TREATMENT OF OYSTER SHELLS AND PREPARING THEM AS AN ADSORBENT SURFACE TO TOLUIDINE BLUE DYE

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ABSTRACT

The presence of dyes in drainage water is one of the important problems that many seek to solve. This study included the preparation of the adsorbent surface using the oyster shells as a basis for the preparation of chitosan, which is a series of carbohydrates and saccharides, by treating them with some simple chemical reactions that grab the acetyl group (de-acetylation), which is a part of the structure of chitin. Then the basic formula of Chitosan is ready to carry positive charges, which act as magnet to attract molecules of any substance beside it. A series of assays were undertaken to assess the efficiency of the adsorption process, such as the weight of oyster shells, equilibrium time, effect of pH, initial concentration of toluidine blue dye, and particle size of the adsorbent. These experiments have shown that the equilibrium time was 120 min, the optimum weight of oyster shells was 0.1 g in 100 mL of dye solution, and the particle size was 150 µm. They also showed there is an effect of the pH on the adsorption of the dye. The adsorption isotherm was well fitted to both the Freundlich and Langmuir models.

Keywords: adsorption, Langmuir model, Freundlich model, toluidine blue, chitosan, oyster shells.

INTRODUCTION

Oyster is a marine animal that belongs to the division of echinoderms and lives in coastal regions and oceans characterized by warm or temperate climates where its shells are glued to the solid bodies found in the sea and ocean bottoms and the sea rocks. The oyster's body is surrounded by a bivalve shell and feeds on organic granules and primitives, and it is known that the vast majority of its kinds live in shallow coastal waters. It is an useful seafood for humans, as it contains mineral salts such as zinc, calcium, phosphorus, iron, manganese, sodium, and potassium, which is why it is an expensive food. And it should be noted that oysters are a source of pearls, which are formed when an interloper, such as a grain of sand, glides in between one of the two shells of the oyster and the protective layer that covers it by secreting calcareous material around them so as not to affect it and turn into pearls [1 - 4]. Chitin, a polyacetylglucosamine with huge functional groups including acetyl amino, primary amino, and the hydroxyl group that have significantly higher adsorption capacities, is the principal main constituent of oyster shells. Moreover, several linear amino sites on every glucose circle of chitin make it simple for the doublet electron pair to join metal ions [3]. A chitin derivative known as chitosan [beta-(1,4)-2-amino-2-deoxy-D-glucose] has been created for a variety of uses, including as an absorbent. Chitosan-based material, which serves as a process to remove numerous oyster shell piles that not only take up land but also induce a multitude of environmental and cleanliness issues, such as mosquito larvae, a strong smell, and poor drainage is more appealing for use as a sorbent compared to other

existing biopolymers [5 - 8].

Due to their ability to prevent light from penetrating, dyes discharged by industry into natural water bodies seriously harm the environment by interfering with biological processes. Moreover, there are numerous poisonous dyes for some organisms that cause the extinction of water groups. The numerous methods include biological processing, coagulation, flotation, adsorption, and oxidation to eliminate colors from industrial wastewaters. Adsorption tends to have the most potential for removing it from industrial wastes among the alternative treatments [9 - 13]. Toluidine blue (TB) is regarded as a natural dye, which is described as a coloring compound produced from naturally occurring resources of either plants or animals. While charcoal and petroleum are the two primary materials used in industrial production [14]. Toluidine blue, also known as 7-amino-8-methylphenothiazin-3-ylidene)-dimethyl ammonium chloride, is a cationic thiazine pigment of the phenothiazine class used in the lab to kill certain microorganisms by activating lighting. The structural formula is shown in Fig. 1, and it is used as an electron receptor assay for pneumonia coating in healthy lungs [15].

Adsorption is a separation method, especially for the ones that can't be done with classic methods such as distillation and absorption, in which a substance dissolved in a liquid is deposited on the surface of another solid substance named an adsorbent. The removal of impurities from wastewater, particularly utilized in industrial applications, is one of the most significant applications of the adsorption technology [16, 17]. There are various models that can be used to explain the adsorption mechanism [18].

This is the first study to evaluate the viability of using oyster shell as a technique to remove TB dye through thermodynamic and kinetic experiments. The effectiveness of oyster shell as an adsorbent for TB dye was examined. TB adsorption as a function of pH, temperature, the starting amount of TB dye, and adsorbent particle size has been also studied.

