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Experimental Investigation on Adsorption of Methyl orange Using eggshells as adsorbent Surface

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Abstract

The role of residues in the adsorption process for removing contaminants from their aqueous solution was highlighted in this study. The adsorption capacity of eggshells were used to remove the methyl orange dye from its aqueous solution. The highest dye adsorption was found to range between (62.30% to 62.33%). The results of using adsorption isotherms (Freundlich, Langmuir, and Temkin) have been revealed that the Freundlich model was followed and that the Langmuir model did not match, as well as the partial applicability of Temkin's model at temperatures (298,308,318) K. The process of adsorption is a physical one. Three kinetic models of the adsorption process were also used, with the results demonstrating the applicability of the pseudo-second-order model. In this study, the thermodynamic functions were estimated using the value of the enthalpy ΔH°, which was negative and equal to (-4.7685 KJ/mole), The process was discovered to be exothermic, and the entropy ΔS° value was also negative, equaling (- 11.5100 J/mole.K), indicating a decrease in the randomness of adsorption when added to the Gibbs free energy ΔG°, indicating that the reaction occurred spontaneously.

Keywords: Adsorption; Pollution; green chemistry; Methyl orange; Eggshell .

1. Introduction

Water contaminated with organic dyes is one of the most dangerous that threaten human life. Industrial dyes are considered a dangerous water pollutant. They are one of the important groups used in the chemical and textile industries throughout the world, and 10% of these dyes were discharged as liquid waste in 1990 AD [1].

Therefore, researchers directed to find many ways to treat and remove water pollutants because of the danger they pose to the environment. Adsorption compared to other methods is one

of the most successful techniques used to treat pollution, because of the high efficiency of this technology, ease of use, and its low economic cost when compared to other techniques, and also because of the availability of Natural resources that can be used as suitable adsorbent surfaces for the adsorption process, An example of absorbent surfaces (activated carbon, vegetable waste, animal waste, clay, etc.) [2].

Adsorption is defined as a physical or chemical bonding process arising from the bonding forces between atoms, molecules or ions of a certain substance called an adsorbate, and it may be liquid or gaseous and porous solid surfaces called (adsorbent). Additionally, the degree of adsorption depends on the surface area of the adsorbent materials and their relationship with the size and nature of the adsorbent material [3].

The structure of Methyl orange is (Sodium 4-[(4 dimethylamino)phenyl]diazenyl benzene-1-sulfonate) Which has negatively charged azo anionic dye [4]. Moreover, methyl orange dye contain orange dye contains a group (R-N=N-R) therefore it is classified among the azo dyes and because this dye contains sulfonate salts ($R\text{-}SO_3$) group, its solubility increases in water [5].**Figure 1.** shows the structural formula of (MO^-).

Recently, green chemistry has emphasized the importance of protecting the environment and human health in a beneficial and economic way aimed at avoiding toxins, reducing waste and avoiding the use of toxic chemicals [6]. With the increase in environmental awareness, it was found that using natural materials is safer for human health [7].

In this study, the (MO-) dye was removed from its aqueous solution by eggshells (ES). The effect of the initial weight of the adsorbent surface, contact time, kinematic constants and the thermodynamic functions of the adsorption process were studied.

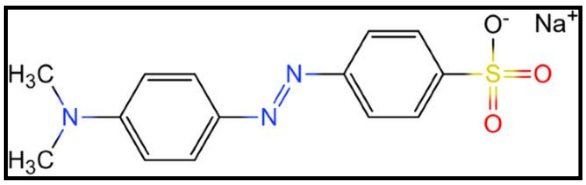

Figure 1. The structural formula of methyl orange.

2. Materials and method

2.1 The adsorbent Surface

Eggs are one of the animal products that consume daily, and eggshells are one of the animal wastes used in the adsorption process. They are a good adsorbent surface because they contain pores in addition to fibers and proteins [8,9]. The eggs were obtained from the local Iraqi markets in Baghdad - Iraq. The internal contents of the eggs were discarded to obtain the shells.

2.2 Preparation of MO^- stock solution

One gram of methyl orange dye was dissolved by nonionic distilled water in a glass beaker, and the solution was diluted in a 1000 ml volumetric vial to obtain the standard solution, to perform the experiments, a series of different concentrations were prepared (10-100 mg/L).

