



Separation, Preconcentration and Spectrophotometric Determination of Rhodamine B by using Cloud Point Extraction coupled with Magnatic Solid Phase Extraction

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Abstract

The aim of this study is extraction, preconcentration and spectrophotometric determination of Rhodamine B (RhB) in aqueous media by developing cloud point extraction (CPE) methods and magnatic solid phase extraction (MSPE). The method includes extraction of the Rhodamine B (RhB) by CPE using a non-ionic surfactant Triton X-114; then stearic acid modified Fe₃O₄ magnetic nanoparticles (MNPs) are used to retrieve the micellar phase. Parameters of CPE and MSPE which effected quantitative extractions were investigated and optimized. the method was linear in the range from 10 to 100 µg Kg⁻¹ with the correlation coefficient (R²) of 0.9861 and detection limit of 9.952 ng g⁻¹.

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KeyWords: the dye Roamine-B, FeCl₂.4H₂O, FeCl₃.6H₂O, Stearic Acid

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Introduction

Dyes are organic compounds that can be used to color fibers. Dyes can be divided into fungal and synthetic. Synthetic dyes are human-made dyes, prepared from other sources such as petroleum based on crude oil, earth minerals and various chemicals. Synthetic dyes are very common used in the textile industries. Because its color is flexible and improves stability[1]

Rhodamine B (RhB) is a derivatives of xanthene dyes.[2] is widely used in many industries such as textiles, leather and food. However, this is a highly toxic colorant that exhibits carcinogenic and mutagenic behavior to any living species.[3] In addition to its use in the dyeing industries, Rh-B in combination with Uramine-O (basic dye) is widely used as biological stains in biomedical research laboratories as well as in the dyeing of leather and paper. but due to their low cost and high effectiveness, these harmful dyes are still used by immoral manufacturers. Therefore, a reliable and sensitive method is directly needed for the simultaneous determination of RhB in various food testers and aquatic environment[4,5], A assortment of analytical methods have been suggested for this purpose, such as voltammetric[6,7] high-performance liquid chromatography[8] electrochemical[9], fluorescence spectrophotometry[10,11] and visible spectrophotometry[12,13]. the traditional chemical separation procedure, such as solid phase extraction (SPE)[14], dispersive liquid-liquid microextraction (DLLME)[15], Supramolecular Solvent Microextraction[16] , and cloud point extraction (CPE)[17,18] has been used to simultaneously detect many analytes. Separation and preconcentration based on CPE are becoming an important and practical application of surfactants in analytical chemistry[19,20] In this work, we combine the advantages of the CPE procedure and MSPE procedure for simultaneous spectrophotometric determination of trace amount of Rhodamine B.

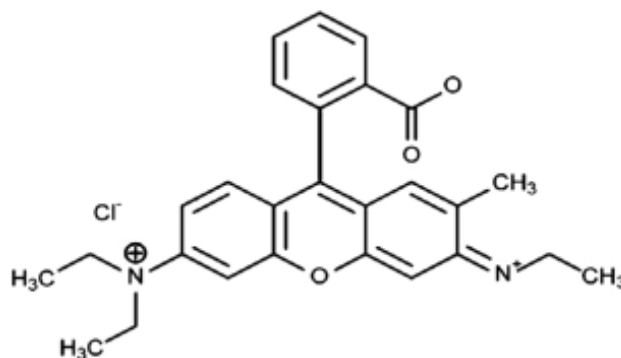


Figure 1. Structure of Rhodamine-B dye.

Experimental:

Apparatus

Jasco 7850 UV Visible Spectrophotometer with 1 cm (0.5 mL) quartz cell was used to record the absorption spectrum and absorption measurements. A 3D device (4000 rpm, UromAzma Corporation) was applied to accelerate the phase separation process. Metrohm 632 pH meter was used with integrated glass pH electrode Measurements All measurements were made at the University of Al-Qadisiyah.

