Reducing the Formation of Adsorbable Organic Halides Using an Ammonium Thiosulfate Chlorine Dioxide Bleaching Process

Yan Li,[a,b,c] Liming Cao,[b,c] Kaiqi Gu,[b,c] Xinyue Wang,[b,c] Yunbiao Pang,[b,c] Qin Wu,[a,c] and Shuangquan Yao [a,b,c]*

Reducing the formation of adsorbable organic halides during chlorine dioxide bleaching (the first stage chlorine dioxide bleaching, D_0) is necessary to obtain clean bleaching processes. A new bleaching agent, ammonium thiosulfate (AT), was investigated to determine its potential for reducing the amount of adsorbable organic halides (AOX). Upon investigating the optimal reaction conditions for an effective reduction in AOX, the authors determined that adding 0.20% of AT 10 min after the beginning of the bleaching reaction, while maintaining a pH of 4 and a temperature of 70°C, yielded the best results. Under these conditions, AOX formation decreased by 22.0%. The bleaching effluent after the addition of AT was analyzed *via* gas chromatography-mass spectrometry, which showed an inhibited production rate of chlorobenzene and chlorophenol, which are both highly toxic and difficult-to-degrade compounds. Therefore, AT not only reduces AOX formation during the bleaching process, but also minimizes the difficulty of treating bleaching effluent. The results of this study provided a new, clean method for reducing AOX formation during chlorine dioxide bleaching.

Keywords: Chlorine dioxide bleaching; AOX formation; Ammonium thiosulfate; Chemical composition

Contact information: a: State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Jinan 250353 P.R. China; b: School of Light Industrial and Food Engineering, Guangxi University, Nanning 530004 P.R. China; c: Guangxi Key Laboratory of Clean Pulp & Papermaking and Pollution Control, Nanning 530004 P.R. China;
** Corresponding author: yaoshuangquan@sina.cn*

INTRODUCTION

Chlorine dioxide bleaching is a common and clean bleaching method, due to its selective delignification properties (Nie *et al*. 2014; Shi *et al*. 2019). Compared to conventional chlorine bleaching, 75% to 85% of adsorbable organic halide (AOX) formation can be reduced by chlorine dioxide bleaching (Zhang *et al*. 2019). However, preparing chlorine dioxide results in chlorine gas formation *via* side reactions. A small amount of chlorine gas is then dissolved in the chlorine dioxide solution, resulting in the formation of hypochlorous acid (Afsahi *et al*. 2019). AOX is generated mainly from the chlorination of hypochlorous acid, lignin, and hexenuronic acid. The predominant AOX species are chlorobenzene and chlorophenol, which are highly toxic compounds that are difficult to biodegrade (Rada *et al*. 2006). Reducing AOX formation during the bleaching process has become an important task, and without achieving it, developments in pulp and papermaking processes are restricted.

