Organic pollutant loading and biodegradability of firefighting foam

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Abstract. Firefighting foam has been widely used as the high-performance extinguishing agent in extinguishing the liquid poor fire. It was concerned for its environmental impacts due to its massive usage. In this study, the organic loading level and the biodegradability of 18 firefighting foams commonly used in China were evaluated and compared. The COD and TOC of firefighting foam concentrates are extremely high. Furthermore, those of foam solutions are also much higher than regular wastewater. The COD/TOC ratio of synthetic foams are higher than protein foams. The 28-day biodegradation rates of 18 firefighting foams are all over 60%, indicating that they are all ready biodegradable. Protein foams (P, FP and FFFP) have the higher organic loading and lower 28-day biodegradation rates compared to the synthetic foams (Class A foam, AFFF and S). The short and long-term impact of protein foams on the environment are larger than synthetic foams.

1. Introduction

Firefighting foams are widely used in preventing, suppressing and extinguishing fuel pool fires. They are also the most effective method to extinguish pool fires. Firefighting foams contain many additional substances, such as surfactants, organic solvents, corrosion inhibitors, and preservatives. Such can achieve suitable foaming and functional properties. The ingredients may pose hazard to living organisms as firefighting foam bubbleding and releasing into soil and water. As public awareness and environmental regulations have increased, concerns about the impact of firefighting foams have on the environment have been raised. Therefore, it is necessary to evaluate the environmental properties of firefighting foams, such as aquatic toxicity, organic loading, biodegradability and foaming.

Firefighting foam is a mixture of many different kinds of chemicals. Due to most manufacturers do not public the ingredients and contents of their foam products. Thus, the conventional methods evaluating the single chemical do not applicable to firefighting foam. There is no test method special used for evaluating firefighting foam's environmental impact. Considering firefighting foam's organic content and biodegradability, Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) can be used to evaluate the organic loading of firefighting foams on natural water. OECD 301 A-F series test standards could be available to test the biodegradability of firefighting foam, among which CO_2 evolution method and manometric respirometry method are commonly used.

Recently, several studies focusing on the biodegradation of firefighting foam have been performed. Ruppert et al. carried out a biodegradation study of six chosen firefighting foams. However, their results could not represent the respective groups of firefighting foams. Bernard et al. reported the biodegradability of 40 firefighting foams commonly used in Europe. Bourgeois et al. compared the biodegradability of three fluorinated firefighting foams, and analyzed the difference of COD and TOC in evaluating the biodegradation of fluorinated firefighting foams. To our best knowledge, the systematic research on the organic loading and biodegradation in China is lack, and the related data is too few to analysis the environmental impact of firefighting foams.

The aim of the present study was to investigate the organic loading level and evaluate and compare the biodegradability of different kinds of firefighting foams commonly used in China. The results of this study could contribute to the development of new environmental friendly foam products, to reduce the environmental risk of firefighting foams.

2. Materials and methods

2.1.Firefighting foam samples

In this study, 18 commercial firefighting foam products commonly used in China were collected. These foam concentrates covered the main varieties on China market, and could be divided into six different kinds of foam types: Class A foam, Aqueous Film Forming Foam (AFFF), Synthetic Foam (S), Protein Foam (P), Fluoroprotein Foam (FP), and Film-Forming Fluoroprotein Foam (FFFP). Details of the firefighting foams samples were shown in Table 1.

Table 1 Details of firefighting foams samples

No.	Foam type	Mixing ratio(%)	Freezing point (℃)
1	Class A foam	1	-
2		1	-
3		1	-
4		1	-
5		1	-
6	AFFF	3	0
7		6	-10
8		6	-10
9		6	-10
10		6	-3
11	S	6	-7
12		3	-5
13		3	-8
14	P	3	-15
15	FP	6	-12
16		3	-15
17		3	-10
18	FFFP	3	-10

As firefighting foam concentrates were highly condensed, the COD and TOC values of concentrates were high that far exceeded the instrument range. So for accurate measurement, 1g firefighting foam sample was added into purified water to make 100 ml foam reserve solution. The concentration of reserve solution was 10000 mg/L. Before carrying out the tests, dilute this reserve solution to proper concentration according to the instrument range and the test requirement.