Chemicals and instrumentations

In this study, no further purification was required in all chemicals and reagents. Brilliant green dye (MF = C₂₈H₃₁N₂O₃Cl M.wt = 479.02 g mol⁻¹, Melting point 484K , dye purity ≥ 90%, approved by the Biological Spots Committee) was obtained from Sigma-Aldrich. 0.1g of dye was weighed and dissolved with 10ml of ethanol in a 100ml volumetric vial and the volume was completed with distilled water to dissolve the amount of dye needed to prepare a stock solution of 1000mg/L BG. Distilled water was used throughout this study. For absorbance of BG dye solutions, a Shimadzu UV-1601PC spectrophotometer set at wavelength 558 nm was used for measurement.

Synthesis of steric acid modified MNPs

Fe₃O₄ nanoparticles were prepared using a simple chemical. Where 5.8 g of FeCl₃.6H₂O and 2.1 g of FeCl₂H₂O were mixed in a triple vacuum flask under nitrogen atmosphere, the mixture was dissolved in 100 ml of deionized distilled water with stirring mediated by a magnetic



stirrer and using a hot plate at 80 °C, then 20 ml was added ml of ammonia solution gradually to the mixture through a burette for 15 minutes, then the solution is poured into a 250 ml beaker where it is washed several times with distilled water to get PH = 7 and after washing it was placed in the oven at a temperature of 50 °C for 6 hours for the purpose of It was dried, and after the drying process it was coated with stearic acid, where every 2 g of nano-material was coated against 1 g of stearic acid by mixing and grinding it into a powder of nano-material coated with acid.

Recommended extraction procedure

In a test tube of volume 10 ml, 2 ml of dye (RB) solution with a concentration of 10 mg/L was taken and 2 ml of the surfactant Triton X-114 was added to it and 1 ml of buffer solution with pH = 3 was added and the volume was completed with distilled water free of ions at the mark limit. It was placed in a water bath at a temperature of 50 °C for 5 minutes until it formed a turbidity and then the test tube was placed in the centrifuge for 5 minutes until the organic layer was separated from the aqueous layer. Then the organic layer was taken and the nanomaterial 0.05 g was added to it. It was placed in sonication for 5 minutes, then the nanomaterial was withdrawn by a magnet and 2 ml of ethanol was added to it and placed in the sonication for 15 minutes, and the absorbance was read for it at the wavelength of 558nm. In the same way, the plank was prepared, but without the presence of dye.

Result and discussion:

Fourier transform infrared (FTIR) spectroscopy for magnetism and ferromagnetism with stearic acid.

When measuring the FTIR of the nanomaterial (Fe₃O₄) before encapsulation, the spectrum was obtained as shown in Figure (1) by taking a sample of the uncoated nanomaterial and using the KBr potassium bromide disc method within the range of positive numbers Cm-1 (4000 - 400). Figure (1) shows the FTIR data for the nanomaterial (Fe₃O₄) as shown

