Immobilization of perfluorooctane sulfonate on modified natural materials: Remediation strategy for contaminated soils

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Abstract
Perfluorinated compounds such as perfluorooctane sulfonate (PFOS) are distributed globally in many wildlife species, as well as ocean waters and even in remote regions far from sources. Limited data available indicate that soil and sediments could act as a major sink for PFOS in the environment. The present work was undertaken to develop a cost effective remediation strategy for the soils impacted with perfluorinated compounds. To this endeavor, a naturally occurring material was modified by our research group and was named as MatCARE^{TM} (patent pending). Results obtained show that MatCARE^{TM} has a very high sorption capacity for PFOS (50 mg PFOS/g MatCARE^{TM}). A treatability study under laboratory conditions was conducted to determine the optimum dosage rate of MatCARE^{TM} for the efficient immobilization of PFOS from contaminated soils over a period of 90 days at 25 and 37^{o}C temperatures. The results showed that total immobilization of PFOS occurred at a dosage of 100g/kg of MatCARE in most of the contaminated soils varying in PFOS concentration in the range of 1.83 to 74.38 mg/kg soil.

Key Words
Perfluorooctane sulfonate, soil, contamination, immobilization, MatCARE^{TM}.

Introduction
Perfluorinated compounds (PFCs) manufactured since the 1960s have a wide range of consumer and industrial applications like coatings for textiles, paper packaging products, upholstery, carpeting, insecticides, fabric treatments, paper coatings, corrosion inhibitors, shampoos, anti-static agents, and in the formulations of aqueous fire fighting foams (AFFFs). Perfluorinated surfactants, including perfluorooctane sulfonate, $C_8F_{17}SO_3^-$ (PFOS) have been recently declared as pollutants of environmental concern. The strong carbon-fluorine (C-F) bond of these compounds impart stability to the molecules enabling them to become resistant to thermal, chemical, and biological degradation. Inevitably they have been found to bioaccumualate in higher trophic level organisms through the food chain (Tomy *et al.* 2004). The detection of PFOS in wildlife even in and around the polar regions indicate the long range transport and global distribution of PFOS and its precursors (Moody *et al.* 2003).

AFFFs containing perfluorinated compunds like PFOS have proven to possess very high capacity to fight class B fires or fires from hydrocarbon burning and thus they have been used routinely by civilian and military fire fighters. Historically, effluents from AFFF fire-fighting activities were not pre-treated prior to their discharge in the environment. As a result they have impacted water bodies and soils of a large number of fire training areas including those located in Australia. The important roles of soils and sediments in determining the environmental fate of hydrophobic organic contaminants have long been understood (Luthy *et al.* 1997). Hydrophobic contaminants such as perfluorinated compounds including PFOS are expected to partition from the water column into organic matter rich sediments and soil particles due to their propensity to adsorb to organic carbon thus causing soils to be the ultimate sink for these compounds (Higgins *et al.* 2005, Nakata *et al.* 2006). Application of conventional treatment techniques such as soil washing for remediating perfluorinated compounds from impacted soils is restricted by technical and/or economical constraints. Due to their strong stability, these compounds are also not amenable to biological treatments. Adsorption to suitable and inexpensive adsorbents could be considered a cost effective method for remediating sites contaminated with PFOS and its precursors. The present study was undertaken with the objective of remediating soils collected from fire training areas in Australia where AFFF formulations are used. With this aim, several natural materials were tested to ascertain the one best suited for the purpose of immobilizing PFOS. Subsequently, an attempt was made to optimize the dose at which the material needs to be applied to mitigate the adverse effects of the AFFF compounds.

Methods

Sorption experiments were conducted with three different naturally modified materials (adsorbents) to determine the one with the highest capacity to adsorb PFOS. The experiments were done by equilibrating each adsorbent with aqueous solutions of PFOS varying in the concentration range of 0 to 500 mg/L for 24 hrs. The solutions were then centrifuged, filtered and subsequently analyzed using HPLC-MS.

PFOS was quantified in the impacted soils using 1:1 ethyl acetate: methanol with 7% orthophosphoric acid as the extracting solvent. Also the physico-chemical properties (pH, organic carbon, anionic constituents) of the soils were assessed following standard procedures. Treatability studies were carried out by the addition of 'MatCARE^{TM}', the naturally modified material with the highest sorption capacity at the rate of 100g/kg to the naturally impacted soils and also in some spiked soils. The treated soils were incubated at 60% maximum water holding capacity in two temperature controlled rooms (25 and 37^{o}C) to observe the effect of temperature on the release characteristics of PFOS. The amounts of PFOS that became bioavailable, as determined by desorption, with time were determined after 0, 15, 30, 45 and 90 days.

Results

Adsorption study

Among the different natural materials (MatU, MatV, and MatCARE^{TM}) tested MatCARE^{TM} (Kambala and Naidu, 2009 Patent Pending) was found to adsorb PFOS at a considerably high level (50 mg/g). Figures 1 and 2 represent the Freundlich and Langmuir isotherms for MatCARE^{TM}.

