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Characterization of nanoparticulate fouling and breakthrough during low-pressure membrane filtration

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ABSTRACT

Low-pressure membranes suffer from particulate, organic and biological fouling during operation. In order to elucidate the impact of nanoparticles on membrane fouling, experiments were carried out with a small membrane test unit operated with artificial and natural waters. Both microfiltration (MF) and ultrafiltration (UF) membranes were used. Artificial waters were made from ultra pure water spiked with polystyrene or magnetite nanoparticles with sizes between 20 and 250 nm in varying particle concentrations. During the filtration tests the permeability decreased with time indicating a blocking of the membrane pores by nanoparticles. During the filtration of small particles (20–30 nm) the permeability dropped to a significantly lower level than during filtration of larger particles (100–250 nm). Under the tested conditions the nanoparticle concentration seemed to have no influence. In natural waters particulate fouling tended to be overlapped by other fouling processes such as organic fouling.

With the test unit the fouling potential of raw waters could be characterized within a short period of time whereas the nanoparticles in the feed waters were characterized by a special analysis based on Laser-induced Breakdown Detection (LIBD). With this highly sensitive quantification method it was possible to determine both nanoparticle size (down to 10 nm in diameter) and concentration (down to a few ng/L) in the feed and the filtrate. In the filtrates of the MF membrane operated with spiked feed waters, nanoparticles were detected indicating their breakthrough. Comparatively, under similar conditions the UF membrane showed a very high retention of such nanoparticles.

Keywords: Laser-induced Breakdown Detection (LIBD); Nanoparticles; Particle analysis; Particulate fouling; Ultrafiltration

1. Introduction

The process of micro-/ultrafiltration is widely applied in drinking water treatment plants in Germany for the removal of particles and microorganisms [1, 2]. Full scale experience has shown that membranes suffer from particulate, organic and biological fouling during operation which is the result of physical, chemical and biological interactions of both dissolved and suspended materials in the feed waters with the membrane as documented by several authors [3, 4, 5, 6]. Membranes need to be backwashed and chemically cleaned in regular intervals in order to restore the permeability. The mechanisms responsible for a decrease in the permeability during water treatment are not fully understood at this time. Until recently most studies typically were conducted for organic fouling [6, 7, 8, 9], biofouling [10, 11] and particle fouling [3, 4, 5]. However, very few investigations have

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studied MF and UF due to nanoparticles. The objective of this study was to characterize nanoparticle fouling and its impact on the MF and UF performance.

2. Material and methods

2.1. Membrane filtration

A small test unit for membrane filtration (SUMF) was designed and operated with artificial and natural waters under constant, realistic flux conditions. Special miniature membrane modules provided by two membrane manufacturers were used in the SUMF. The first manufacturer provided special modules consisting of a single multibore membrane fibre of 20 cm length potted into a PVC tubing. It has an effective membrane area of 24 cm² (membrane type A). A second manufacturer produced mini modules containing about 50 fibres with a total membrane area of 150 cm² (membrane type B). Some specific details about the membranes are given in Table 1. Although the mini modules do not represent the length and packing density of the large-scale modules, they can be used to show excellent the interactions between the water and the membrane under practical operation conditions regarding flux during filtration and backwash and backwash frequency. However, the test cannot be used to optimize operational conditions. A schematic illustration of SUMF is given in the top of Fig. 1. The modules were connected to the pump and the measuring devices for flow and pressure difference by flexible tubing. The SUMF is fully automated with regard to the filtration and backwash processes and contains a data logger for monitoring the pressure difference and the flow rate.

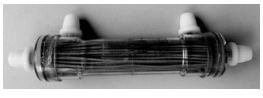
Each experiment with SUMF was carried out over a period of at least 5 h. Within this time period several backwashes took place so that it was guaranteed that each test ran under stable conditions. Before starting a run the respective membrane was operated with ultra pure water (UPW, see section *artificial waters* below) to exclude side effects such as membrane compaction until the transmembrane pressure (TMP) was constant. The increase of TMP over time due to fouling effects was measured and any changes of temperature which also influence permeability were monitored. The permeability was calculated and normalized to a standard temperature of 20°C.