2.3 Preparation of ES

The white eggshells were collected through daily use of eggs available in the local Iraqi markets in Baghdad governorate. After disposal of the contents of the eggs, they were washed by deionized distilled water 6 times to remove the rest of the contents of the eggs and the pollutants suspended on the surface of the eggshells, then the shells were left to dry for (24 hour) at room atmosphere . The eggshells were ground by a dry electric mill for the purpose of obtaining a fine powder of the shells, then it was sieved by a sieve of granular size (≤75 mμ), the sieving process was repeated more than once to get the sufficient quantity for the purpose of the study.

2.4 Determination of λmax for MO^- dye

To measure the maximum wavelength (λmax) of methyl orange dye, a standard solution was prepared. It was recording in a visible and ultraviolet spectrophotometer, within the range (190-800) nm. The greatest absorption of the dye (464) nm . A quartz cell with a thickness of (1 cm) was used for the purpose of measurement. **Figure 2.** shows the absorption spectrum of MO- dye.

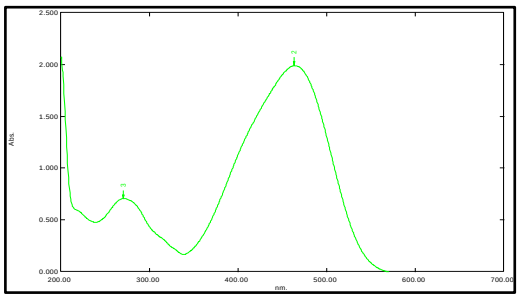

Figure 2. UV-visible absorption spectrum of MO^- dye.

3. Results and discussion

3.1 Effect of the adsorbent weight surface (ES) on the adsorption

In order to determine the ideal weight for adsorption of methyl orange dye on the surface of the eggshells, the effect of the weight of the ES was studied using an initial concentration of the dye 100 mg/L against a series of different weights of the adsorbent surface (0.05-0.7)g and at (298) K. From observing the results,in **Figure 3.** it was found that the percentage of removal (%R) increased continuously with the increase in the weight of the ES (0.05-0.3) g, which was equal to (62.14 -62.30) %, due to the increase in the number of active sites prepared for adsorption of MO^- , and that by increasing these sites the efficiency of the adsorbent surfaces are able to remove the MO^- dye from its aqueous solution. Then we notice that at the ideal weight of (0.4)g of the ES, the %R begins to remain stable, which was equal to 62.3% [10].

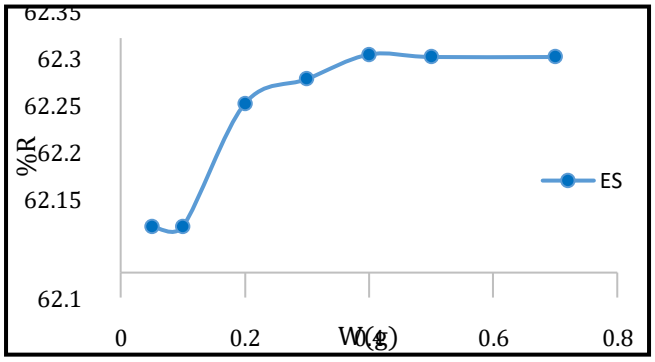

Figure 3. Effect of the weight of the adsorbent surface (ES) for adsorption of MO^- dye.

3.2 Effect of equilibrium time

The effect of the equilibrium time of eggshells with the aqueous solution of MO^- dye was studied by using initial concentration of the dye 100 mg/L and at different temperatures (298,308,313) K , granule size (≤ 75µm) and the ideal weight of ES (0.4g) under study. **Figuer 4**. shows the effect of time on the adsorption process of the adsorbent surface ES. The results showed that (25 min) is the equilibrium time required for the MO^- dye adsorption process on ES.

