First report on the environmental friendliness of OBS, an alternative to PFOS in fire-fighting foams and oil production agents in China

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Introduction

As required by the Stockholm Convention, all parties including China is now seeking for right alternatives to phase out PFOS and related chemicals in main applications. It's an important fact that most alternatives in current market are still organfluorine chemicals. As indicated in Madrid Statement, the environmental friendliness of these alternatives have aroused great concerns by many scientists [1]. For example, some short chain alternatives have been found to be of similar persistence, bioaccumulation or toxicity (PBT) to PFOS [2-5].

Sodium *p*-perfluorous nonenoxybenzene sulfonate (OBS, also known as "SPBS", CAS No.: 70829-87-7) was firstly synthesized in Japan and widely used in China since 1980s. It was mainly used in fluoroprotein foams and oil production agents. Recently, OBS has been detected in water samples from urban wastewater treatment plant (WWTP) and local rivers in oilfield area in North China [6]. However, there's no available data about its environment related properties. The present study is aiming at the investigation on the PBT properties of OBS, as well as its stability under typical advanced oxidation process (AOP). The results can be useful for understanding this alternative which has largely produced and widely used in China.

Materials and methods

OBS was obtained from 3F corporation (Shanghai, China) and prepared at concentration of 100 mg/L. H_2O_2 (30%) was obtained from Beijing Modern Eastern Fines Chemical Co. (China). The UV irradiation or UV/H_2O_2 experiment was performed in quartz glass tube contained 300 mL OBS solution in photochemical reactor (RPR200, Southern New England Ultraviolet (Rayonet) Co., USA). The tube was placed in the middle of the reactor and surrounded by four UV lamps (254 nm) at room temperature. The fluorine ion and sulfate ion were detected by ion chromatograph (Dionex ICS 2000, USA). OBS was determined by high-performance liquid chromatography (LC-20AT, Shimadzu, Japan) equipped with UV/VIS detector at 275 nm (SPD-20A, Shimadzu, Japan).

The persistence of OBS was assessed by Closed Bottle Test method of Organization for Economic Cooperation and Development (OECD) guidelines for testing of chemicals 301 D. The bioaccumulation of OBS and PFOS were all calculated by using EPI Suite v 4.11 (Arnos-Gobas BCF&BAF Methods), and Kow of OBS and PFOS were calculated by ECOSAR v1.10, both softwares are from US Environment Protection Agency. The toxicity of OBS was tested according to OECD guidelines for testing of chemicals 203 (Fish, Acute Toxicity Test). The UV and UV/H_2O_2 system were adopted to assess the stability of OBS under typical AOP.

Results and discussion

Persistence assessment Based on the OECD guideline 301D, the secondary effluent from a municipal wastewater treatment plant was adopted to inoculate in all testing solution. The BOD of OBS solution exerted after each time period was calculated by subtracting the oxygen depletion (mg O_2/L) of the inoculum blank from that exhibited by the test substance (Table 1). Calculate the biodegradation percentage by dividing the specific BOD by the specific ThOD, and the degradation efficiency were showed in Table 2. It was not surprising that OBS was non-readily degraded during 28 days, namely, it possess potential persistence when entering into the natural environment.

Table 1: Consumption of dissolved oxygen in closed BOD bottles during 28 days

Days	Blank（mg/L）			Reference group（mg/L）			OBS（mg/L）		
	Bottles1	Bottles2	Average	Bottles1	Bottles2	Average	Bottles1	Bottles2	Average
0	8.99	9.03	9.01	9.06	9.11	9.085	9.07	9.07	9.07
4	8.96	8.84	8.90	4.76	4.88	4.82	8.80	8.83	8.82
7	8.85	8.91	8.88	4.88	3.80	4.34	8.98	8.74	8.86
11	8.75	8.75	8.75	3.33	3.62	3.48	8.75	8.76	8.76
14	8.68	8.64	8.66	3.39	4.35	3.87	8.69	8.71	8.70
18	8.69	8.63	8.66	3.09	3.19	3.14	8.63	8.48	8.56
21	8.76	8.72	8.74	3.00	3.36	3.18	8.82	8.92	8.87
25	8.49	8.51	8.50	3.95	3.04	3.495	8.54	8.52	8.53
27	8.49	8.47	8.48	2.85	3.13	2.99	8.48	8.52	8.50
28	8.41	8.43	8.42	3.40	3.56	3.48	8.48	8.69	8.59

Table 2: Biodegradation efficiency of OBS and reference substance in closed BOD bottles during 28 days

	Average degradation efficiency after n days（%）									
Days	0	4	7	11	14	18	21	25	27	28
$C_7H_5NaO_2$	0	62.2	69.1	80.1	72.8	83.8	84.4	76.1	83.3	75.0
OBS	0	3.1	1.7	1.2	0.4	3.5	0	0.6	0.8	0

Bioaccumulation assessment Both log BAF and log BCF were calculated by using EPI Suite v4.11, and log Kow was calculated by ECOSAR v1.10. All properties were calculated using the components of corresponding substance. As showed in Table 3, OBS and PFOS possesses same level oil-water partition coefficient, and bio- accumulation/concentration factor, hence, we have reason to believe that OBS is also tend to accumulate in body, and further, cause similar reproductive and developmental toxicity.