In order to be able to carry out several experiments with the same membrane and guarantee that the membranes status is the same at each start-up, it was cleaned with sodium hypochlorite solution (concentration 150 mg/L) for one hour. This procedure has been evaluated as most suitable out of a series of tests with varying concentration and contact time. Thus, after each run the permeability could be fully restored by this chemical cleaning to its original value. Finally the obtained permeability was correlated with the number, size and composition of nanoparticles in the feed in order to quantify their fouling potential.

2.2. Particle analysis

The number and size of nanoparticles in feed and filtrate were analyzed by a patented, not yet commercially available Nano-Particle Analyzer based on Laser-induced Breakdown Detection (NPA/LIBD) developed at the Karlsruhe Research Center (Germany). The NPA/LIBD is a highly sensitive nanoparticle detector that allows the online detection of particles within a size range of approximately 10 to 1000 nm at concentrations as low as 1 ng/L and a corresponding number concentration as low as approximately 10^7 particles/L. Any sample pretreatment is not required. The method and applications of the NPA/LIBD was described in detail previously [12, 13, 14]. The calibration of NPA/LIBD was carried out with commercially available polystyrene reference particles with mean diameters in the range of 20 to 1000 nm (Duke Scientific Corporation, Palo Alto, California). In this study SUMF and NPA/LIBD were directly coupled in order to determine operational parameters of the membrane (TMP, flux) as well as nanoparticle counts in feed and membrane filtrate; the experimental setup is illustrated in Fig. 1.

Table 1
Membrane specification for SUMF.

Membrane type	A		B
Membrane material	Polyethersulfone		Polyvinylidene fluoride
Pore size	app. 20 nm		app. 100 nm
Type	Multibore capillary		Singlebore capillary
Number of fibres	1		50
Membrane area, cm²	24		150
Flux, L/m²/h	100		100
View of module			

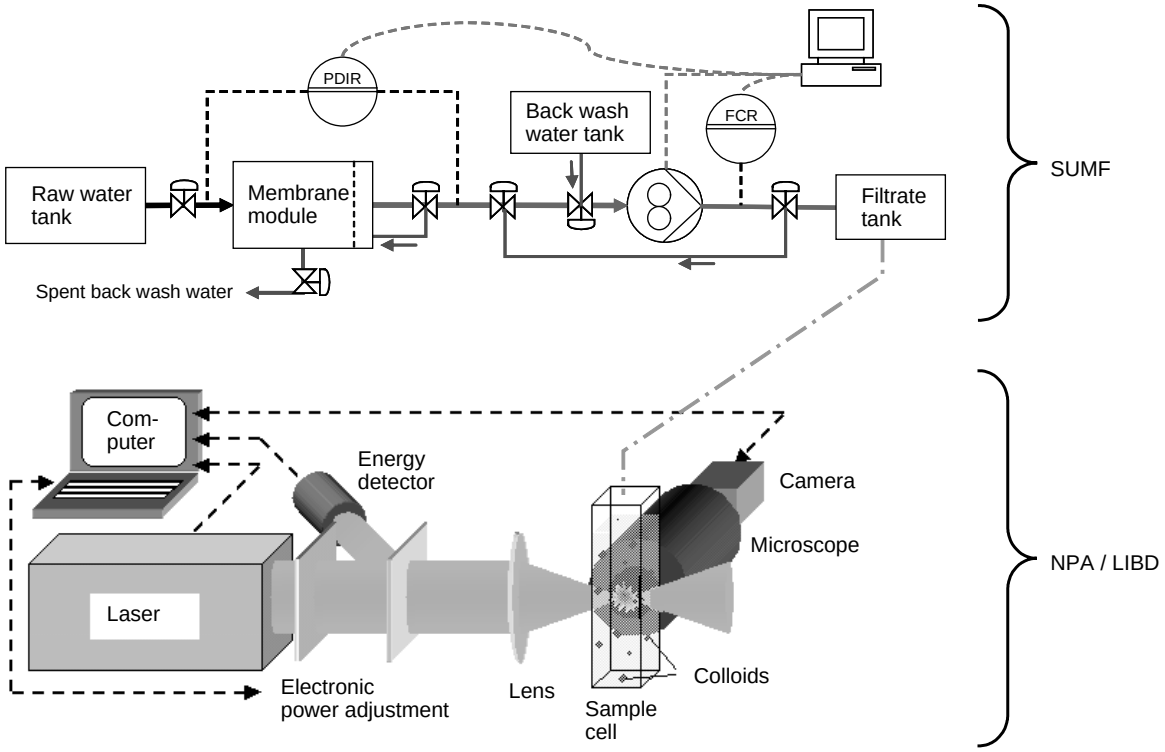


Fig. 1. Schematic illustration of the direct coupling of SUMF filtration unit and NPA/LIBD particle detector.