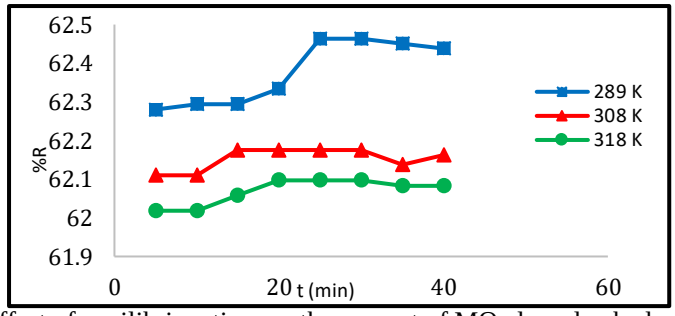

Figure 4. Effect of equilibrium time on the amount of MO^- dye adsorbed on the surface of ES.

3.3 Adsorption Kinetics Models studies

Three kinetic models were applied to follow the adsorption of methyl orange on eggshells pseudo-first-order (PFO), pseudo-second-order (PSO) and the Elovich kinetic model.. The linear form of PFO is given as follows [11]

$$\ln(q_{e-}\, q_t) = -K_1\, t + \ln q_e \qquad 1$$

q_t (mg/g) represents that the adsorption capacity at time, q_e (mg/g) is the adsorption capacity at equilibrium and K_1(min $^{-1}$) is the rate constant for adsorption of (PFO). K_1 gotten from the slope of the linear plot of in (qe-qt) Vs time (t) as shown in **Figure 5.**

(PSO) constants calculated by the equation (2) [12]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e{}^2} + \frac{t}{q_e} \qquad 2$$

K_2 (g mg^{-1} . min $^{-1}$) represents that the rate constant for the adsorption for (PSO) reaction. K_2 is gotten from the intercept of the linear plot of in t/qt Vs time (t) as shown in **Figure 5.**

(Elovich) constants ∝ , β calculated by the equation (3) [13]

$$q_t = \frac{1}{\beta}\ln(\beta \propto) + \frac{1}{\beta}\ln t \qquad 3$$

∝ represents that the initial adsorption rate constant in units of (mg.g^{-1}.tim^{-1}) and β is the desorption process constant in units of (g.mg-1). And that both β and ∝ are computed from slope and intercept of plotting at against Lnt in **Figure 5.**

Through the results shown in **Table 1.** and by following the values of the correlation coefficient (R^2) for the three Kinetic models, it is shown that the PSO applies to the first because the values of (R^2) have high, in addition to the convergence of the theoretical (qe) values from the practical (qe) values [14] , then followed by the partial applicability of the Elovich Kinetic model due to its weak correlation coefficient, which was less than 0.9 [15]. In addition to the non-applicability of the PFO model because the practical (qe) values did not approach the theoretical values in addition to the very few (R^2) value [16].

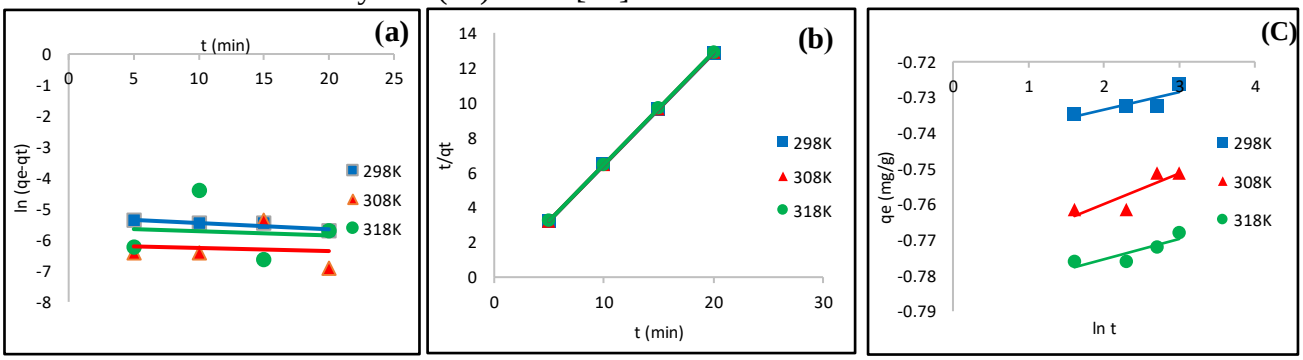

Figure 5. The PFO (a), PSO (b), Elovich (c) kinetic models for the adsorption of the MO- dye on the surface of the ES at different temperatures.