Table 3 Estimated log BCF, log BAF and log Kow of OBS and PFOS

Properties	OBS	PFOS	Software
log Kow	4.48	4.49	ECOSAR v1.10
log BAF	3.89	3.28	BCFBAF v3.01 (EPI Suite 4.11)
log BCF	3.43	3.23	BCFBAF v3.01 (EPI Suite 4.11)

Toxicity assessment Based on OECD guideline 203, the zebra fish (*brachydanio rerio*) was adopted as subjects in acute hazards test to the aquatic environment. The median lethal concentration (96 h-LC_{50}) and

95% confidence interval was calculated use *probit.exe* from U.S. Environmental Protection Agency. The 96 h-LC_{50} of OBS and PFOS were respective 17.0 and 31.0 mg/L (Table 4), though the OBS seems less toxic to fishes, they all belong to Hazard Category 3 according to Globally Harmonized System of Classification and Labelling of Chemicals, which means they all harmful to aquatic life.

Table 4 Medium lethal concentration of OBS and PFOS to zebra fish for 96 h exposure

Sample	96 h-LC_{50} (mg/L)	95% confidence interval (mg/L)
OBS	31.0	28.5~33.8
PFOS [7]	17.0	11.4~28.0

Stability assessment Unlike PFOS, which is highly resistant to AOPs, OBS can be readily decomposed in both UV and UV/H_2O_2 system (Figure 1). Though the concentration of OBS was also decreased rapidly in UV irradiation, it still detectable 120 min later, it can't be detected after 20-min reaction in UV/H_2O_2 system. The fluorine ion recovery ratio for OBS in both system were very low, it was 14.8% under UV and 16.1% under UV/H_2O_2 respectively, namely, the mineralization of OBS was quite limited under both conditions. The distinct difference of recovery of sulfate ion indicated that the benzene sulfonic groups in OBS molecular could be completely destroyed by UV/H_2O_2 rather than UV irradiation (Figure 2).

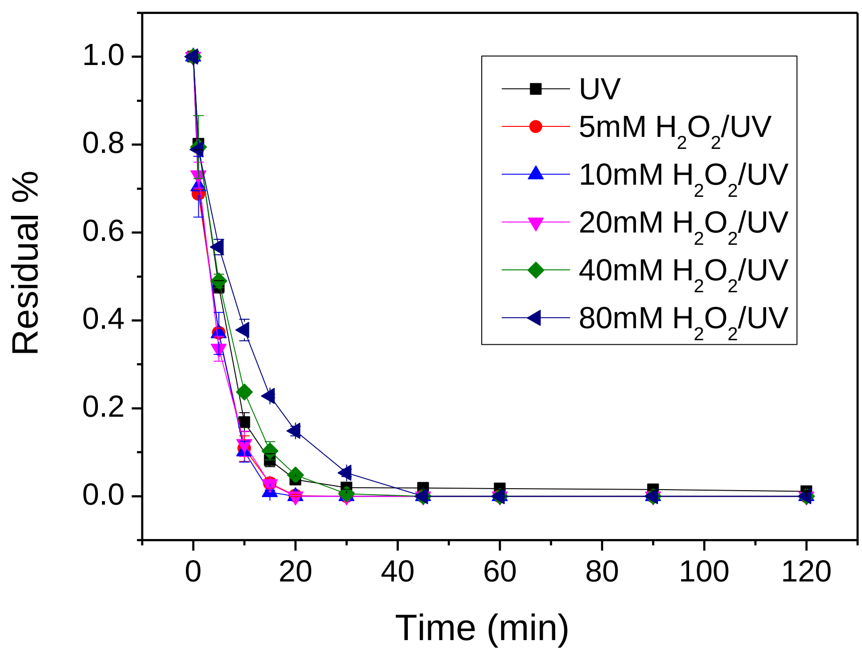

Figure 1 Degradation of OBS in UV and UV/H_2O_2 system

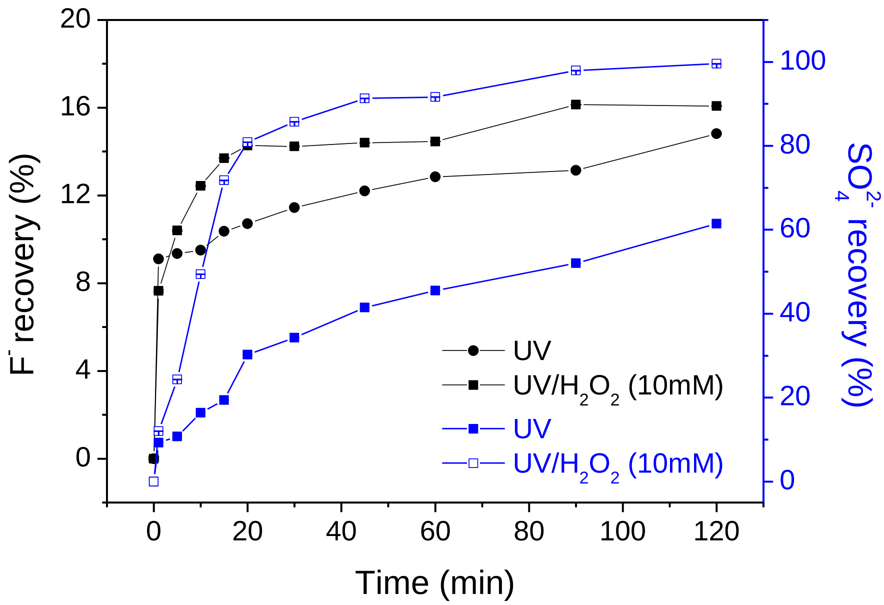

Figure 2 Recovery ratio of fluorine ion and sulfate ion for OBS in UV and UV/H_2O_2 system

In conclusion, OBS is similar to PFOS in PBT properties. However, OBS can be easily decomposed by conventional AOPs, or even by simple UV irradiation. It means that its treatability is completed different from that of PFOS. It's worthwhile to notice that the mineralization of OBS in AOPs was limited. Therefore further studies are needed to investigate the detailed degradation mechanism with the optimization of operating parameters to eliminate the potential risk caused by the intermediates.

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