Performance evaluation of the characteristic features of the MDGELs

The optimal amount of mercury and argon gas in the MDGELs exposed to microwave irradiation was obtained by examining the spectral peak intensities of the vacuum-UV (VUV), UV and visible wavelengths (Fig. 2). The spectral features of the emitted VUV/UV radiation were recorded with a JASCO VUV-201 spectrophotometer (130–260 nm), whereas the ultraviolet, visible and near-infrared wavelength spectral outputs of the MDGELs were monitored using a Fastevert S-2400 UV spectrophotometer (Soma Optics Ltd.). Note that the spectral intensities observed from these two measurements were different. Accordingly, the spectra were synthesized by normalizing the various peak intensities to the intensity of the 280 nm wavelength for both sets of spectra. A 150-W microwave source was used to irradiate the MDGELs device positioned in the multimode microwave applicator. The emitted VUV light was attenuated by the ozone generated from the oxidation of atmospheric oxygen. However, this decrease in irradiance was minimized by purging the multimode applicator with nitrogen gas. The main peaks in the VUV and UV range were 185 nm (6.7 eV) and 254 nm (4.9 eV), respectively. These peaks are similar to the wavelengths emitted by the rod-shaped MDEL [5] and by the Hg lamp in the UV region.

The microwave power consumption necessary to ignite the 20 MDGELs in the MW/Photo reactor was investigated and compared with the power required for the rod-shaped MDEL using circulated pure water with the experimental setup of Fig. 1b. About 80 W was necessary to light the MDGELs, whereas 160-W microwaves were necessary to achieve a stable ignition/lighting of the rod-shaped MDEL. Variation between the power levels is likely due to three reasons. (i) *First*, the 20 MDGELs were packed in the reactor (Fig. 1c) in such a way that the microwaves efficiently irradiated all the MDGELs. By contrast, the rod-shaped MDEL did not completely pack the space in the reactor (Fig. 1d) so that the microwaves irradiated the MDEL and were absorbed by the aqueous medium. (ii) *Second*, the reactions among the filler gases (Hg and Ar) in the MDGELs and the MDEL, summarized by reactions (1)–(4) [24], indicate that under microwave irradiation an accelerated electron collides with a gaseous Ar atom and yields an excited argon atom, Ar^*, formed through the cationic Ar^+ intermediate:

$$e^- + \text{MW} \rightarrow e^-(\text{accelerated}) \quad (1)$$

$$e^-(\text{accelerated}) + \text{Ar} \rightarrow \text{Ar}^+ \rightarrow \text{Ar}^* \quad (2)$$

$$\text{Ar}^* + \text{Hg} \rightarrow \text{Hg}^* + \text{Ar} \quad (3)$$

$$\text{Hg}^* \rightarrow \text{Hg} + h\nu \quad (4)$$

Subsequently, energy transfer from Ar^* to Hg gas atoms ensues a Penning effect, yielding excited Hg^* atoms that ultimately emit the wavelengths observed in Fig. 2. The surface temperature of the rod-shaped MDEL was not stabilized by the circulated water from the top-end of the reactor. Cooling the MDEL surface controls the gasification of the mercury in the MDEL device. The liquefied mercury is not excited by the Ar^* species, so that a greater microwave power input of 160 W was necessary to stabilize the lighting of the rod-shaped MDEL. (iii) *Third*, the power consumption of the microwaves per unit volume of one of the MDGELs (ca. 0.33 cm^3) was 0.004 W cm^{-3}, whereas for the rod-shaped MDEL (volume, ca. 12 cm^3) the estimated power consumption was ca. 0.08 W cm^{-3}, nearly 20-fold greater for the latter. We suspected that when one of the MDGELs in the reactor is ignited under microwave irradiation it may become a trigger for the argon gas excitation in other MDGELs that did not ignite by the emitted VUV light from the ignited MDGEL. Accordingly, next we examined the possibility of a VUV/UV-assisted ignition of a MDEL device that was set up in the wave guide without the metal cone; under these conditions, 600-W microwaves were needed to ignite the device. On the other hand, using the VUV/UV light emitted by a low-pressure electrode Hg lamp that irradiated the MDEL device through the five holes ($D = 2$ mm) on the wave guide side necessitated only 552 W of microwave power to ignite the MDEL device. Thus, an energy saving of about 8% by this VUV/UV light-assisted process is achievable. Clearly, the microwave irradiation efficiency can be improved by filling the reactor with the MDGELs that can lead to a chain ignition of other MDGELs through the assistance of the emitted VUV/UV light.