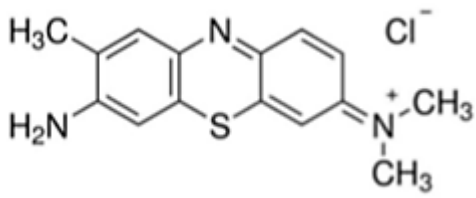


Fig.1. (7-amino-8-methylphenothiazin-3-ylidene)-dimethyl ammonium chloride) TB dye.

EXPERIMENTAL

Apparatus

Shimadzu UV-Vis spectrophotometer (1650 PC) was used in spectral studies. Also, pH-meter (WTW3), Electric shaker (Barnstead International), Sensitive analytical balance with four decimal places (Denver Instrument), and Heater (Ardeas 51) were used.

Preparation of the adsorbent (Oyster shells)

The process of preparing the surface of the adsorbent begins by taking samples of oyster shells from the bank of the Euphrates River overlooking the Al-Hashemite area in the city of Hilla. The samples were cleaned up, the oyster's body inside was removed, and they were washed with warm water for half an hour to get rid of mud and other plankton, then washed with distilled water and dried by exposure to the sun for 6 hours, and then they were crushed with a special rock grinder. After the grinding process, the powder of the oyster shells is treated with the following chemicals and several steps:

- Deproteinization: This step involves boiling the powder in a solution prepared from 3 % NaOH for 60 min. It takes 1 g of the powder to make 10 mL of the prepared sodium hydroxide solution (1:10, w/v) and then washing the model with distilled water.
- Demineralization: The powder is placed in a solution of acid (1 N HCl) for 30 minutes at room temperature in 1g to 15 mL of prepared acid solution (1:15, w/v), and then the form is washed with distilled water.
- Deacetylation is the process of converting chitin to chitosan by removing the acetyl group. This is achieved by adding a NaOH solution (40 - 50 %) usually at 100^{o}C or higher for 30 min to remove the acetyl groups from the polymer, which is 1 g of the powder to 10 mL of the prepared NaOH solution (1:10, w/v). Then it is washed with distilled water and dried. In the last step, the adsorbent is separated into different grain sizes using special sieves. Fig. 2 illustrates the synthetic form of chitin and chitosan, which was prepared after removing the acetyl groups.

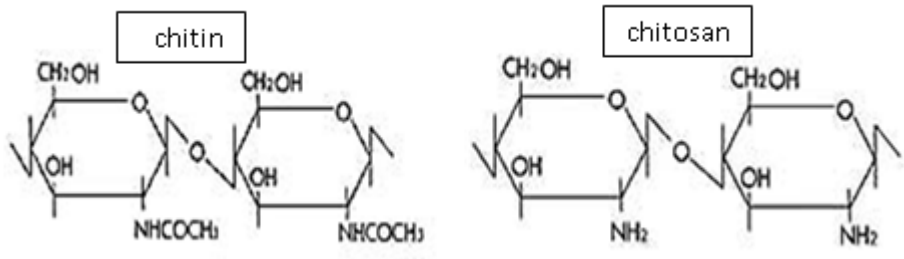


Fig. 2. The structural formula of chitin and chitosan.

Preparation of the adsorbate

The parameters of the dye are shown in Table 1 after 1 g of TB dye has been dissolved in 1000 mL of distilled water to create the stock solution of 1000 mg L^{-1}. Hydrochloric acid (0.1 M) or sodium hydroxide (0.1 M) solutions are used to adjust pH.

Batch equilibrium and thermodynamic studies

The equation 1 was used to determine the quantity of TB dye adsorbed onto the oyster shell powder (mg g^{-1}):

$$q_e = (C_\circ - C_t) \times m / V \quad (1)$$

where q_e corresponds to the quantity of dye absorbed on the adsorbent mass (mg g^{-1}); Co and Ct (mg L^{-1}) are the initial and equilibrium TB dye concentrations in the aqueous medium, respectively; V (L) is the solution's volume; m (g) is the adsorbent mass.

The well-known Freundlich and Langmuir models are used to describe the distribution of the compound studied between the liquid and the adsorbent, which is a measurement of the adsorption equilibrium, (Eq. 2).