The reduction of AOX formation in the chlorine dioxide bleaching process has been achieved through various methods, including process optimization (Xie *et al*. 2016), acid/alkali pretreatments (Shimizu *et al*. 2018), enzyme pretreatments (Sharma *et al.* 2014; Nie *et al.* 2018b), hydrothermal pretreatments (Yao *et al*. 2015; Zhu and Yadama 2016; Huang *et al*. 2020), and introducing chemical additives (Yao *et al*. 2016). High temperature chlorine dioxide bleaching (Zhang *et al*. 2018a,b) is a typical process optimization method (Barroca *et al*. 2001), whereby AOX formation can be reduced by up to 50%. However, cellulose degradation is promoted at higher bleaching temperatures. As previously mentioned, AOX primarily form due to the chlorination of lignins or hexenuronic acid by hypochlorous acid. However, these components can be removed by different pretreatment methods (Nie *et al*. 2018a; Bian *et al*. 2019, 2020), thereby effectively reducing the formation of AOX. Acid or alkali pretreatments have been shown to reduce the total AOX formation (Francis *et al*. 1997), but also to increase the chemical oxygen demand (COD) in bleaching effluent (Li *et al*. 2010; Kim *et al*. 2016). It is well known that biological enzymes are easily inactivated due to changes in environmental conditions (Thakur *et al.* 2012; Dai *et al*. 2016; Gangwar *et al*. 2016). Therefore, it is necessary to develop enzymes with strong applicability. A large amount of hemicellulose and a small amount of lignins were dissolved during hydrothermal pretreatments (Yao *et al*. 2015; Ge *et al.* 2020; Huang *et al*. 2020), which decreased the probability of these components reacting with hypochlorous acid, thus inhibiting AOX formation (Yao *et al*. 2017a). However, cellulose was dissolved and degraded, which resulted in a decrease in the pulp yield. Different from pretreatment reduction technology, AOX reduction technology for bleaching processes has been improved by employing chemical additives (Nie *et al.* 2016; Yao *et al*. 2016). The results show that the molar ratio of S/Cl is an important factor affecting the inhibition efficiency of AOX generation by chemical agent. By introducing sodium sulfide at a 2.00% dosage, AOX formation was reduced by 20.0%, but the brightness of the pulp was also decreased by 6.3%. The mechanism of AOX reduction by sulphur-based auxillaries can be mainly attributed to two points based on a large number of studies. First, the chlorine source generated by AOX is consumed, such as chlorine dioxide, hypochlorous acid, and chlorine. The second effect is that the main components of AOX, chlorobenzene and chlorophenol, are sulfonated, which significantly reduces the formation of AOX. In fact, lignin in unbleached pulp reacts quickly in chlorine dioxide solution, and AOX is generated rapidly in the initial stage of bleaching reaction. Therefore, the ineffective consumption of bleach agent and the production of chlorobenzene and chlorophenol are reduced by adding this chemical agent at the appropriate time of the bleaching process. In addition, the above studies show that nitrogenous chemical agents have an effect on AOX reduction (Yao *et al*. 2016). The results showed that AOX formation decreased by 10% when 0.05% of amino sulfonic acid was added, which indicated that sulfur-nitrogen compounds could drastically reduce AOX formation. This indicates that chemical agent with a higher S/N molar ratio has a more significant effect on AOX reduction. The results provide theoretical support for further reduction of AOX during bleaching.

In this study, a chemical agent with a higher S/N molar ratio, ammonium thiosulfate (AT) was selected. The inhibitory effect of AT on AOX formation was analyzed. The effects of it addition time and dosage, as well as the reaction pH and temperature, on AOX formation were studied. The chemical composition of the bleaching effluent was also analyzed *via* gas chromatography-mass spectrometry (GC-MS).

EXPERIMENTAL

Materials

The unbleached bagasse pulp was purchased from a local pulping mill (Guangxi, China). The kappa number of the pulp was 13.91, the viscosity was 1211 mL x g^{-1}, and the brightness was 42 %ISO. The effective chlorine present in the chlorine dioxide solution was 16.00 g x L^{-1}. All chemicals used were of analytical grade. AT was obtained from Sigma-Aldrich (St. Louis, MO), and all other reagents were purchased from Aladdin Biotechnology Co., Ltd. (Shanghai, China).

Methods

Bagasse pulp (10 g) with a 10% pulp concentration was added to the plastic bag. The pH value of bleaching effluent was adjusted by the addition of sulfuric acid. The dosage of chlorine dioxide was 1.60% and 0.10% to 0.30% of AT was added at 0 min to 50 min after the bleaching process began. The bleaching reaction was carried out at a temperature range of 40°C to 90°C and at various pH values between 1.49 and 6.03, and the plastic bag was rubbed every 10 min to ensure sufficient contact between the pulp and bleaching agent. The solution was collected for analysis after each reaction.

The AOX formation in the bleaching effluent was analyzed *via* a multi-X2500 AOX analyzer (Analytik Jena, Jena, Germany) and quantified *via* the micro-coulomb titration method (Yuan *et al*. 2012). Each sample was measured three times and averaged. The chemical compositions of the bleaching effluent were analyzed *via* an Agilent 6990-5973 GC-MS (Santa Clara, CA) (Yao *et al*. 2017).

RESULTS AND DISCUSSIONS

Effect of AT Addition Times on AOX Formation

Sulfur precipitates out of AT solutions after long periods of time and gradually decomposes at temperatures greater than 50 °C. Therefore, the addition time of AT during bleaching can drastically influence its performance. The effect of the addition time on AOX formation was studied (as shown in Fig. 1), where AT was added at various times (0 min to 50 min), using a dosage of 0.30%. In fact, the formation of AOX in bleaching effluent without AT was 42.8 mg x L^{-1} under the same bleaching conditions.