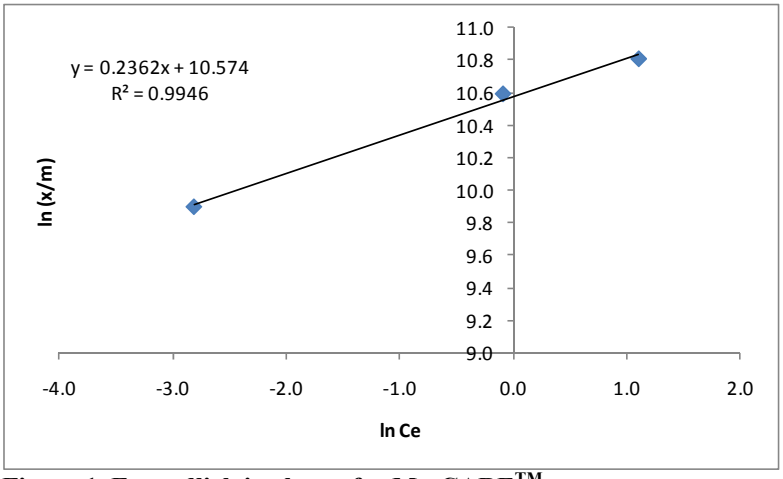

Figure 1. Freundlich isotherm for MatCARE^{TM}.

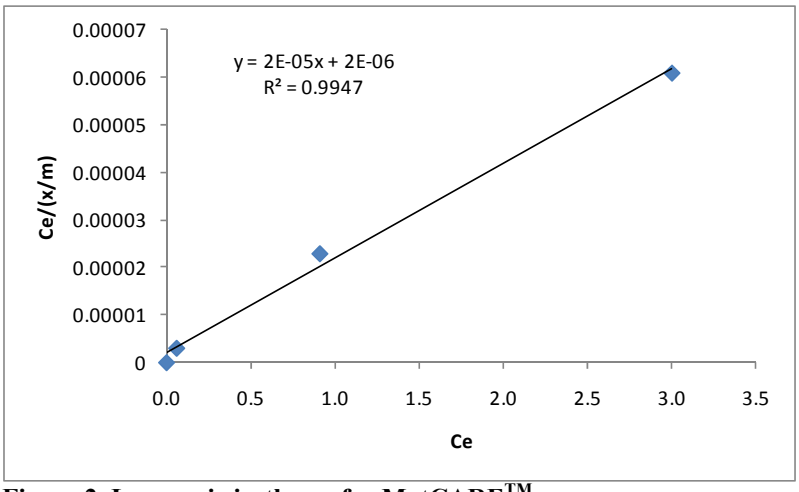

Figure 2. Langmuir isotherm for MatCARE^{TM}

Determination of physico-chemical properties of soil

Four different types of contaminated soils were collected from the impacted sites located in Darwin, Northern Territory, Australia. These soils varied in their physico-chemical properties as can be seen from the data presented in Table 1.

Table 1. Physico-chemical properties of the soil.

Soil	pH	DOC (mg/kg)	TOC (%)	Moisture content (%)
Tindal SS01	6.46	30.57	2.03	9.64
RBD	4.37	3.07	0.96	1.94
RBD (Moist)	5.90	32.22	1.63	24.56
Tindal FTA 064	8.10	4.55	0.29	3.02

Treatability studies

Results from the treatability study performed on the field contaminated soils show that the MatCARE^{TM} has a very high capacity to adsorb PFOS and hence to immobilize it. Only in a few cases, insignificant amount of desorption could be found during the entire 90 days incubation period. Figures 3(A) and (B) presents findings of desorption study at 25 and 37°C temperatures. Four soils (RBD, RBD moist, Tindal FTA064, and Tindal SS01) from the impacted areas were amended with MatCARE^{TM} at 100 g/kg dosage rate. While the untreated soils showed significant levels of bioavailable PFOS both at 25 and 37^{o}C temperatures as measured by desorption, MatCARE^{TM} treated soils showed zero or very low levels of bioavailable PFOS. The RBD soil with a residual concentration of 1.83 mg kg $^{-1}$ PFOS, showed no desorption during the entire 90 day period irrespective of the incubation temperatures (25°C and 37°C). Similar results can be found in case of the Tindal FTA064 soils, which had a PFOS concentration of 16.17 mg/kg. For these soils no release occurred even for the spiked samples with PFOS concentration of 102 and 116 mg/kg, respectively. In case of the RBD moist soil, which had a very high PFOS concentration (74.38 mg/kg), no release could be detected for the naturally contaminated field samples, but for the spiked ones containing 175 mg/kg PFOS, only 3.75 mg/kg PFOS was desorbed at 37°C after 90 day incubation period. The results are similar for the Tindal SS01 soil. While no release could be detected for the naturally contaminated soil with a PFOS concentration of 9.26 mg/kg, only 1.48 mg/kg release was observed in the case of the spiked samples with PFOS concentration of 100 mg/kg. However, no release of PFOS was detected even for the spiked RBD moist and Tindal SS01 soils incubated at 25°C.