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (2)$$

where q_e is the amount adsorbed in milligrams per gram of absorbent at equilibria; q_m is adsorption capacity maximum (mg g^{-1}); Ce is the dye concentration at equilibrium; K_a is the equilibrium adsorption coefficient.

The sorption of black tea is monitored via the Langmuir isotherm model, as shown by the plot of C_e/q_e against Ce as shown in Eq 3.

$$\frac{C_e}{q_e} = \frac{1}{q_e K_a} + \frac{C_e}{q_m} \quad (3)$$

Table 1. Physical and chemical characteristics of the TB dye.

Parameter	Value
Molecular formula	$C_{15}H_{16}ClN_3S$
Molecular mass	305.82 g mol^{-1}
C.I. Name	52040
Absorption maxima	590 nm
Nature	Salt-free dye

A dimensionless constant called the equipoise factor, denoted by the letters RL [19, 20], is discernible through Eq. 4.

$$R_L = \frac{1}{1 + bC_o} \quad (4)$$

where b is Langmuir constant; C_o is initial concentration.

The value of RL indicates whether the line's outline is unavailing (RL >1), linear (RL = 1), positive (0< RL<1), or irreversible (RL = 0).

The sorption of TB through oyster shells was also functionally accomplished by the Freundlich model [21], (Eq. 5).

$$\log q_e = \left(\frac{1}{n}\right) \log C_e + \log K_f \quad (5)$$

Freundlich factors, also known as K_f and n, offer an idea of the vantage and K_f[mg g^{-1}(L mg^{-1})1 n^{-1}]. In the linearized form (Eq. 5) n is found from the slope of the line and K_f- from the intercept from the y-axis.

RESULTS AND DISCUSSION

Calibration Curve

The varied quantities of TB dye solutions in the range of 0.5 - 35 mg L^{-1} were created after measuring at λ_{max}= 590 nm. The calibration graph of the TB dye and correlation coefficients (R^2 = 0.9985) were provided while measuring the absorbance values of the various concentrations at the maximum value λ_{max}, Fig. 3.

Determining the optimum conditions

Impact of the oyster shells' mass

A collection of masses in the range of 0.1 - 1.5 g in 100 mL of dye at a quantity of 100 mg L^{-1} of dye were used to study the impact of the oyster shell's mass on the adsorption of TB dye. After 3 hours of contact time, it was discovered that 0.1 g is the best mass to obtain the highest removal ratio at the lowest price. The removal percentage increased incrementally with weight gain, from 66.03 to 95.75 %, indicating high adsorption as well as a large number of effective sites, as shown in Fig. 4(a) and 4(b) [20]. Equation 6 is used to get the dye's adsorption percentage for each mass of the components (Eq. 6).

$$R\ (\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (6)$$

where R is the removal extent, %; C_0 is the initial concentration of TB; C_e is the equilibrium concentration of TB.

Impact of the contact time

Eight conical flasks were used to study the impact of contact time. Each flask contained 0.1 g of the adsorbent (oyster shells) and 100 mL of TB dye with a concentration of 100 mg L^{-1}. Fig. 5 depicts the impact of contact time on the adsorption process after samples were placed in the shaker instrument for times ranging from 20 to 180 min. It was discovered that 120 minutes is the optimal contact time during which equilibrium is established. It is caused by the saturation of the active sites [22].

Impact of sorbents' size of particles

Using a variety of particle sizes (75 – 850 μm), the impact of particle size on the TB adsorption was

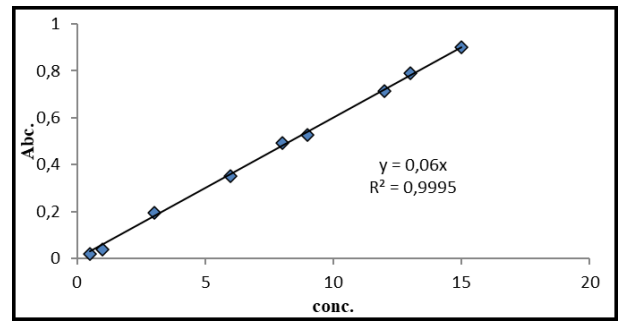


Fig. 3. The calibration curve of TB dye.