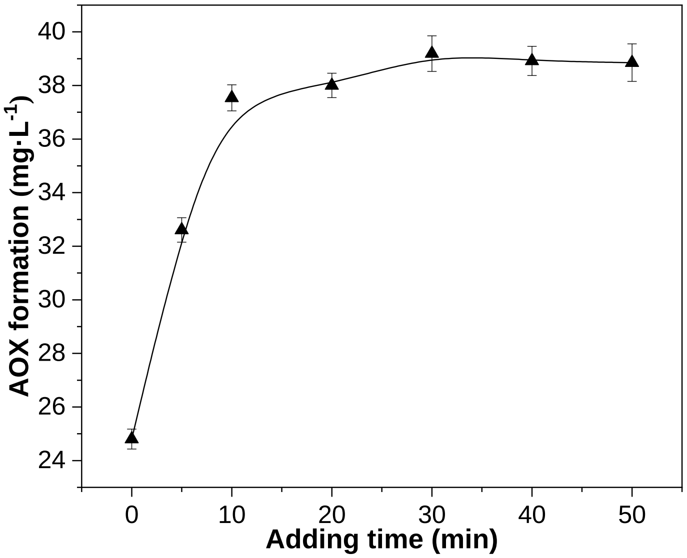

Fig. 1. Effect of different AT addition times on AOX formation during bleaching

Figure 1 shows that AOX formation gradually increased as AT addition time was extended. AOX formation was the lowest (24.8 mg x L^{-1}) when it was added at the initial stage of the bleaching process, and it rapidly increased when it was added at 10 min to 37.5 mg x L^{-1}. Although AOX formation increased in this case, it was reduced overall by 12.3% when compared to the AOX formation of conventional chlorine dioxide bleaching (42.8 mg x L^{-1}). Moreover, the formation of AOX remained unchanged after 10 min, which was due to two reactions that occur during bleaching that involve lignin (Nie *et al*. 2014). The primary reaction is the oxidative degradation of lignin by chlorine dioxide, and the other is the chlorination of lignin by hypochlorous acid. Both reactions rapidly occur to remove lignin and bleach the pulp. The excess chlorine dioxide and hypochlorous acid in the bleaching solution then reacted with hemicellulose and cellulose, which led to AOX formation and cellulose degradation (Zhang *et al*. 2018b). However, AT consumes the excess chlorine dioxide and converts it into a sulfate (Cseko *et al*. 2018) or a nitrate (Malouki *et al*. 2005, Song *et al*. 2019). This is the primary route for reducing AOX formation. Unfortunately, the lignin removal and pulp bleaching were affected by this excessive consumption of chlorine dioxide. Therefore, the authors determined that the best time to add AT was after 10 min, since the oxidative degradation of chlorine dioxide and lignins was essentially completed by this time.

Effect of AT Dosages on AOX Formation

The primary purpose of adding AT is to consume excessive bleaching agent; thus, the effect different dosages had on AOX formation was studied. Dosages of 0.10%, 0.15%, 0.20%, 0.25%, and 0.30% were tested. It was added after 10 min. The results are shown in Fig. 2.