Table 1. The values of the kinetic constants of the adsorbent ES surface at different temperatures.

T (K)	First Pseudo order			Second Pseudo order			Elovich		
	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 ($g.mg^{-1}.min^{-1}$)	q_e (mg/g)	R^2	β ($g.mg^{-1}$)	∝ ($mg.g^{-1}.min^{-1}$)	R^2
298	0.0282	0.0059	0.8939	67.4673	1.5588	1	125	$1.2465*10^{-43}$	0.8863
308	0.0101	0.0021	0.0101	60.9756	1.5552	1	116.2791	$4.9141*10^{-42}$	0.7403
318	0.0136	0.0037	0.0083	50.5561	1.5530	1	116.2791	$8.4899*10^{-43}$	0.7423

3.4 The adsorption isotherms

A series of different concentrations of Methyl Orange 20-120 mg/L and at temperatures (298,308,318) K, the ideal adsorbent surface weight (ES) (0.4) g, particle size (≤75µm) and equilibrium time (25 min) were used to study the adsorption isotherms. The **Figure 6**. drawn shows the relationship between (q_t (mg/g)) and (Ce (mg/L)) isotherms of adsorption of methyl orange dye on ES at different temperatures.

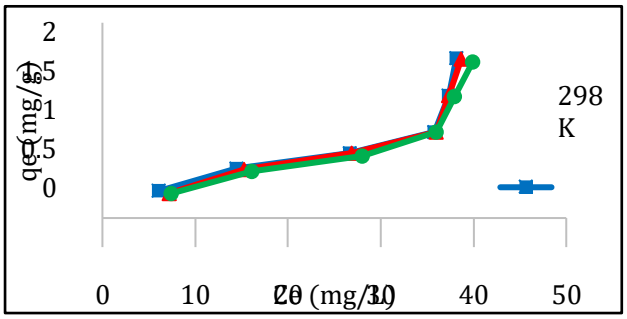

Figure 6. Isotherm of the adsorption process of MO- dye on ES

Figure 6. Isotherm of dye adsorption on the surface ES of type (S_3), which is based on the principles of Freundlich for the adsorption process, and this indicates, according to Giles classification, that the adsorption process occurs with different forces on the adsorbent surface, where the amount of the adsorbent substance on the adsorbent surface decreases with the increase in the covered part of the adsorbent surface Through the adsorbate[17]. In addition that the

adsorption process occurs perpendicular to the adsorbing surface, meaning that the adsorbate will occupy a smaller amount of the adsorbent surface portions, so the adsorption will be high due to the availability of a vacant space on the surface [18].

3.5 Adsorption Isotherm Models

The collected data were subjected to three models of the adsorption process isotherm, and **Table 2**. displays the values of the three model constants, Freundlich, Langmuir, and Temkin, as well as the correlation coefficients. The isotherm models of the adsorption process are shown in **Figure 7.** The Freundlich Isotherm adsorption model constants (K_f (mg/g)) and (n) were calculated using the equation (4) [19]

$$\log(q_e) = \log(K_f) + (1/n)\log(C_e) \qquad 4$$

The equation (5) was used to derive the Langmuir constants KL(L/mg) and qemax (mg/g). [20]

$$\frac{C_e}{q_e} = \frac{C_e}{q_{e\,max}} + \frac{1}{q_{e\,max}K_L} \qquad 5$$

The equation (6) was used to calculate the Temkin constants KT (L/mg) and BT(J/mol). [21]