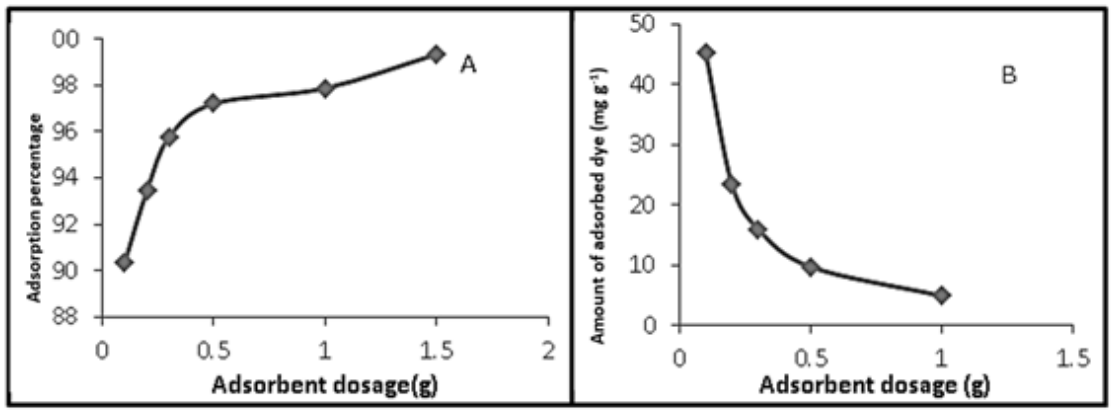


Fig. 4. Effect of adsorbent amount in the removal of TB dye via oyster's shells (a)Adsorption percentage. (b) Amount of dye adsorbed (mg g^{-1}).

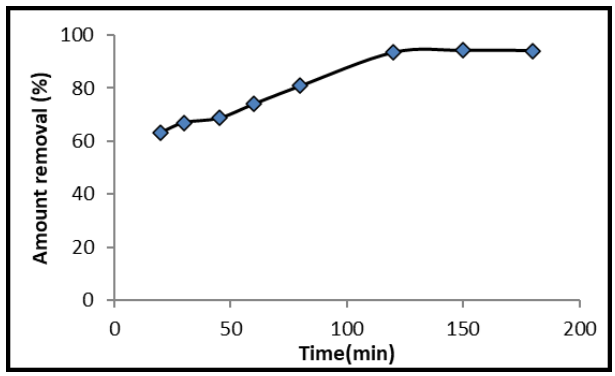


Fig. 5. The impact of contact time on the removal of TB dye.

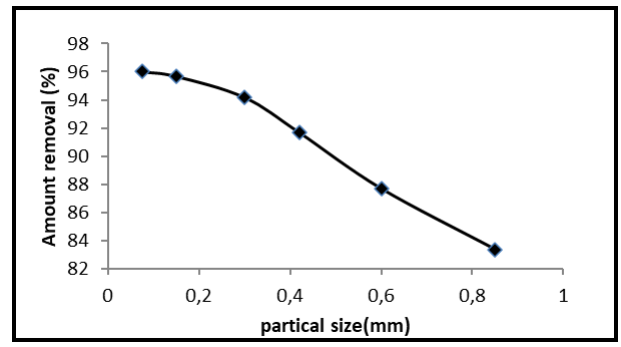
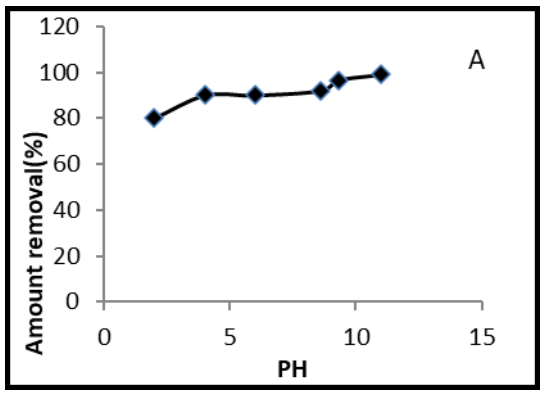


Fig. 6. The impact of particle size on the removal of TB.