2.2. COD and TOC analysis of foam samples

Chemical oxygen demand (COD) of diluted foam samples was measured according to ISO 6060-1989. The foam reserve solution was diluted to 500-1000 mg COD/L, and the COD value was measured with the use of COD photometer. The COD values of foam concentrates and foam solutions were calculated as the COD values multiplied by the dilution factor.

An Elementar Vario TOC Analyzer was used to determine TOC of diluted foam samples. The foam reserve solution was diluted to 30-50 mg TOC/L. The TOC values of foam concentrates and foam solutions were calculated as the TOC values multiplied by the dilution factor.

2.3.CO_2 evolution test for biodegradability

The 28-day CO_2 evolution test (OECD 301B) was conducted using self-made experimental device showed in Figure 1. The test bottle was filled with inoculated mineral nutrient medium, containing 15 mg TOC/L of foam sample as the nominal sole source. The test bottle was aerated by the passage of carbon dioxide-free air at the rate of 50-100 ml/min in the dark at 22±2 °C.

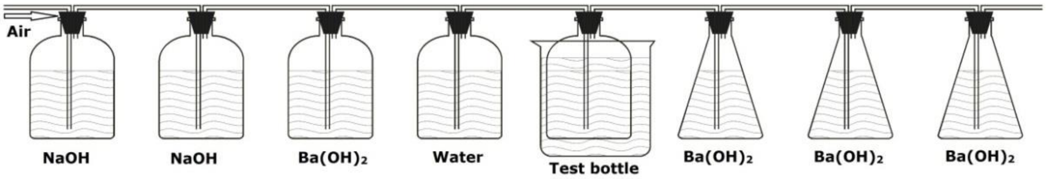

Figure 1. Schematic diagram of the experimental device

The inoculum was selected as activated sludge from the aeration tank of a wastewater treatment plant treating primarily domestic wastewater in Tianjin, China. The sludge was washed by mineral nutrient medium and aerated for 2-3 days at the test temperature. The inoculation concentration in the test bottle was 30 mg MLSS/L.

In order to check the procedure, sodium benzoate employed as reference compound was tested by setting up an appropriate bottle in parallel as part of normal test runs.

Degradation was followed over 28 days by determining the carbon dioxide produced. The CO_2 was trapped in barium hydroxide and was measured by titration of the residual hydroxide. CO_2 analysis of samples was performed on the 1, 2, 3, 4, 5, 10, 15, 20, 25 and 28 day.

Eq. 1 was used to calculate the biodegradation rate of firefighting foam.

$$\text{Biodegradation rate (\%)} = \frac{\sum \text{CO}_2 \text{ produced}}{3.67 \times \text{TOC added}} \times 100 \qquad (1)$$

3. Results and discussion

3.1 evolution test for biodegradability

In general, firefighting foam is produced, stored and transported in the form of foam concentrate.It mixed with water at certain mixing ratio to give a foam solution in the fire scene. In this study, both foam concentrate and foam solution were tested and the COD and TOC values were listed in Table 2.

Table 2. COD and TOC values of firefighting foam samples

No.	Mixing ratio(%)	COD (mg/L)	Foam solution COD(mg/L)	TOC (mg/L)	Foam solution TOC(mg/L)
1#	1	1443750.00	14437.50	265004.72	2650.04
2#	1	1024250.00	10242.50	212501.68	2125.02
3#	1	992250.72	9922.51	173850.43	1738.50
4#	1	723666.56	7236.67	128110.89	1281.11
5#	1	1226919.06	12269.19	283899.20	2838.99
6#	3	348040.00	10441.20	92595.58	2777.87
7#	6	121285.67	7277.14	35463.61	2127.82
8#	6	330704.73	19842.28	98052.92	5883.18
9#	6	205383.81	12323.03	56157.64	3369.46
10#	6	182540.83	10952.45	51271.70	3076.30
11#	6	168817.63	10129.06	49685.19	2981.11
12#	3	154992.63	4649.78	52986.04	1589.58
13#	3	168483.89	5054.52	54135.74	1624.07
14#	3	313607.85	9408.24	114900.08	3447.00
15#	6	287203.67	17232.22	108473.04	6508.38
16#	3	424425.87	12732.78	170949.84	5128.50