2.3. Artificial waters

Feed waters were prepared by spiking UPW with nanoparticles. UPW was produced from tap water by means of a multistage treatment (ion exchange, reverse osmosis, ultrafiltration), the last step being an ultrafiltration with a commercially available device (Arium 611, Sartorius AG, Göttingen, Germany). Polystyrene reference particles with a mean diameter between 20 and 200 nm in size (same as for NPA/LIBD calibration) were employed in this study. Additionally, Fe_3O_4 (magnetite) particles (micromod Partikeltechnologie GmbH, Rostock, Germany) of 130 and 250 nm in size were chosen to examine the fouling potential of inorganic particles. The nanoparticle concentrations ranged from 10^4 to 10^9 particles/mL. Previous examinations of polystyrene nanoparticles with NPA/LIBD and ESEM had shown that nanoparticles did not agglomerate in feed solutions for the SUMF.

2.4. Natural waters

In order to assess the fouling potential of natural waters the SUMF was operated with waters of different origin and biochemical composition (Ca^{2+}, NOM), also with regard to physical parameters like turbidity, UV absorption at 254 nm and colour (UV absorption at 436 nm). Turbidity was measured according to DIN EN 27027 with a turbidimeter (Nephla, HACH-LANGE GmbH, Düsseldorf, Germany). The UV absorption at 254 and 436 nm was determined with a spectrophotometer (CADAS 200, HACH-LANGE GmbH, Düsseldorf, Germany) using 10 and 50 mm quartz cells.

3. Results and discussion

3.1. Artificial waters

About 40 test runs were carried out in which the SUMF was operated with artificial waters spiked with polystyrene or magnetite particles with differing size and concentration. In one test run UPW was spiked with different quantities of 25 nm polystyrene nanoparticles in order to obtain different feed concentrations. The test run started with a concentration of 1.2×10^5 particles/mL in the feed and was increased gradually up to 1.2×10^7 particles/mL. As shown in Fig. 2 the permeability steadily decreased with increasing specific throughput. From this follows that particles gradually blocked the membrane pores. However, there were not yet enough particles to block the membrane completely as the slope of the decrease of permeability seems to be independent of the applied feed concentration. At a specific throughput of 10.5 m^3/m^2 the dosage of nanoparticles was stopped and the SUMF was operated with UPW resulting in a constant permeability for the time of operation. There