$$q_e = B_T \ln K_T + B_T \ln C_e \qquad 6$$

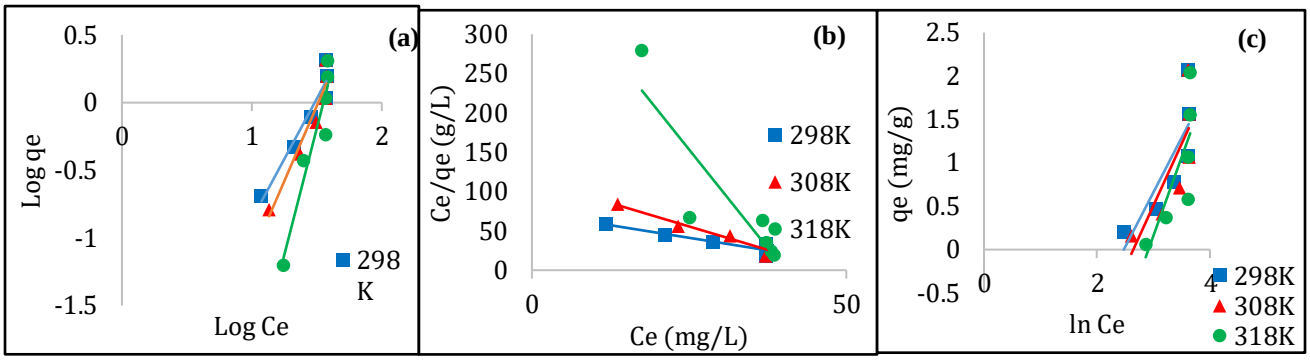

Figure 7. Freundlich (a), Langmuir (b), Temkin (c) isotherm for the adsorption of the MO- dye on the surface of the ES at different temperatures.

Table 2. The values of the isotherm constants of the adsorbent surface ES at different temperatures.

T (K)	Freundlich			Langmuir			Temkin		
	K_f (mg/g)	n	R^2	K_L (L/mg)	qe_{max} (mg/g)	R^2	K_T (L/mg)	B_T (J/mol)	R^2
298	0.0731	1.2186	0.8779	0.0091	5.5804	0.1412	0.2122	0.7025	0.6710
308	0.0459	1.0526	0.9008	0.0017	23.5849	0.0099	0.1679	0.7918	0.6990
318	0.0418	1.0363	0.9012	0.0003	135.1351	0.0003	0.1597	0.7926	0.6991

Table 2. shows that Freundlich 's lsotherm equation is well applicable to the adsorption process in this investigation, with values of (n) confined between (1-10) indicating that adsorption is governed by physical forces. In addition, when the temperature under examination rises, the Freundlich constant (Kf) for the adsorbent surface (ES) decreases, confirming the exothermic character of the adsorption process. And the adsorption process took place on heterogeneous surfaces with various adsorption energy locations [22].Because of the very weak linear correlation coefficient at the same temperatures used, the Langmuir model does not fit, according to the data in **Table 2.**[23] in addition Temkin 's model is only partially applicable because the surface correlation coefficient at all temperatures is less than 0.9 [24].

3.6 Calculation thermodynamic functions

The influence of temperature on adsorption is critical for calculating thermodynamic functions (standard enthalpy (ΔH°), Gibbs free energy (ΔG°), and standard entropy (ΔS°) as well as comprehending the adsorption process' behavior. The values of thermodynamic functions for adsorption of a MO- dye on ES[25] are shown in **Table 4**.

Equation (7) was used to compute the equilibrium constant for the adsorption process of MO dye on the adsorbent surface (ES) and at each temperature to discover the values of thermodynamic functions[26].

$$K_{eq} = \frac{qe * w(g)}{Ce * V(L)} \qquad 7$$

While Keq is the adsorption process' equilibrium constant, qe is the amount of adsorbate on the adsorbent surface in units (mg/g), W is the weight of the ideal adsorbent surface in units (g), V is the volume of the MO dye solution in units (L), and Ce is the equilibrium dye concentration in solution in units (mg/L).

Table 3. values of the thermodynamic equilibrium constants for adsorption of MO^- dye on the adsorbent surface of eggshells and at different temperatures.

Adsorbent	T (K)	ΔG° KJ/mole	ΔH° KJ/mole	ΔS° J/mole.k
Eggplant Peels	289	-1.3486	-4.7685	-11.5100
	308	-1.2021		
	318	-1.1198		

The linear equation for calculating ΔH° and ΔS° was obtained by plotting **Figure 8**. between lnKeq and 1/T. The standard enthalpy of adsorption and standard entropy were determined at each temperature inside the system under these conditions using the linear connection in **Figure 8**. where the slope represents (-ΔH°/R) and the intercept represents ΔS°/R, using equation (8).

$$\text{Ln Keq} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad 8$$

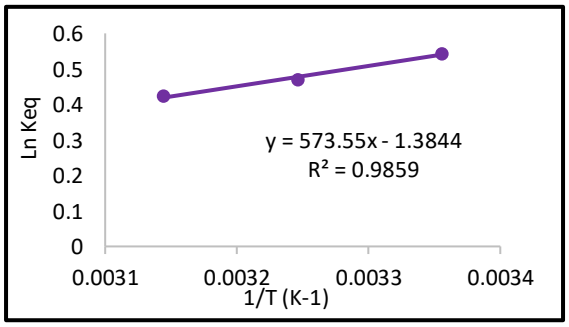

Figure 8. Vant Hof's equation for adsorption of methyl orange dye on the adsorbent surfaces of eggshells .