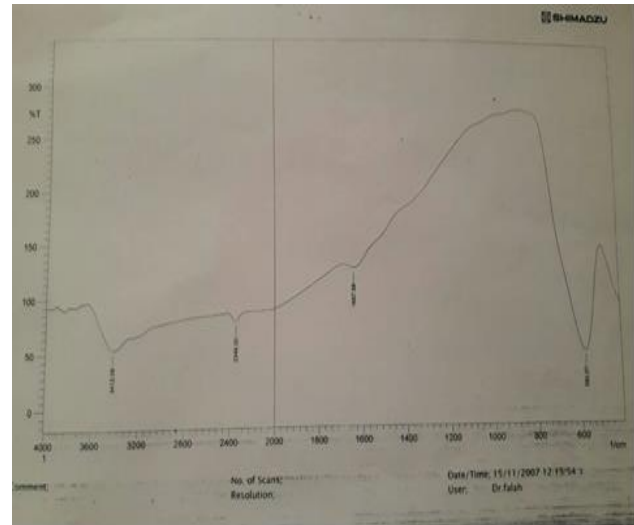


Figure 1 Infrared spectrum of iron nanoparticles before encapsulation

Table (1) Infrared Spectrum Data (400 - 4000) Cm-1 for Fe₃O₄

IR Bond	Wave Number(Cm-1)
O-H	3022
CO ₂	2340
Fe-O	580

6447

The infrared spectrum of the FTIR scale composed of iron oxide with fatty acids shown in Figure 4 showed a broad band in the range 3022 cm⁻¹ where this band is due to the stretching vibrations (O-H) within the carboxyl group, in addition to the appearance of a peak in the range of 1703.14 cm⁻¹, due to the (C=O) bond stretching vibration of the carboxylic group, the appearance of peaks between 2918.30 - 2854.65) cm⁻¹ due to symmetric and asymmetric stretching vibrations of the (-CH₂) group, and the appearance of peaks in the range 1456.26 cm⁻¹ due to bending vibrations (-CH₃) and (-CH₂) have an aliphatic group. Also, the appearance of the peak in the -1111,1 cm⁻¹ range is due to distorted vibrations (-CH) and (CH) grouping of the acid. For the bands that appeared in the range-1 cm 680.78-551.64, they indicate the Fe-O bond of the repaired compound.



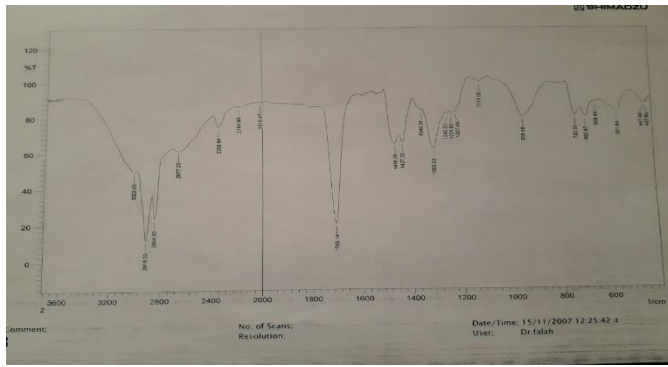


Figure 2 FT-IR Fe2O3 form coated with Stearic acid

Table (2-) Infrared Spectrum Data (400 - 4000) Cm-1 for stearic acid modified Fe3O4 magnetic nanoparticles

IR Bond	Wave Number(Cm-1)
O-H	3022
C-O	1703.14
CH2-	2854.65
CH2- و CH3-	1456.26
(CH- Stearic acid) و CH-	1111.00
Fe-O	551.64-680.78

The infrared spectrum of the FTIR scale composed of iron oxide with fatty acids shown in Figure 4 showed a broad band in the range 3022 cm⁻¹ where this band is due to the stretching vibrations (O-H) within the carboxyl group, in addition to the appearance of a peak in the range of 1703.14 cm⁻¹, due to the (C-O) bond stretching vibration of the carboxylic group, the appearance of peaks between 2918.30 - 2854.65) cm⁻¹ due to symmetric and asymmetric stretching vibrations of the (-CH₂) group, and the appearance of peaks in the range 1456.26 cm⁻¹ due to bending vibrations (-CH₃) and (-CH₂) have an aliphatic group. Also, the appearance of the peak in the -1111,1 cm⁻¹ range is due to distorted vibrations (-CH) and (CH) grouping of the acid. For the bands that appeared in the range-1 cm 680.78-551.64, they indicate the Fe-O bond of the prepared compound.

scanning electron microscope(SEM)

An analytical technique used to determine the surface appearance and particle size of prepared samples. Figure(3)shows the SEM analysis of Fe₃O₄ iron oxide nanoparticles if irregular

spherical shapes are observed with a clear increase in the partial accumulation rate. While Figure (4) complex (Fe₃O₄, stearic acid) shows the presence of heterogeneous nanoshells with irregular distribution resulting from the synthesis of iron oxide by stearic acid. The increase in the rate of aggregation of particles indicates the success of the physical bond due to iron oxide with stearic acid. The average particle size of the superimposed iron oxide is 50 nm and 70 nm, respectively. The interpreted results are similar to a set of previous studies.