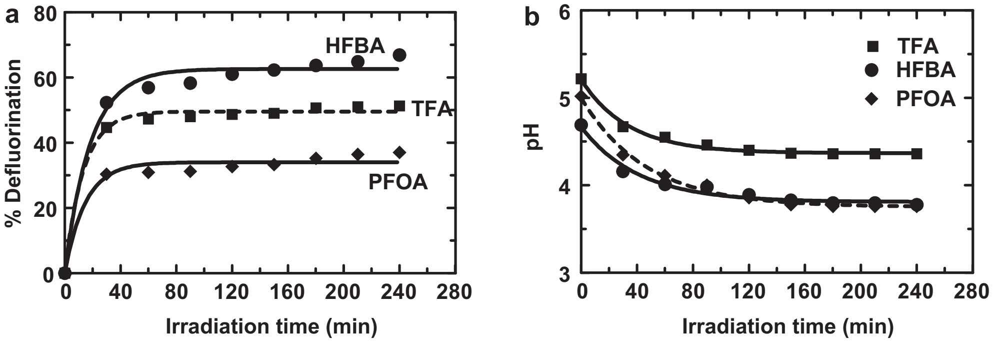


Fig. 3. (a) Percent defluorination and (b) pH changes during the photoassisted defluorination of trifluoroacetic acid (TFA), heptafluorobutyric acid (HFBA) and perfluorooctanoic acid (PFOA) in aqueous solutions with the single rod-shaped MDEL device in the MW/Photo reactor; initial concentrations of the perfluoroalkylated acids, 0.10 mM.

3.2. Photoassisted defluorination of TFA, HFBA and PFOA contaminants in aqueous media

The extent of defluorination and changes of pH during the photoassisted defluorination of trifluoroacetic acid (TFA), heptafluorobutyric acid (HFBA) and perfluorooctanoic acid (PFOA) in aqueous solutions (0.10 mM) was first examined using the rod-shaped MDEL system; results are displayed in Fig. 3. After 30 min of irradiation, the defluorination levels were 45% for TFA, 53% for HFBA and 30% for PFOA, after which defluorination slowed considerably upon further microwave irradiation leveling off at 51% (TFA), 67% (HFBA), and 37% (PFOA) for an irradiation period of 240 min. The pHs of the initial aqueous solutions were 5.2 (TFA), 4.7 (HFBA), and 5.0 (PFOA), which decreased to 4.4, 3.8 and 3.8, respectively, after this irradiation period. The corresponding dynamics of defluorination (up to 240 min) were 7.5×10^{-2} min^{-1} (TFA), 5.5×10^{-2} min^{-1} (HFBA) and 6.8×10^{-2} min^{-1} (PFOA). To the extent that the initial pHs could have influenced the defluorination dynamics, we next examined the dynamics of defluorination of all three perfluoroalkylated acids in alkaline media at an initial pH of 10. Note that PFOA, HFBA and TFA are strong acids (p*K*a of PFOA = −0.5; p*K*a of TFA = −0.3, and p*K*a of HFBA ≈ 0.4 [25]) and are highly soluble in water. Accordingly, at the pHs of the aqueous media used in the present study (pH = 4.7–5.2 and pH = 10), these perfluoroalkylated acids exist in their anionic form. As decomposition and defluorination progressed, the pH of the aqueous media decreased from pH = 10 of the initial solution to pH ca. 4.5 indicating the formation of acids in the degradation/defluorination processes.

The time profiles of the photoassisted defluorination of the perfluoroalkyl acids in aqueous solutions adjusted to pH = 10 are illustrated in Fig. 4a for the rod-shaped MDEL device as the irradiation source and in Fig. 4b for the 20 MDGELs as the light source. With the MDEL light source, defluorination of TFA and HFBA was 100% complete within 120–135 min of irradiation, whereas the extent of defluorination of PFOA was only ca. 80% after 200 min. The initial pH 10 of the aqueous solutions decreased to ca. pH = 4 after an irradiation period of 150 min. With the MDGEL system, defluorination of TFA and HFBA was complete within 105 min of irradiation, whereas 100% defluorination of PFOA necessitated ca. 400 min of irradiation. The initial pH of 10 of the aqueous solutions in the MDGELs reactor decreased to about 4.5 after ca. 40 min of irradiation.