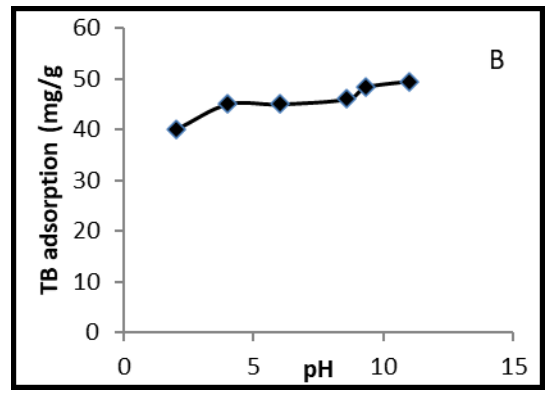


Fig. 7. Adsorption of TB dye by oyster shells at different pH.

examined. Six conical flasks are filled with 0.1 g of each of these six types after being weighed with 100 ml of TB dye solution with a concentration of 100 mg L^{-1} and shaken for 120 min. It was established that the smaller the oyster shell's particle size, with regard to a specific quantity of them, the increased is the surface area that exists, and as a result, the better the total of obligatory findings accessible [20 - 23], and the particle size was maintained at 150 µm. This is illustrated in Fig. 6.

Impact of pH

The adsorption capacity was affected by the pH of the medium. The dye adsorption was analyzed at various pH values using six conical flasks, each with 100 mL of dye at 100 mg L^{-1} concentration; the pH was controlled at (2 - 11) using dissolved HCl or NaOH, each adding 0.1 g of oyster shells at 150 µm particle size, and then shaking for 120 minutes. Fig. 7 shows the impact of pH on the adsorption mechanism, with an optimum value of pH = 2.

Impact of the initial TB dye concentration

Various dye concentrations (50 - 250 mg L^{-1}) were introduced to six conical flasks containing 0.1 g of oysters with 150 µm particle sizes in order to study the impact of the initial concentration of TB dye on the effectiveness of the adsorption. The flasks were then shaken for 120 min. Fig. 8 shows that as the dye

concentration is increased, more TB is collected onto the adsorbent. This is as a result of the concentration gradient's driving power being stronger with increasing initial dye concentrations [24 - 27]. The values for the adsorption capacity ranged from 24.75 to 119.9617 mg g^{-1}.

Isothermal analysis

The Freundlich and the Langmuir models were employed to explain the connection between the dye and the surface of the adsorbent. The two equations (3, 5) can be used to describe these concepts, and Table 1 shows that both the Langmuir and Freundlich isotherms are satisfied by the adsorption of TB dye using oyster shells. Fig. 9 (a, b), illustrates the applicability of both models to the adsorption of TB dye on the surface of oyster.

Fig. 10 shows the relationship between the separation factor (RL) and the initial TB concentration. The oyster shells' RL value was found to be in the range of 0 to 1, indicating that the adsorption method was successful.

Fig. 11 illustrates how the models fit the experimental

Table 2. Isotherms data for the removal of the dye.

Langmuir	Freundlich
q_m(mg g^{-1}) = 166.666	K_F($mg^{-1}g$)($1mg^{-1}$)$^{1/n}$ = 32.673
Ka(L mg^{-1}) = 0. 208	1/n = 0.5423
R^2 = 0.9206	R^2 = 0.9750
0.877 – 0.0189)) R_L	

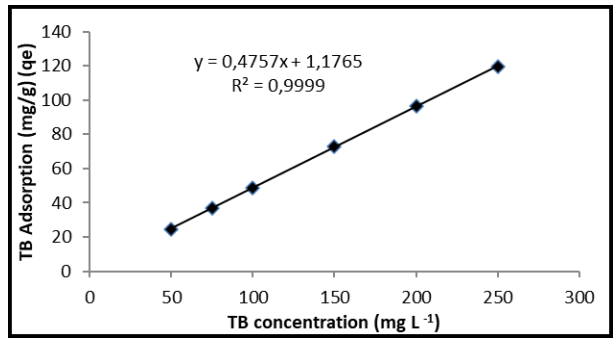
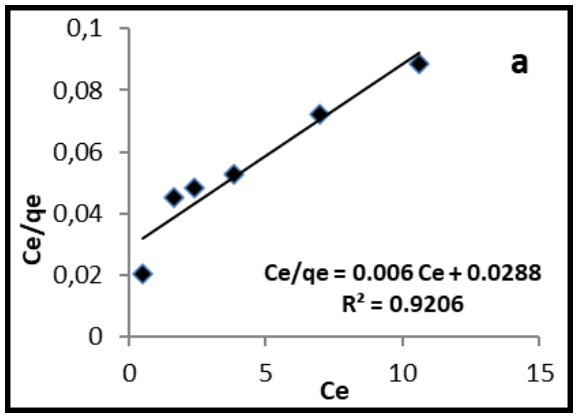