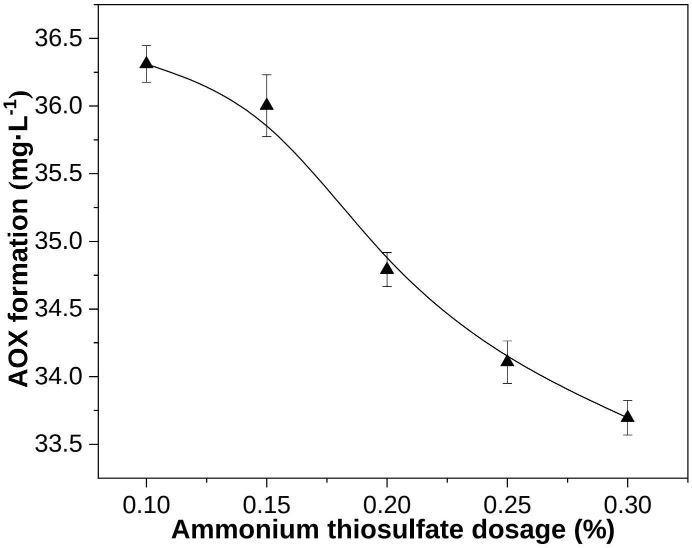

Fig. 2. Effect of AT dosages on AOX formation during bleaching

Figure 2 shows that when AT dosage increased from 0.10% to 0.20%, the AOX formation decreased by 3.6%, from 36.1 mg x L^{-1} to 34.8 mg x L^{-1}. When the dosage was increased to 0.30%, AOX formation decreased to 33.7 mg x L^{-1}, which was 1.1 mg x L^{-1} less than the decrease seen with a 0.20% dosage. This indicated that the rate of AOX formation gradually decreased as the dosage increased. Synthesis of C-Cl is reduced by the addition of the chemical agent. The chlorination level of the reaction product is reduced (Griffin 1986). In addition, a small amount of chlorine gas in chlorine dioxide solution is converted to HCl (Raghunathan and Gullett 1996). The degree of chlorination is reduced. AOX formation is suppressed. Small amounts of sulfur and sulfur dioxide are produced from the decomposition of AT. Since this increases the pollution load of bleaching effluent. The addition of excessive AT was unfavorable. The optimal dosage of AT was 0.20%.

Effect of pH Values on AOX Formation

As the decomposition rate of chlorine dioxide (Zhang *et al*. 2019) and its reactions with sulfur (Cseko *et al*. 2018) and nitrogen compounds (Zhong *et al*. 2019) are affected by pH, the reaction system with ammonium thiosulfate was studied at various pH levels. The initial pH values of the reaction system were 1.49, 2.15, 3.00, 4.06, 5.08, and 6.03. AT dosage of 0.20%; and it was added after 10 min. The results are shown in Fig. 3.

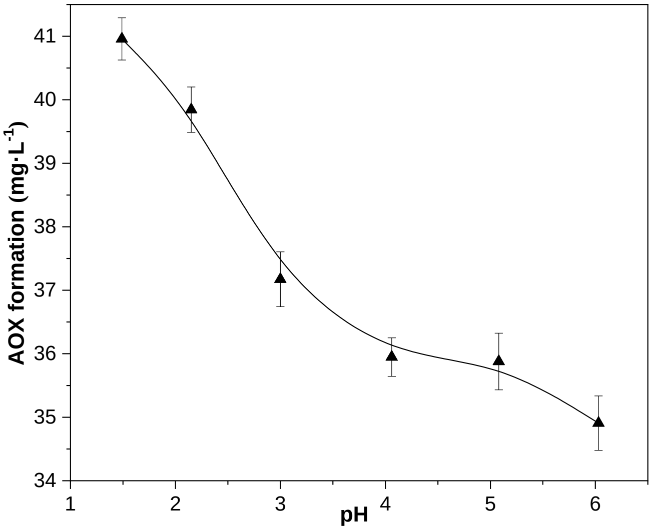

Fig. 3. Effect of pH values on AOX formation during bleaching

Figure 3 shows that AOX formation decreased as the pH value increased. At a pH of 1.49, the amount of AOX formed was 41.0 mg x L^{-1}, and when the pH was increased to 4.0, the amount of AOX formed was 36.0 mg x L^{-1}. However, the trend of a decreasing amount of AOX formation slowed when the pH value exceeded 4.0, where an additional decrease of only 1.0 mg x L^{-1} was observed at pH 6.03. This was due to increased chlorine dioxide decomposition in lower pH (Liu *et al*. 2020), which produced more chlorine and hypochlorous acid that subsequently increased AOX formation. In addition, the decomposition rate of chlorine dioxide was the lowest at pH 3 to 4. AT was oxidized to sulfate and nitrate at pH 5 to 9. Therefore, the quality of the bleached pulp was affected if the pH of the reaction system was too high or too low. Combined with the conditions of a traditional chlorine dioxide bleaching, the optimal pH value of the bleaching system containing AT was 4.0.

Effect of Reaction Temperatures on AOX Formation

The bleaching and decomposition rate of chlorine dioxide are drastically affected by the reaction temperature. Therefore, the effect of different reaction temperatures on AOX formation in this new system was studied. The temperature was 40°C, 50°C, 60°C, 70°C, 80°C, and 90°C, respectively. AT dosage was 0.20%, and it was added after 10 min. The results are shown in Fig. 4.