The corresponding dynamics for the photoassisted defluorination of TFA, HFBA and PFOA in aqueous media at an initial pH of 10 are reported in Table 1. A significant difference in the defluorination dynamics was observed for TFA and HFBA between the rod-shaped MDEL and the 20 MDGELs. By contrast, the defluorination dynamics for the PFOA substrate was independent of the light source used, namely the rod-shaped MDEL versus the 20 MDGELs. Interestingly, however, the dynamics for the rod-shaped light source correlate well with the carbon chain length and with the number of C–F bonds in the three substrates as illustrated in Fig. 5. The limited data preclude offering an explanation as to why the data for the MDGELs (Table 1) do not correlate as well.

Estimated on the basis of per unit surface area of the rod-shaped MDEL (ca. 35.6 cm^2) and the twenty MDGELs (33.3 cm^2; one MDGEL, area ca. 1.66 cm^2), the defluorination dynamics paralleled similar observations with the rates for TFA and HFBA using the MDGEL system being about 1.8–2.0 times greater than with the rod-shaped MDEL system. This was not unexpected, as in the case of the MDGEL system the aqueous solutions were irradiated efficiently while passing through the space between the MDGELs inside the MW/Photo reactor. Curiously, however, the photoassisted defluorination of PFOA was not enhanced by the MDGEL system. With regard to the defluorination dynamics estimated on a per-unit of

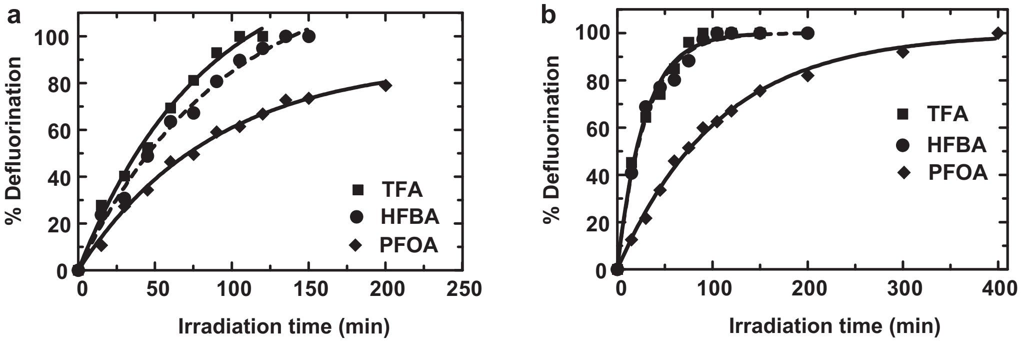


Fig. 4. Time profiles of the extent of the photoassisted defluorination of trifluoroacetic acid (TFA), heptafluorobutyric acid (HFBA) and perfluorooctanoic acid (PFOA) in aqueous solutions at an initial pH of 10 (initial concentrations of the perfluoroalkylated acids, 0.10 mM); (a) in the photoreactor that used the single rod-shaped MDEL system, and (b) in the photoreactor containing the 20 MDGEL system.

Table 1

Dynamics of the photoassisted defluorination of trifluoroacetic acid (TFA), heptafluorobutyric acid (HFBA) and perfluorooctanoic acid (PFOA) in air-equilibrated aqueous solutions (0.10 mM; pH = 10) under VUV and UV irradiation using the rod-shaped MDEL and the 20 MDGELs, together with defluorination rates per unit surface area of the lamp(s) and defluorination rates per unit applied MW electric power. The surface areas of the lamps immersed in the solutions were: rod-shaped MDEL, 35.6 cm^2; the 20 MDGELs, 33.3 cm^2; U-shaped Hg lamp, 115.2 cm^2. Microwave power levels used were: rod-shaped MDEL, 160 W; MDGELs, 80 W.