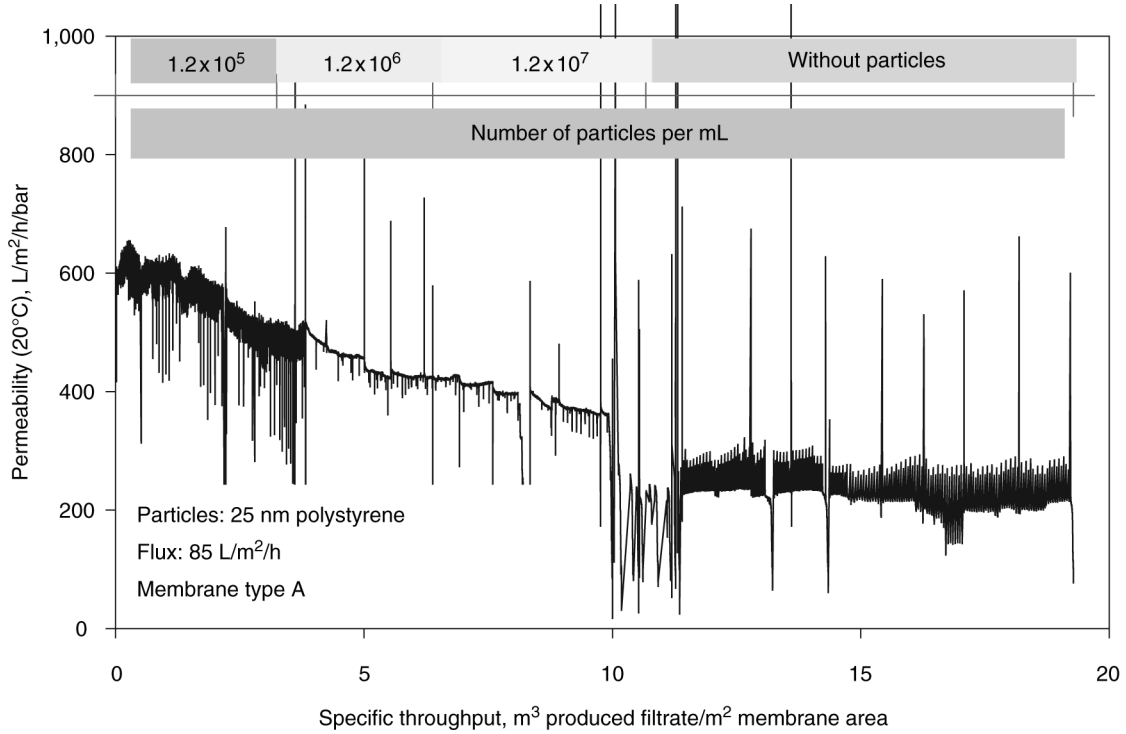


Fig. 2. Permeability decrease caused by nanoparticles of the same mean diameter but different concentration in the membrane feed.

was no backwash of the membrane which means that all particles deposited on the membrane surface during the beginning of the test run remained there. Though there was no further blocking by nanoparticles during the filtration of UFW the water flow was still hindered by these particles. It can be concluded from these experiments that the concentration of the feed solution seems to have only a minor influence on particulate fouling of low-pressure membranes in the tested range.

In order to examine the influence of the particle size on membrane fouling, different feed solutions were prepared using 25 nm polystyrene particles alone and in a mixture with 100 nm. Moreover, magnetite particles with sizes of 130 nm and 250 nm were also taken into account. As shown in Fig. 3, 25 nm polystyrene particles alone showed the highest increase of the transmembrane pressure during the operation of SUMF. Combining the 25 nm with 100 nm particles in the feed solution surprisingly caused a lower increase of TMP compared to the 25 nm particles alone. The lowest increase of TMP was found for the inorganic magnetite particles. Also in this comparison, the smaller 130 nm particles lead to more fouling than the larger 250 nm particles. From these experiments it may be concluded that increasing the particle size in the feed will lead to a decreased fouling potential because of the presumably lower packing density of the deposited fouling layer on the membrane surface. Moreover, particle size will have a higher influence on particulate fouling than particle concentration, at least in colloidal dimensions. This finding is in agreement with experiences from full scale membrane filtration plants: Shock loads of larger inorganic particles can be better handled (i.e. they have a smaller fouling effect) than shock loads with organic substances.

Since artificial waters as described above do not contain any other compounds than particles, their effect on membrane fouling can be more precisely investigated and quantified. This is of particular benefit since the

Table 2
Results of NPA/LIBD and SUMF measurements with artificial waters (experiments with membrane type A).

Water origin	Mean particle diameter nm	Concentration µg/L	Slope of TMP-increase h^{-1}
Ultra pure water (UPW)	12	0.05	0.01
UPW with polystyrene particles	20	-	0.02
SUMF filtrate	21	0.24	0.01