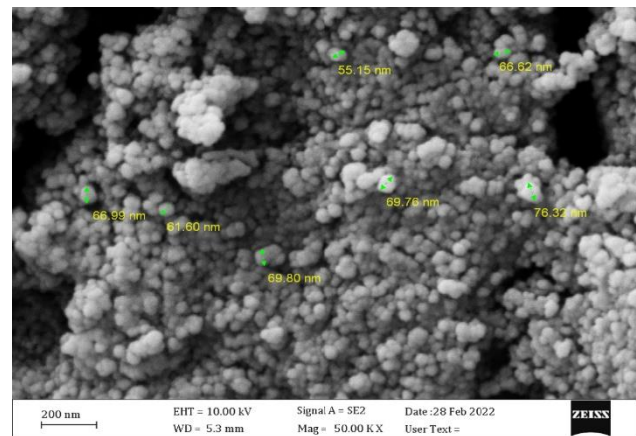


Figure 3 SEM analysis of Fe₃O₄ . iron oxide nanoparticles

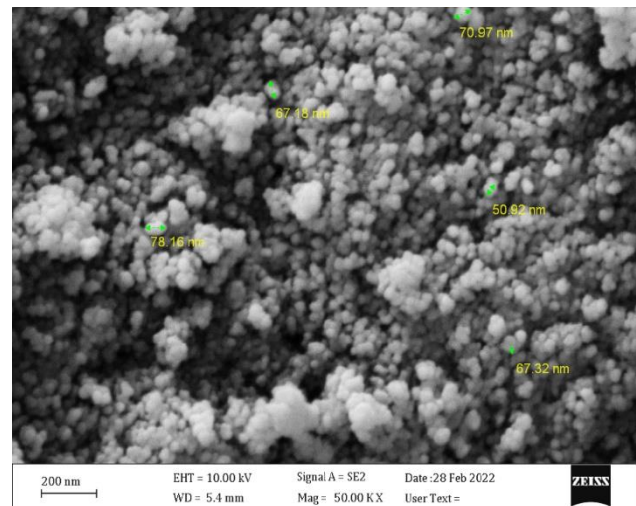


Figure 4 Compound Fe₃O₄, Stearic Acid

Absorption Spectra of Rhodamine-B

The UV-visible spectrum of Rhodamine-B was measured at a concentration of 10ppm, and it was noted from Figure (5) that the highest absorption of Rhodamine-B dye at the wavelength (558nm).



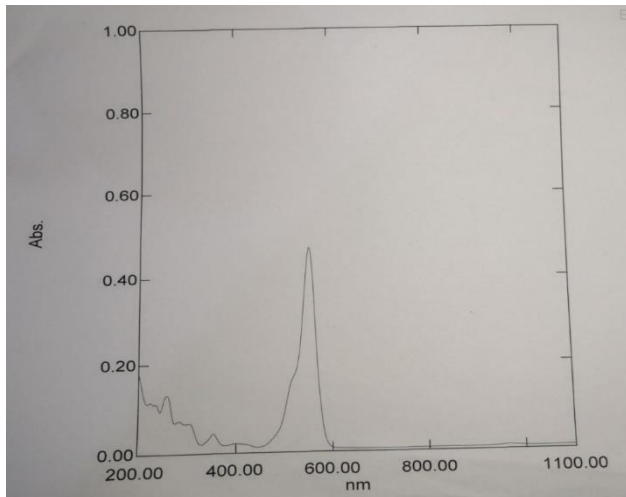


Figure 5 VIS-UV spectrum of rhodamine-b dye

Effect of the type of surfactant:

The effect of partridge, surfactants on the absorbance of the organic layer extracted from the dye was studied. Surfactants (Teween80, Teween20, TritonX-100, TritonX-114, SDS, CTAP) were used. The results are shown in Figure 8. As shown in Figure 8, where The surfactant TritonX-114 gave the highest absorbance for the extracted organic layer. Therefore, TritonX-114 was chosen as the optimum pH for the absorption of the dye by the organic layer at the wavelength of the largest absorption = 558 nm.