Dynamics	Rod-shaped MDEL			20 MDGELs			Low-pressure electrode Hg lamp (24 W)
	TFA	HFBA	PFOA	TFA	HFBA	PFOA	PFOA
Defluorination (10^{-2} min^{-1})	2.2	1.8	0.93	3.5	3.4	0.94	0.067
Defluorination per unit surface area of lamp (10^{-2} min^{-1} cm^{-2})	0.062	0.051	0.026	0.11	0.10	0.028	0.00058
Defluorination per unit of applied MW electric power (10^{-2} min^{-1} W^{-1})	0.014	0.011	0.0058	0.044	0.042	0.012	0.0028

microwave power consumed (rod-shaped MDEL, 160 W; twenty MDGELs, 80 W), defluorination was 3–4 times faster for TFA and HFBA with the MDGEL system than with the MDEL device. On this basis, the dynamics of defluorination of the PFOA substrate was twofold faster with the MDGELs. Overall, significant energy saving can thus be achieved on using the MDGEL system.

For comparison purposes we also examined the defluorination of PFOA in aqueous media with the 24-W low-pressure electrode Hg lamp shown in Fig. 1e setup. The 300-mL aqueous PFOA solution (0.10 mM, pH = 10) was likewise circulated in the MW/Photo reactor. The extent of defluorination under UV irradiation (alone) was 3% after 50 min, 6% after 100 min, and 10% after 150 min yielding a defluorination rate of ca. 0.067 min^{-1}, significantly slower than the dynamics encountered with the MDGEL and MDEL methods but significantly faster than the defluorination rate for PFOA ($k = 0.0016$ min^{-1}; pH = 3.7) reported by Chen et al. [14] who used a 15-W Hg lamp. Defluorination rate per unit surface area of this low-pressure electrode Hg lamp (ca. 115 cm^2) was 0.00058 min^{-1} cm^{-2}, and per unit applied electric power (24 W) it was 0.0028 min^{-1} W^{-1}. Clearly, the MDGELs light source offers significant advantages over the Hg lamp for the photoassisted defluorination of PFOA in aqueous media with regard to both surface area and power consumption.

3.3. Plausible pathway for the photoassisted defluorination of perfluorooctanoic acid (PFOA)

The electrospray mass spectra recorded in the negative ion mode (M^-) in the photoassisted defluorination of PFOA in aqueous media (molecular mass, 414 g mol^{-1}; 0.10 mM; initial pH = 10) was examined for the samples of Fig. 4b for irradiation times of 0, 30 and 90 min using the twenty MDGEL system and are displayed in Fig. 6; the mass peak for PFOA was seen at $m/z = 413$ (Fig. 6a). At 0 time, the LC–MS spectrum also included a mass peak at $m/z = 369$ that we attribute to an impurity present in the initial aqueous solution of PFOA, namely $CF_3(CF_2)_5CF_2H$, that could have been formed by decarboxylation of PFOA during electrospray ionization in the LC–MS apparatus. Other LC–MS spectral intermediates were seen at $m/z = 363$, 313, 263, 213, 163 and 113 subsequent to the 30- and

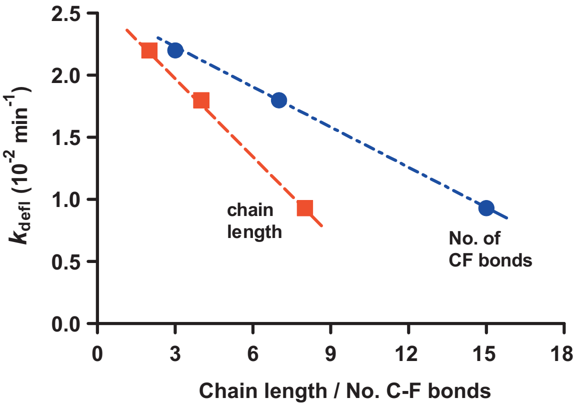


Fig. 5. Kinetic data correlation with the carbon chain length and with the number of C–F bonds in PFOA, HFBA and TFA systems at pH 10 when the latter were irradiated with the rod-shaped light source.