The temperature-dependent changes in AOX formation during the bleaching process used for this study can be divided into two stages: (1) increased AOX formation (from 34.6 mg x L^{-1} to 38.2 mg x L^{-1}) when the temperature increased from 40 °C to 60 °C; and (2) decreased formation at temperatures greater than 60 °C. The increased AOX formation was primarily attributed to the reaction activity of lignin and the thermal decomposition of chlorine dioxide, which increased as the temperature increased and consequently promoted lignin chlorination and increased AOX formation during bleaching. The decreased formation was ascribed to the enhanced reaction between chlorine dioxide and AT as the temperature increased, as the increased consumption of chlorine dioxide inhibited hypochlorous acid generation, which resulted in a decrease in AOX formation. In addition, the autohydrolysis of hexenuronic acid produced during bleaching was enhanced as the temperature increased, which also reduced AOX formation.

Furthermore, ineffective decomposition of chlorine dioxide occurred at 80 °C, which weakened the bleaching effect. Therefore, the optimal bleaching temperature of the new system was 70 °C.

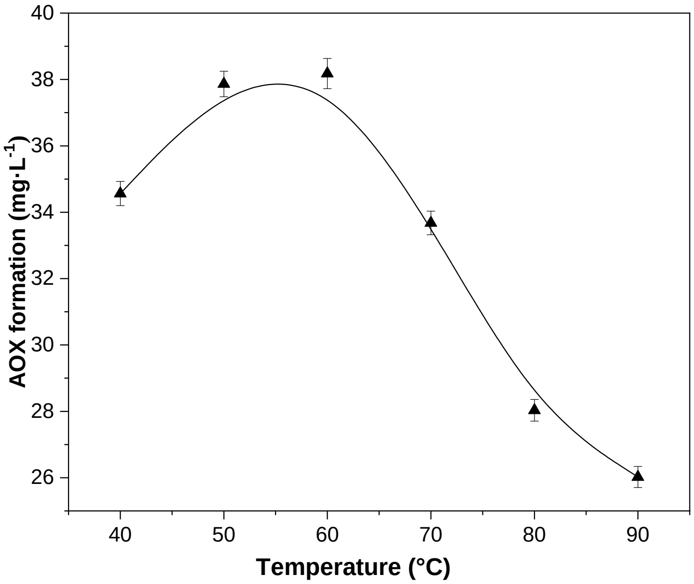

Fig. 4. Effect of temperatures on AOX formation during bleaching

The optimal conditions that the determined for employing AT in chlorine dioxide bleaching were as follows: AT was added after 10 min, it dosage 0.20%, pH 4.0, and reaction temperature 70 °C. Under the optimal conditions, AOX formation was reduced by 22.0%, which demonstrated that adding AT during the bleaching had a strong inhibitory effect on AOX formation.

Component Analysis of the Bleaching Effluent

The above evaluation showed that total AOX formation during the chlorine dioxide bleaching was reduced after AT addition. However, AOX have many components and properties, *e.g.*, volatility, toxicity, and durability. The difficulties of processing each AOX component are directly related to their properties. The components of the bleaching effluent, with and without the addition of AT, were analyzed *via* GC-MS. The results are shown in Fig. 5.

The changes in chemical composition of the bleaching effluent with and without AT addition are shown in Table 1. The results showed that 1,1-dichloroacetone, 1,2,3-trichloroacetone, 3-chloro-phenol, and 2,4,6-trichlorophenol disappeared in effluents that had AT added. In addition, the amounts of 1,2,4-trichlorobenzene, 1,3-dichlorobenzene, and 6-chloro-purine were reduced. The results showed that chlorobenzene, chlorophenol and other cyclic organic chlorides were inhibited. In fact, they are highly toxic, refractory, and persistent components of AOX. The findings indicated that the environmental hazards of bleaching effluent were reduced by adding AT. Furthermore, the tetrachloroethane, trichloromethane, and 1,1,3,3-tetrachloroacetone content all increased, and ethyl 2-chloro-propionate was detected. This indicates that the inhibitory effect of AT addition on small molecules of organochlorine was low. This was attributed to the fact that the oxidative degradation of lignin by chlorine dioxide was not affected by AT addition. The organic chlorides of these small molecules are low toxic and volatile. They are low risk to the environment and easy to handle. The results showed that adding AT in the bleaching process not only reduced the amount of AOX, but it also reduced the toxicity and treatment difficulty of bleaching effluent. The reduction in chlorobenzene and chlorophenol is due to sulfonation. This results in an increase in the relative content of small molecules of chlorinated products. In addition to the influence of AT on the content and composition of bleaching effluent, their retention time was also changed. The retention time of trichloromethane and chloropurine was the most obvious. This is due to the fact that chlorobenzene and ring substances have been sulfonated by AT. At the same time part is retained, but is derived, resulting in retention time changes on GC-MS.