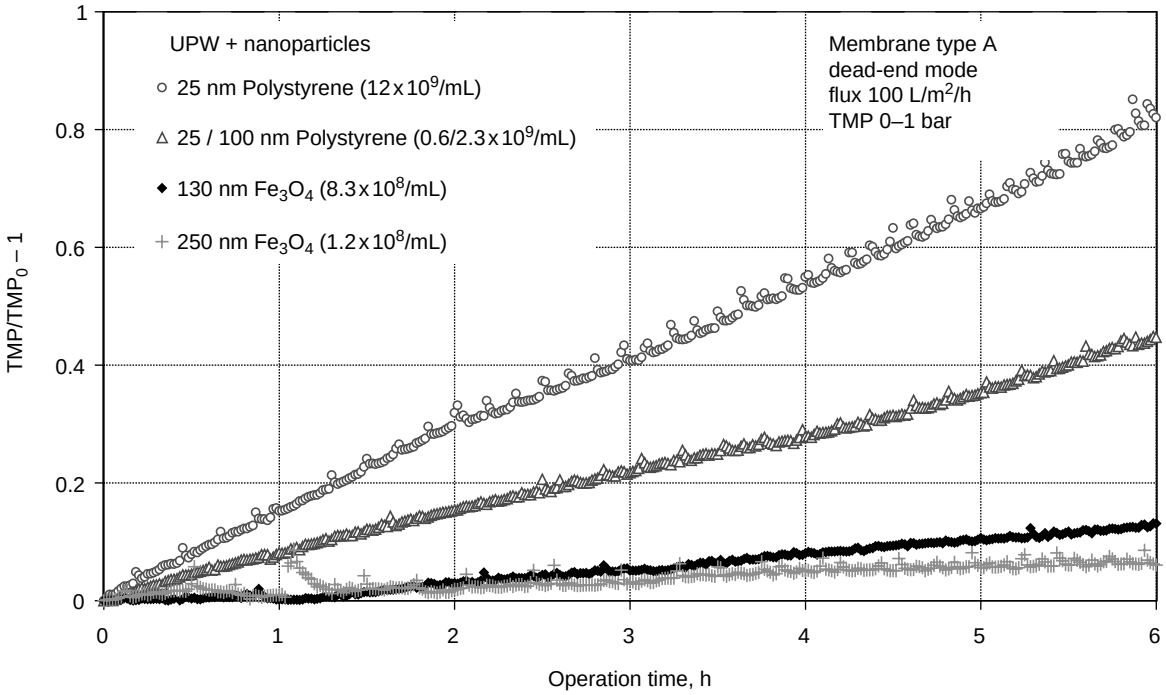


Fig. 3. Effect of size and concentration of nanoparticles on the TMP increase.

Nano-Particle Analyzer based on LIBD (NPA/LIBD) does not distinguish between artificially added particles and natural water content; in the latter case the NPA/LIBD measurements need to be thoroughly interpreted.

3.2. Natural waters

The SUMF was operated with different natural waters including untreated dam water as well as dam water after different treatment steps. The natural waters were characterized by NPA/LIBD with regard to the mean diameter and the concentration of natural nanoparticles. As shown in Table 3, particles sizes in the natural waters used in this study ranged from 20 nm to 300 nm while the concentrations were quite different. In order to quantify the influence of particle size on the fouling potential, a normalized transmembrane pressure ($TMP/TMP_0 - 1$) increase was determined. The results indicate that particles larger than 100 nm tend to cause a smaller TMP increase (slope < 0.2 h^{-1}) compared to smaller particles which caused a higher TMP increase (values > 1 h^{-1}). However, it can also be seen that particulate fouling is superimposed by other fouling processes. For this interpretation chemical composition of the waters is given in Table 4. If NOM was removed that is UV-254 is decreased by coagulation-filtration the resulting water was less prone to fouling, resulting in lower rates of TMP increase (0.04 h^{-1}). This observation is also well-known from large-scale UF plants treating surface waters [1, 2, 15, 16].

Table 3
Results of NPA/LIBD and SUMF measurements with natural waters of different origin and after different treatment steps (experiments with membrane type A).

Water origin	Mean particle diameter nm	Concentration µg/L	Slope of TMP increase h^{-1}
SUMF filtrate	21	0.24	0.01
a) After rapid sand filtration	40 ± 9	127 ± 13	1.30
b) After conventional filtration	76 ± 28	11 ± 4	0.11
c) Reservoir water	100 ± 22	256 ± 9	0.20
d) Prefiltered water + ozone + coagulant	208 ± 14	955 ± 189	0.04
e) Untreated spring water	285	1370	0.17

Table 4
Chemical composition of waters from Table 3.