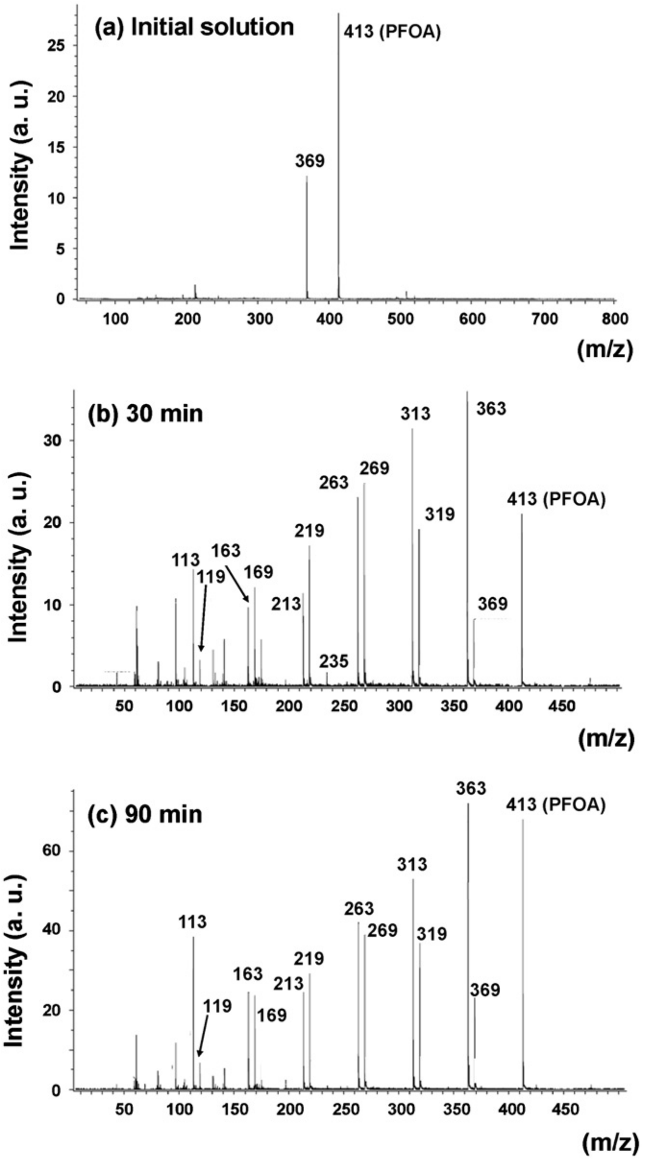
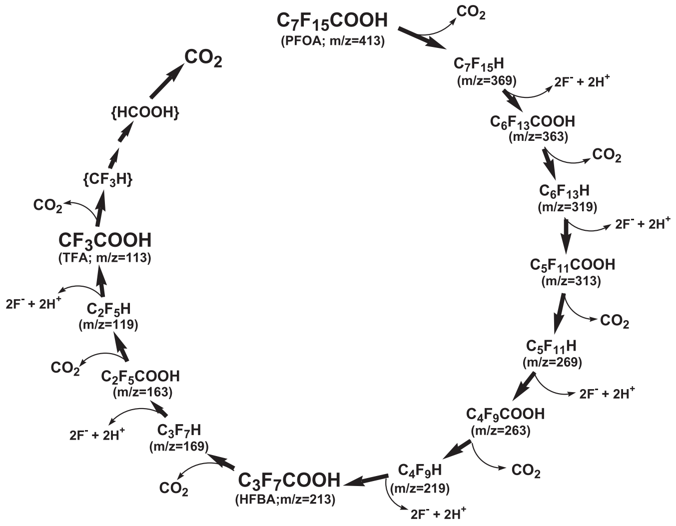


Fig. 6. Electrospray mass spectra recorded in the negative-ion mode (M^-) during the photoassisted defluorination of PFOA in the circulated aqueous media by the 20 MDGEL system for 0, 30 and 90 min of irradiation.



Scheme 1. Suggested path of the photoassisted decomposition and defluorination of PFOA using the twenty MDGEL system as the light source. LC–mass spectra were recorded in the negative-ion mode (M^-). Note that although the perfluorinated acids existed in their anionic form in solution, we have followed the practice of others in the scheme showing the protonated form.

90-min irradiation periods (see Fig. 6b and c). The mass peaks correspond to species obtained from the sequential loss of $–CF_2$ units during the photoassisted decomposition of the PFOA substrate. The mass peaks at $m/z = 319, 269, 219, 169$, and 119 are the corresponding intermediates produced by loss of CO_2 through prior oxidation of the perfluoroalkylated species yielding perfluoroalkylated acids followed by decarboxylation.