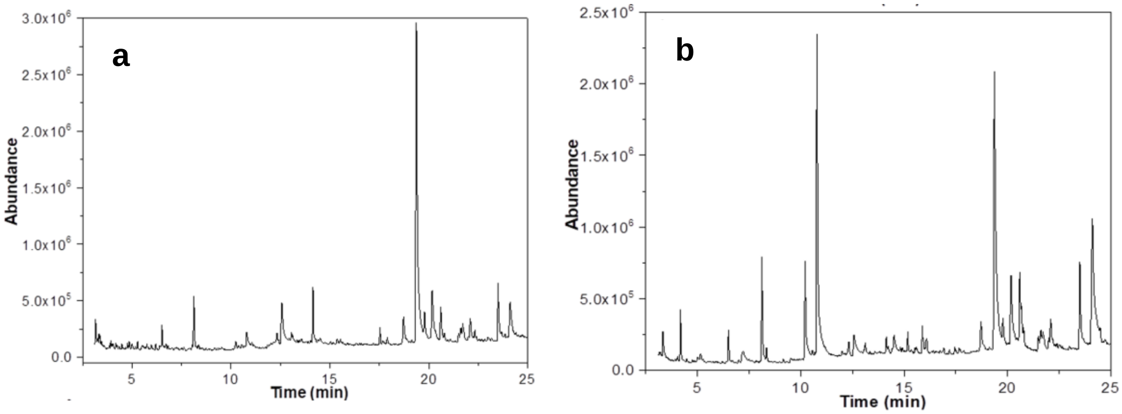

Fig. 5. GC-MS of the bleaching effluent (a) with and (b) without AT addition

Table 1. Composition of Bleaching Effluent with and without AT Addition

Retention Time (min)		Composition	Relative Amount (%)	
Without $(NH_4)_2S_2O_3$	With $(NH_4)_2S_2O_3$		Without $(NH_4)_2S_2O_3$	With $(NH_4)_2S_2O_3$
4.037	—	1, 1-dichloroacetone	0.06	—
4.648	4.636	tetrachloroethane	0.15	0.54
6.502	—	1,2,3-trichloroacetone	0.26	—
8.126	8.132	1,1,3,3-tetrachloroacetone	0.03	0.09
9.455	9.545	1,2,4-trichlorobenzene	0.32	0.01
12.668	12.328	trichloromethane	0.08	0.09
13.123	13.255	1,3-dichlorobenzene	0.22	0.10
—	13.468	ethyl 2-chloro-propionate	—	0.06
15.533	—	3-chloro-phenol	0.12	—
16.673	—	2,4,6-trichlorophenol	0.15	—
20.176	20.168	2-chloro-p-chlorophenol	1.29	0.65
22.091	21.528	6-chloro purine	0.38	0.15
Note: $(NH_4)_2S_2O_3$ is AT				

CONCLUSIONS

1. The effective use of ammonium thiosulfate (AT) as a new chlorine dioxide bleaching treatment was demonstrated. The effects of various reaction factors on chlorine dioxide and its subsequent formation of absorbable organic halides (AOX) were studied after the addition of AT.
2. The results showed that ammonium thiosulfate has a strong inhibitory effect on AOX formation, owing to its consumption of excess chlorine dioxide. Under the optimal conditions determined in this study, AOX formation was reduced by 22.0%. Among the AOX that were decreased by the addition of AT were chlorobenzene and chlorophenol, which are highly toxic compounds that are difficult to degrade. This study has established a new system for clean chlorine dioxide bleaching.

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