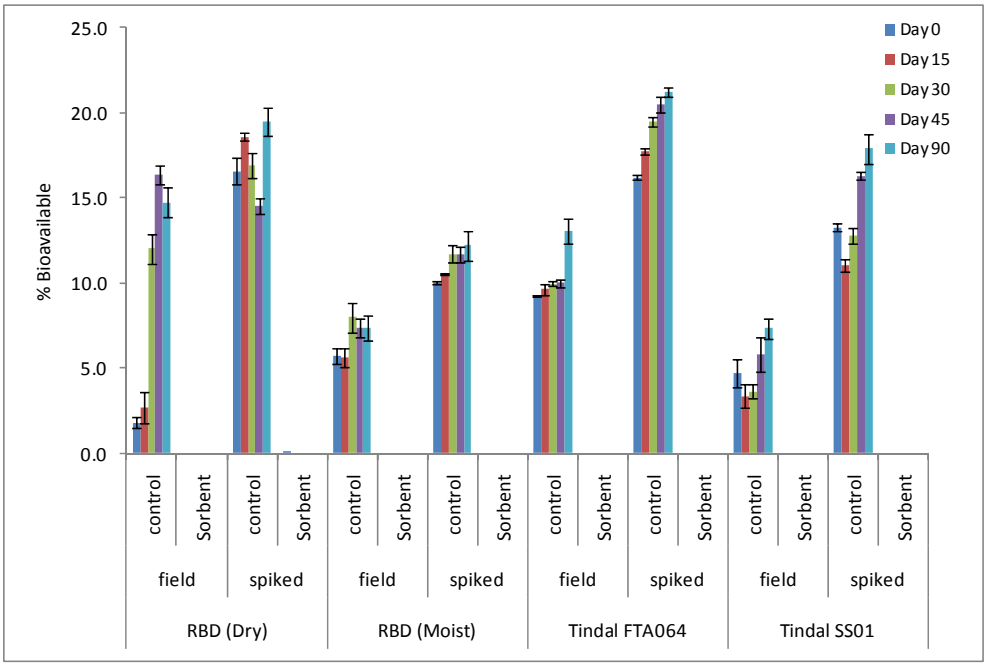

Figure 3A. Results of desorption study for four different field contaminated and spiked soils at 25^{o}C.

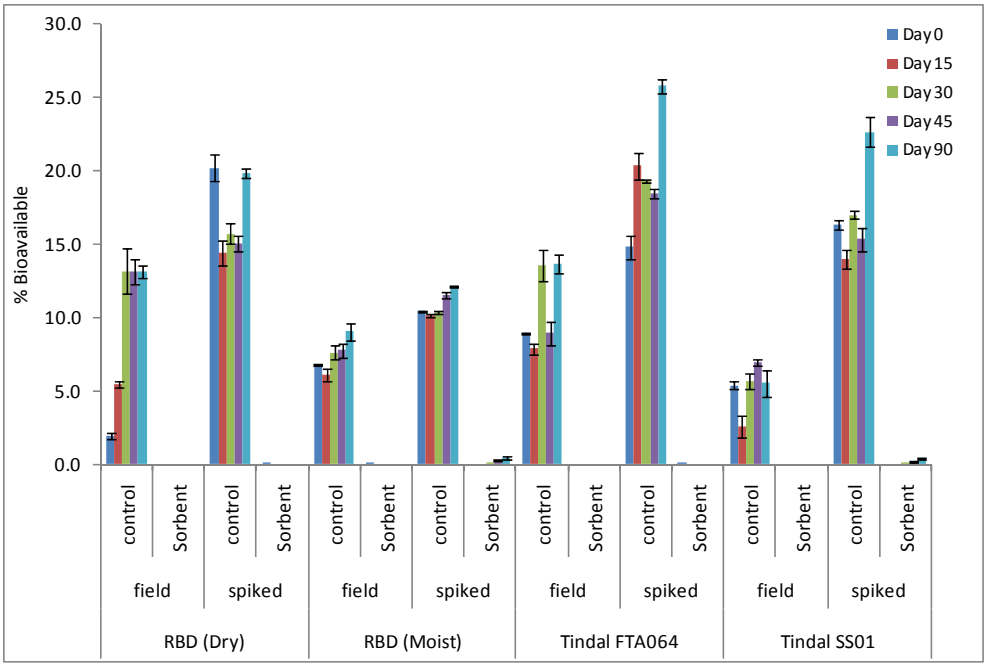

Figure 3B. Results of desorption study for four different field contaminated and spiked soils at 37°C.

Conclusions

It has long been recognized that the transfer of contaminants within the soil profile and their uptake by plants depend to a large extent on the bioavailability of these compounds. Our main strategy to remediate the fire training areas impacted with AFFF compounds was to reduce their bioavailability by adsorption to an inexpensive and nontoxic natural material. 'MatCARE^{TM}' developed by CRC CARE/CERAR laboratories was found to be a promising material to immobilize PFOS. Laboratory studies have shown potential outcomes for a field scale remediation trial.

Acknowledgements

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