To calculate the change in the Gibbs free energy, equation (9)[27] is applied

$$\Delta G^\circ = -RT\ln K_{eq} \qquad 9$$

Where ΔG° represents the change in Gibbs free energy in units of (KJ.mol-1), and R represents the general constant of gases in units of (J/mol.K).

Table 4. Thermodynamic values of the adsorption of MO^- dye on the adsorbent surface of the ES at different temperatures.

Adsorbent	T	1/T (K-1)	K_{eq}	Ln K_{eq}
Eggplant Peels	298	0.0034	1.7235	0.5443
	308	0.0032	1.5991	0.4695
	318	0.0031	1.5274	0.4236

The enthalpy of the adsorption process of the adsorbing surface (ES) reveals the nature of the adsorption process, which was exothermic, and the enthalpy values were less than (40 KJ/mol), indicating that adsorption is physical adsorption [28]. The dye molecules deposited on the adsorbing surface and overlapping are regular and less random when the adsorption process begins, as indicated by the negative entropy values. The Gibbs free energy estimates for MO- dye adsorption on ES are negative, indicating that the adsorption process happens spontaneously [29].

3.7 Effect of ionic strength

The effect of salt concentration on methyl orange adsorption from aqueous solution using sodium chloride (NaCl) on ES with different concentrations (0.05, 0.1, 0.2, 0.3)M with the stability of other factors such as the initial concentration of MO- (100 mg/L), granular size (75m), ideal weight (0.4g), equilibrium time (25 min), and at a temperature of (298K).**Table 5.** and **Figure 9.** show the effect of ionic strength on the amount of dye adsorbate on the adsorbent surface.

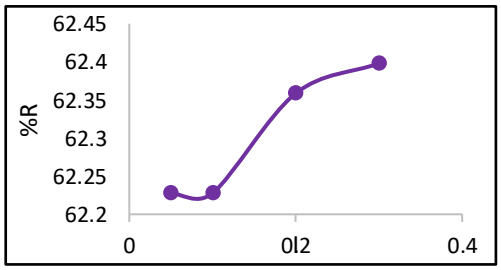

Figure 9. Effect of the ionic strength of adsorption of MO^- dye on the adsorbent surface (ES).

Table 5. data of adsorption of MO^- dye on the surface of ES at different concentrations of NaCl and a temperature of 298K.

I [M]	Eggplant Peels	
	qe (mg/g)	%R
0.05	1.5557	62.2277
0.1	1.5557	62.2277
0.2	1.5590	62.3586
0.3	1.5599	62.3979

Table 5. shows that the amount of adsorbate material on the ES surface increases as the salt concentration rises, as does the percentage of removal. To increase the amount of adsorbate substance on the adsorbent surface and the percentage of MO- dye removed from its aqueous solution [30]. This is due to the salt's higher solubility in aqueous solution than the dye's, resulting in an increase in the MO dye's bonding ability to the adsorbent surface (ES), resulting in a higher

percentage of the methyl orange dye being removed from its aqueous solution and a higher amount of the adsorbate substance on the adsorbent surface [31].

4.Conclusions

In conclusion to this study, Methyl Orange dye was adsorbed by eggshells in this experiment. The results of the applied kinetic constants revealed that the (PSO) model provided the best fit. in addition from being compatible with the Freundlich isotherm. The negative ΔH° value indicated that the adsorption process is exothermic, and its value was less than (40 KJ/mol), indicating that the adsorption process is physical, and the negative ΔS° value indicated a decrease in randomness, in addition to the negative ΔG° values, indicating that the adsorption process is spontaneous**.**

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