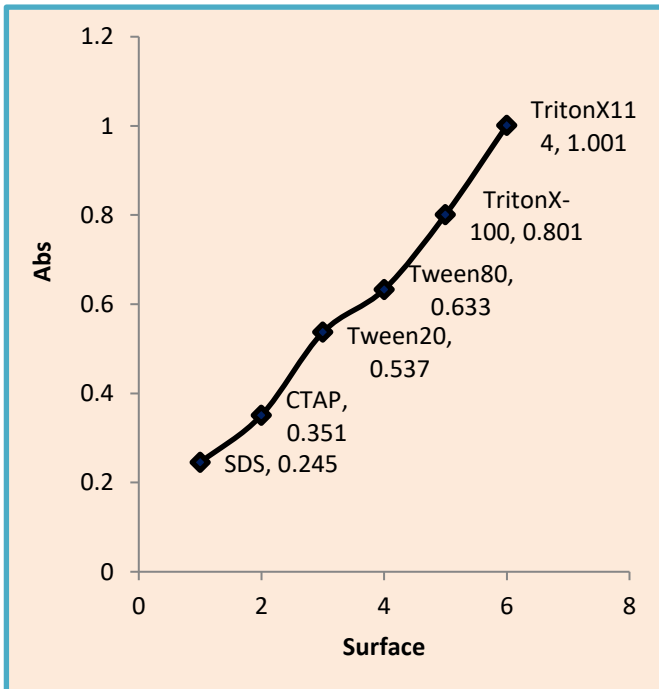


Figure 6 Extraction solvent type

Effect of the (PH)

The effect of “pH in the range” 2 to 9 “was studied using different pH acetate buffer solutions. The results are illustrated in Fig. 7. As can be seen from Figure 7, the absorption first increased with increasing pH and reached a maximum of pH 3.0 Subsequently, the absorption decreased due to “partial dissociation of higher pH”. Therefore, pH 3.0 was chosen as the optimum pH for the adsorption of the organic layer of the dye for it at the wavelength of the greatest Absorption max = 558nm.

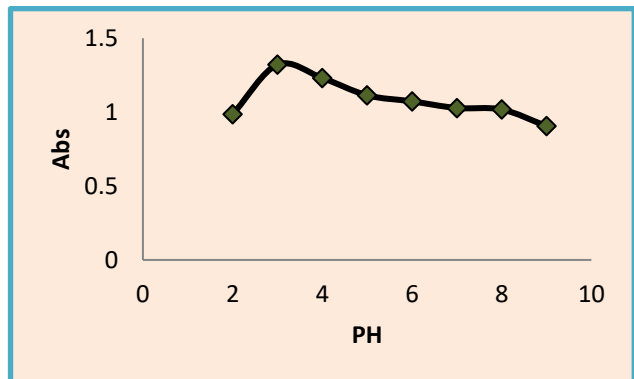


Figure 7 Effect of pH on the adsorption of the organic layer of berlint dye [Conditions: 1 ml of dye, 2 ml of Triton X - 114 PH solution= 3]

Effect of time:

The ideal time that provides the ideal condition for measuring the absorbance of The effect of the “time effect in the range” from 2 to 10 was studied using Triton X-114 solution and the results are illustrated in Figure 8. As can be seen from Figure 8, the absorption first increased with increasing time, reaching a maximum of 5 minutes. Subsequently, the absorption decreased due to the “upper time partial dissociation”. Therefore, the time 5 min was chosen as the optimal time to measure the absorbance of the organic layer extracted from the dye at the wavelength of maximum absorbance = 558nm.



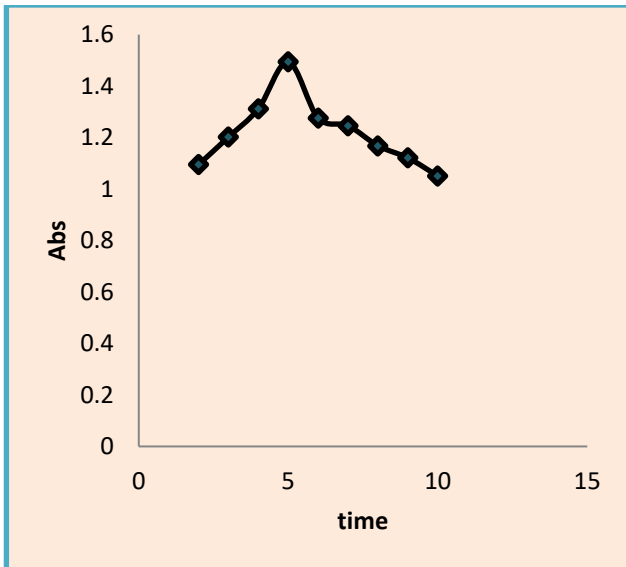


Figure 8 Effect of time on the adsorption of the organic layer of perlint dye [Conditions: 2 ml of dye, 2 ml of Triton X - 114 solution pH 3, time 5 minutes].