17#	3	477624.58	14328.74	163850.99	4915.53
18#	3	450757.58	13522.73	162956.55	4888.70

In general, COD and TOC are the index of the organic pollution level in drinking water and wastewater. In this study, the COD and TOC of 18 foam concentrates range in 121286-1443750 mg/L and 35464-283899 mg/L respectively (Table 2). Comparing to wastewater, the COD and TOC of firefighting foam concentrates are extremely high. It may cause serious environmental disaster as releasing into natural environment without pretreatment. This indicate that there are servours organic pollutant in the loading of foam concentrates. Thus, it is strongly recommend to prevent any leakage of foam concentrate in the course of transportation and storage.

As mentioned above, firefighting foam is bubbled and releases into natural water in the form of foam solution at fire sense. Therefore, the COD and TOC value of foam solution is more meaningful than concentrate when considering the firefighting foam's environmental impact. After dilution, the COD and TOC values of foam solutions range at 4649-14437 mg/L and 1281-6508 mg/L respectively. The range of COD and TOC is consistent with the values of AFFF and FP which is reported by Bourgeois et al. Although these values are much lower than the guide concentrates, they are still much higher than COD and TOC values in wastewater and natural water. It can kill fish and plant, and thus causing a red tide, suggesting it has the aquatic toxicity. Surfactant is the key component and the main source of COD and TOC in firefighting foam. It may cause organic loading shock and raw sludge discharge, leading to the disrupting of wastewater treatment as the wastewater rich in surfactant runs into wastewater treatment plant in a short time.

In this study, 18 firefighting foams were tested. Class A foams have the highest COD and TOC values in concentrates, while it was not the highest in foam solutions. This may due to its lower mixing ratio than other foams. Generally, the highest mixing ratio of Class A foam is 1%. however, the other low expansion foam is 3% or 6%. The high dilution of Class A foam leads to its low organic loading in foam solution. For Class A foam, AFFF, and S, which collectively called synthetic foam, the COD and TOC values vary greatly. These materials are directly related to the amount of active ingredients contained, and active ingredients vary greatly depending upon the specific application for which a product is designed. For P, FP, FFFP, the difference in COD and TOC is not so large, and the values are all much higher than synthetic foams mentioned above. The main ingredient of these protein foams is protein hydrolysate, which contains large amount of organics. This main ingredient makes protein foams have higher organic loading than synthetic foams, especially TOC content.

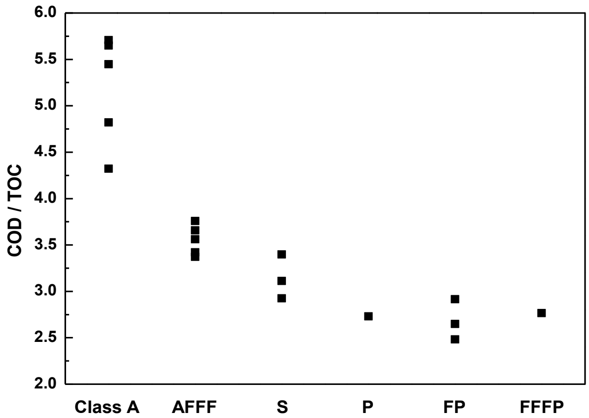

Figure 2. COD/TOC ratio of different firefighting foams

Figure 2 shows the difference of synthetic and protein foams in the form of COD/TOC. The COD/TOC ratio is 2.67 for single organic wastewater. As shown in the Figure 2, there is a clear trend for different kinds of foams. The average COD/TOC for Class A foam, AFFF, S, and protein foam is 5.19, 3.55, 3.15 and 2.73 respectively. Class A foams have the highest COD/TOC ratio, followed by AFFF and S, the lowest COD/TOC ratio was protein foam. The ratio of protein foam is close to the ideal value, but the ratio of synthetic foams is much higher. The difference in COD/TOC ratio indicates that the key ingredients difference that synthetic and protein foams employed.

3.2 Biodegradation of firefighting foam

In this study, all the foams have the similar 28-day biodegradation curve. The typical biodegradation curve of firefighting foam in Figure 3 indicates that the biodegradation process goes through stagnation phase, log phase and stationary phase in 28-day test period. The biodegradation results of 18 foams are showed in Figure 4.