Thus a plausible path for the photoassisted decomposition and defluorination of the PFOA contaminant in aqueous media can now be described (Scheme 1) on the basis of the above electrospray mass spectral results. In this regard, Chen et al. [14] showed that photolysis of PFOA with a light source emitting both 185 nm and 254 nm wavelengths was much faster compared with photolysis with 254 nm radiation alone. Thus we infer that the 185-nm wavelength emitted by the MDGELs was chiefly responsible for the photoassisted decomposition and defluorination of PFOA in aqueous media. These authors also showed that PFOA has an absorption band at ca. 190 nm so that the 185-nm wavelength can cause formation of the excited state PFOA* followed by cleavage of the $CF_3(CF_2)_5CF_2–$ and –COOH bond to yield the $^{\bullet}C_7F_{15}$ and $^{\bullet}COOH$ radicals (reaction (5)), with the former subsequently reacting with water to yield the intermediate $C_6F_{13}COOH$ (reaction (6)) [14], which would undergo further decarboxylation to lower fluorinated intermediates to ultimately complete decomposition. Subsequently, the $^{\bullet}COOH$ radical is converted into carbon dioxide (reaction (7)). Note that no oxalic acid was detected in the mass spectra that might have resulted from dimerization of this radical.

$$C_7F_{15}COOH \overset{185\,nm}{\longrightarrow} {}^{\bullet}C_7F_{15} + {}^{\bullet}COOH \qquad (5)$$

$$^{\bullet}C_7F_{15} + 2H_2O \rightarrow C_6F_{13}COOH + 2F^- + 2H^+ + H^{\bullet} \qquad (6)$$

$$^{\bullet}COOH \rightarrow CO_2 + H^{\bullet} \qquad (7)$$

The 185-nm wavelength also causes the photolysis of water yielding the reactive oxygen species $^{\bullet}OH$ radical, the $H^{\bullet}$ radical and the aqueous electron, e^-. However, it is unlikely that the $^{\bullet}OH$ radical will oxidize the perfluoroalkylated acids through electron transfer as this would involve significant reorganizational energies in transforming $^{\bullet}OH$ radicals into OH^- ions in aqueous media [26]. Alternatively, the perfluoroalkyl radical $^{\bullet}C_7F_{15}$ may react with the $^{\bullet}OH$ radical and molecular oxygen to form a peroxyl radical followed by $C_7F_{15}OH$, which then undergoes HF elimination and forms the acid fluoride $C_6F_{13}COF$ [20]. Subsequent hydrolysis of the latter yields $C_6F_{13}COOH$ that undergoes further photoreaction producing $C_5F_{11}COOH$ and so on until complete defluorination and degradation have been achieved. Moreover, we cannot preclude an electron reductive process. Our data infer continuous decarboxylation (loss of CO_2) and loss of $–CF_2$ units from the perfluorinated alkoxy intermediates. Small amounts of CF_3H and C_2F_6 were also detected as reaction products together with acetic acid and formic acid by Qu et al. [22] in the photoreductive defluorination of PFOA in water. In addition, Scheme 1 explains the drop of the initial pHs during the photodegradation process.

4. Concluding remarks

This study has demonstrated that self-ignition of the MDGELs light source immersed in an aqueous solution contaminated with perfluoroalkylated acids can occur at low microwave power levels (80 W), thereby demonstrating some advantages of miniaturizing MDELs and packing the photoreactor with these mini-MDGEL systems. The penetration depth of the 185 nm radiation in water is shorter than for the 254 nm wavelength, and the 185-nm light intensity decreases by ca. 50% from the surface of the water at a distance of 2 mm [27]. Accordingly, the photodegradation of the perfluoroalkyl contaminants by the VUV light of 185 nm likely takes place near or at the lamp surface. An advantage of miniaturization of MDEL systems is the greater surface area achieved for light irradiation of the contaminated model wastewaters even in a small flow-through reactor. The greater efficiency of the MDGEL system in the photoassisted decomposition and accompanying defluorination of three perfluoroalkylated acid contaminants has been demonstrated in this study and intermediates have been identified by LC–MS techniques that allowed us to infer a path for the transformation of the highly perfluorinated carboxylic acid (PFOA) to complete defluorination and decomposition to carbon dioxide and fluoride ions.

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