Effect of temperature

The effect of temperature in the range from 30 to 100 °C was studied using solutions of dye and Triton X-114. The results are shown in Fig. 9. As shown in Fig. 9, the absorption increased first with increasing temperature and reached a maximum temperature of 50. After That is, the absorption decreased due to “higher temperature partial dissociation.” Therefore, the temperature of 50 °C was chosen as the optimum layer of the dye for it at the wavelength of the largest absorption =558 nm.

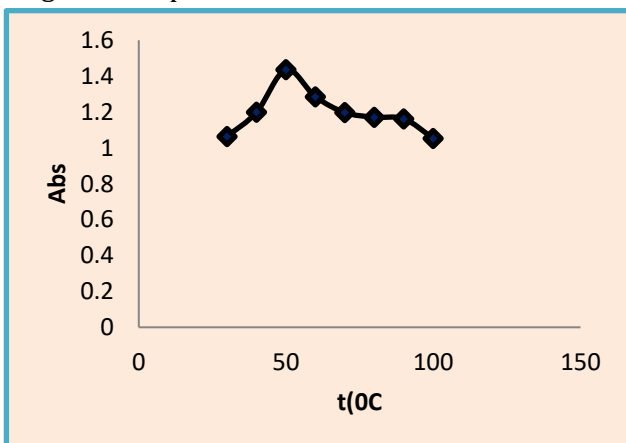


Figure 9 Effect of temperature on the adsorption of the organic layer of pearlescent

dye [Conditions: 2 ml of dye, 2 ml of Triton X - 114 solution pH 3, and temperature. 50 ° C, time 5 minutes].

Effect of the amount of nanomaterial:

The effect of the amount of nanomaterial on the adsorption of organic matter extracted from the dye was studied using dye solutions and Triton X-114. The results are shown in Figure 10. As shown in Figure 10, the absorbance increased first with the increase in the amount of nanomaterial added, with a maximum absorbance of 0.05g. Therefore, the amount of nanomaterial added 0.05g was chosen as the optimum amount for the absorption of the organic layer of the dye at the wavelength of the largest absorption = 558 nm.

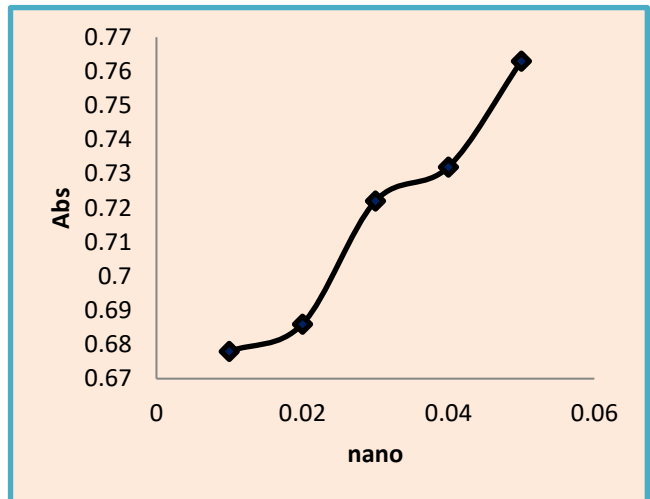


Figure 10 Effect of the amount nanomaterial on the adsorption of the organic layer of the dye [Conditions: 2 ml of dye, 2 ml of Triton X - 114, solution pH 3, and temperature. 50 ° C, time 5 minutes, when using 0.05 g of nano-material].

Analytical performance of the optimized method

Under the experimental conditions, the calibration curve was linear over the concentration range of 10-100 µg Kg-1 with R2 of 0.9861. Solutions for the construction of calibration curve were prepared by spiking appropriate amounts of RhB working solutions and subjected to the proposed CPE-MSPE procedure following the enhanced measurements. The limit of detection (LOD=3.3Sb/m, where Sb is the standard



deviation of replicate measurements of blank solution and m is the slope of the calibration curve) was found to be 9.952 ng g⁻¹.

Conclusion

The combination of (CPE) and - Stearic acid modified Fe₃O₄ - MSPE was effectively used as a capable sample pretreatment procedure for extraction and determination RhB dye The analytical method has many benefits, including small organic solvent feasting ,acceptance of operation and high pre-concentration component, Additionally, the style has ability for the detection of RhB dye traces in different samples

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