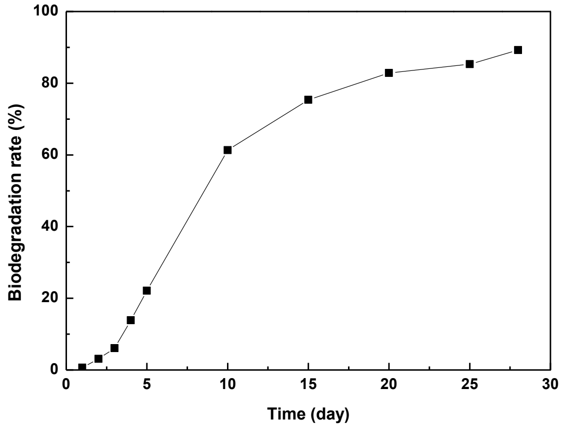

Figure 3. Biodegradation curve of typical firefighting foam in 28-day period

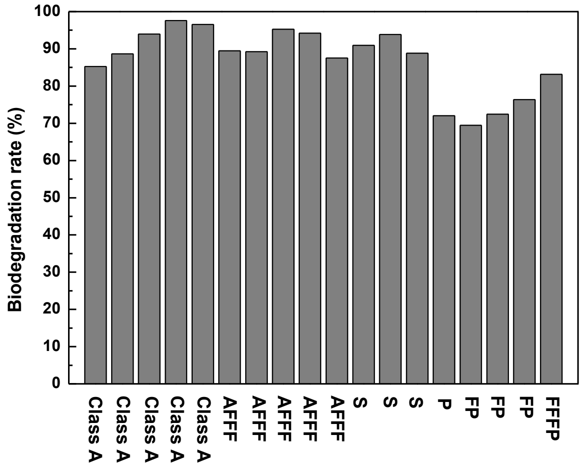

Figure 4. The 28-day biodegradation rates of firefighting foams

Biodegradability is the capability of a chemical or mixture to be decomposed by biological means. In OECD 301,the pass level of ready biodegradability is 60% of CO_2 production for the CO_2 Evolution test method. This pass level has to be reached in a 10-day window within the 28-day period of the test. According to this standard, the 28-day biodegradation rates of 18 firefighting foam samples in this study are all over 60%, suggesting that they were ready biodegradable.

The biodegradation rates of Class A foam, AFFF and S were ranged from 85.27% to 97.61%. this indicates that the rates of different foam types do not have significant differences for these three kinds of foam. however, the biodegradation rates of P, FP and FFFP, were significantly lower than the synthetic foams mentioned above. Their biodegradation rates were ranged from 69.45% to 83.17%. In this study, the synthetic foams (Class A, AFFF and S) are much easier to biodegrade than protein foams (P, FP and FFFP).This trend is similar with the results reported by Ruppert et al. and Bernard et al. However, there was difference between this study and those report. In their research, the biodegradation rates of protein foams were below 60%. In contrary, they were more than 60% in this study. The main reason of this defference may be that the microbial inhibitors added to extend the life of protein foam life reduce its biodegradability in the nature environment, although protein hydrolysate is usually considered to be easily biodegradable.

Based on the organic loading and biodegradation discussed above, protein foams have the higher organic loading and lower 28-day biodegradation rates compared to the synthetic foams such as Class

A foam and AFFF. Thus, they pose a high threat on the environment. Once protein foams enter the natural water, they may lead to the organic content raised significantly in water, consuming more dissolved oxygen. Also their relative poor biodegradability make them persistent in the environment, poisoning plant and animals in the water for a long time.

4. Conclusion

In this study, the COD, TOC and biodegradation of 18 firefighting foams were tested. The COD and TOC of firefighting foam concentrates are extremely high, and those of foam solutions are also much higher than regular wastewater. The COD/TOC ratio of synthetic foams are higher than protein foams. The 28-day biodegradation rates of 18 firefighting foams are all over 60%, meaning they are all ready biodegradable. Protein foams have the higher organic loading and lower 28-day biodegradation rates compared to the synthetic foams. So their short-term and long-term impact on the environment are larger than synthetic foams.

Acknowledgments

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