Water origin	Electrical conductivity mS/m	Turbidity NTU	UV-254 m^{-1}	VIS-436 m^{-1}
SUMF filtrate	4	0.01	-	<0.1
a) After rapid sand filtration	4	0.30	6.5	0.3
b) After conventional filtration	4	0.02	1.6	<0.1
c) Reservoir water	4	0.6	6.8	0.3
d) Prefiltered water + ozone + coagulant	4	1.3	1.1	<0.1
e) Untreated spring water	19	6.9	2.8	0.4

Table 5
Membrane breakthrough of polystyrene nanoparticles during filtration of artificial waters determined by means of NPA/LIBD (experiments with membrane type A and B).

		Feed		Filtrate		
Membrane	Mean particle diameter nm	Particle number #/mL	Concentration* µg/L	Particle number #/mL	Concentration* µg/L	Rate of breakthrough** %
A (UF)	21	$1.2 \cdot 10^9$	6.1	$0.6 \cdot 10^8$	0.3	5
	21	$0.5 \cdot 10^9$	2.5	$4.1 \cdot 10^8$	2.1	84
B (MF)	46	$1.2 \cdot 10^9$	64.4	$1.6 \cdot 10^8$	8.5	13
	73	$1.2 \cdot 10^9$	257.4	$0.1 \cdot 10^8$	2.6	1

*The mass concentration is calculated from the particle number and the particle volume (derived from the particle size) by using a density of polystyrene of 1.05 g/cm^3.
**Rate of breakthrough = filtrate particle number/feed particle number.

Compared to the natural waters used as feed solution the SUMF filtrates are characterized by considerably smaller particle sizes and lower particle concentrations. If the SUMF filtrate was used as feed in a subsequent SUMF experiment, then no TMP increase was observed within the experimental time frame. So obviously the most active fouling components had been removed in the first run; these may have been natural organic matter (NOM) or also biological material. Further experiments in this direction should be carried out to learn more about the selective removal efficiency for components of natural water. Nonetheless, it can be summarized that SUMF filtration experiments can predict the fouling behaviour of raw waters to be treated in MF/UF plants reasonably well and within a beneficially short period of time.

3.3. Particle breakthrough

By means of NPA/LIBD online analysis it is easily possible to determine the particle removal efficiency of membranes during filtration. It could be shown in repeated experiments (see Table 5 for detailed results) that small particles (21, 46 and 73 nm) were not totally removed by membranes of type B. This was expected since type B was specified as a MF membrane with a pore size of approximately 0.1 µm. Particles larger than 100 nm were totally removed, which proves that NPA/LIBD is a suitable tool to quickly determine the membrane cut-off in this pore size range. Membrane type A, which was a UF membrane with a molecular weight cut-off of 100 kD corresponding to a pore size of approximately 20 nm, was capable of removing particles as small as 20 nm with high efficiency (Table 4).

Additionally to the experiments with artificial waters a particle breakthrough has also been detected with natural waters. In SUMF filtrates of membrane type A a mean nanoparticle size of 20 nm has been measured regardless of the type of water used for filtration. As NPA/LIBD is able to quantify nanoparticles in natural waters in the range of 20 to 300 nm as shown in Table 3 it is assumed to be able to also detect particle breakthrough caused by defects in the membranes. This may be a chance to use this method as an online monitor for UF membrane integrity. Up to now no such method is available for such purpose [17, 18]. However, further research has to be carried out to prove this.

4. Conclusions

Low-pressure membranes are prone to fouling by particles and other constituents of the feed water causing an increase of TMP over time. SUMF experiments are a simple and practical tool to get an idea of the fouling potential of raw water independently of the mechanism responsible for the permeability decline.

Studies with artificial waters have shown that small particles (e.g. 25 nm) cause a stronger fouling effect than larger particles (e.g. > 100 nm) of the same nature. Additionally, a particle breakthrough was detected by NPA/LIBD online measurements of MF/UF filtrates, showing that the NPA/LIBD method may be a promising tool for an effective online monitoring of the integrity of UF/MF membranes.

In natural waters additional factors contribute to fouling. This includes organic substances such as polysaccharides or natural organic matter (mostly humic acids); depending on the exact composition and particle size distribution, organic fouling may mask particulate fouling. Application of both NPA/LIBD for the quantitative characterization of the nanoparticle content and other tools such as (LC-OCD) analysis (Liquid Chromatography-Organic Carbon Detection) for an improved qualitative characterization of organic fouling may further advance the understanding of how to reliably assess the fouling potential of raw waters.

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