Fig. 8. The influence of the initial TB dye concentration on the adsorption capacity.



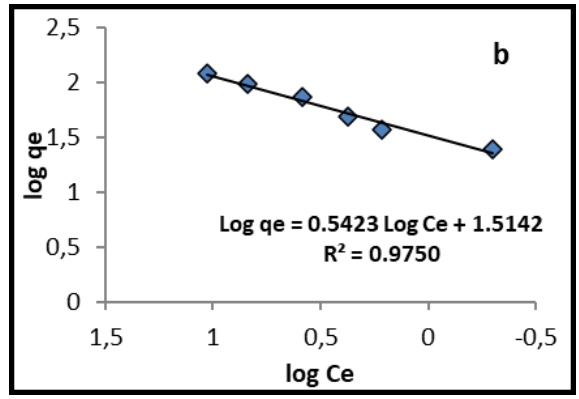


Fig. 9. Linearized TB dye isotherms on oyster shells (a) The Langmuir model; (b) The Freundlich model.

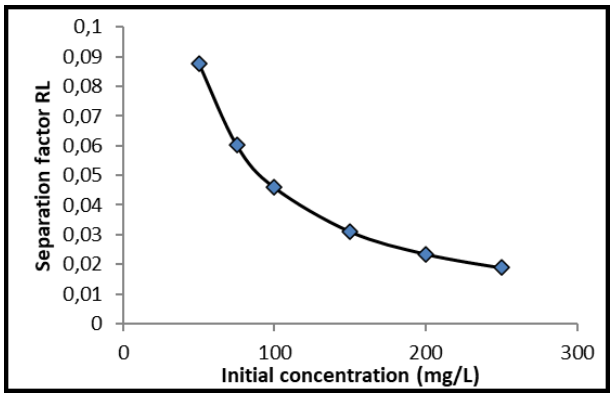


Fig. 10. Initial TB concentration onto oyster shells against separation factor.

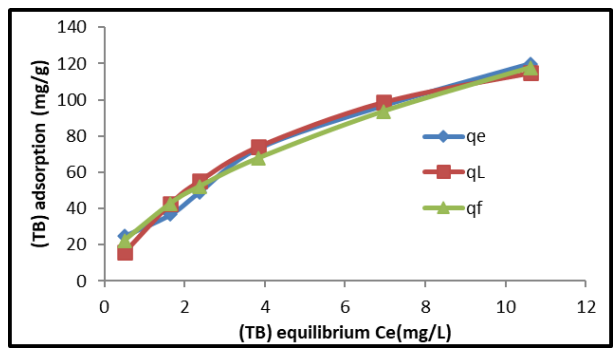


Fig. 11. Langmuir and Freundlich line information for the TB-oyster shell adsorption.

data. It seems that the two isotherms could effectively describe the TB dye adsorption on the oyster shells.

This discovery relates to the character of oyster shell surfaces, which suggests that each TB molecule has equalized adsorption energy of stimulation. The results also demonstrate the make-up of the TB monolayer clouding at the oyster shell's exterior surface.

CONCLUSIONS

The oyster shells were used as effective adsorbent for removing TB dye from aqueous solutions. The initial concentration of TB dye, pH, particle sizes and the contact time have an impact on the oyster shells' ability to absorb the dye (0.1 g, pH = 2, 150 μm, 120 minutes) and the values for the adsorption capacity ranged from 24.75 to 119.96 mg g^{-1}. Oyster shells' adsorption properties are similar to those of established Freundlich and Langmuir adsorption isotherm models. As a cheap and accessible alternative adsorbent for the removal of TB from aqueous systems, oyster shells have a great deal of potential.

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