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Batch Adsorption Studies on Removal of Dye using Agro-Waste

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Abstract: Purification of industrial waste water polluted by anionic dye was carried by adsorption process. Anionic dye (i.e. Acid Yellow 24) from waste water can be effectively taken out by Madhuca Longifolia Seeds Hull (MLSH) as adsorbent in the sorption technique. MLSH is a low cost and easily available agricultural waste in our ambience. Batch equilibrium method was followed to study the effects of some physico-chemical experimental conditions such as pH, agitation time and adsorbent dose. Equilibrium adsorption isotherm was also studied and found to be suitable with Freundlich isotherm. Kinetic parameters were in conformity with pseudo-second order. The present research projects towards applicability of MLSH in designing low cost adsorbent and for treating effluent water in industries or other adsorption processes. The observations and findings were interpreted at laboratory scale.

Keywords: Adsorption, Acid Yellow 24, Madhuca Longifolia, Agriculture waste, Freundlich isotherm, effluent

I. INTRODUCTION

Attraction for natural colors is known for many years, but natural colors had many disadvantage[1-4]. To mitigate the disadvantages, researchers had developed synthetic dyes with interesting properties. Textile industries are one of the major consumers of the synthetic dyes. However, along with many benefits, the effluents released from these industries are polluting our domestic rivers. These dye pollutants are imposing adverse results directly to the aquatic life and indirectly to human beings.

There are many methods, processes, phenomenon etc. reported in the literatures to clean the water from the coloring impurities[5]. Adsorption as a method to eliminate the dyes from water has many advantages like simple, cheap over other methods in the literature[5].

Experimental studies proved that the effective removal of dyes is obtained using several cheaply available non-conventional adsorbents[6]. Therefore, studies related to efficient and low cost adsorbent derived from existing sources are gaining importance for removal of the dye. Use of agricultural wastes as solid adsorbent proved efficient and eco-friendly. These wastes are cheap and easily available in nearby areas; hence its use makes whole process a low cost removal of dyes from industrial effluents[5].

These raw agricultural wastes are chemical activated to increase their porosity and surface area which makes it highly active adsorbent. Many agricultural wastes are reported in the literature with more or less efficiency, to add in studies, this research is an attempt to use *Madhuca longifolia seed hull* (MLSH) as a low cost agricultural adsorbent.

The effect of various parameters such as effect of time, pH, temperature, adsorbent dose, isotherms and kinetic studies had been investigated in batch experiment using Acid Yellow 24 dye and agricultural waste adsorbent as *Madhuca longifolia* seed hull (MLSH).

A. *Aim And Objective*

1) To study the efficacy of adsorption of acid yellow dye by adsorbent MLSH and to research the affecting constraints such as pH, adsorbent dose.
2) To optimize the process of adsorption for effective removal of dye from aqueous solution.
3) To investigate the adsorption isotherms and kinetic behavior of the process of removal of dye.

II. MATERIAL AND METHODS

1) *Material:* Preparation of the Adsorbent:

Adsorbents like MLSH collected from the local areas of Raigad district of Maharashtra. The seed hull collected and dried at temperature (~110^{0}C) for 10 hrs to remove moisture present in the seed hull. The dried material was washed with doubly distilled

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water till washings gave constant pH. After carbonization with concentrated H_2SO_4 in the ratio of 1:1 (w/v), it was further dried and activated by heating at 1100^0C for 5 hours in hot air oven. The dried mass was grinded and sieved[7].

All chemicals were used of high purity, commercially available analytical grade. Stock solution of 1 gm/Liter of dyes was prepared using doubly distilled water.

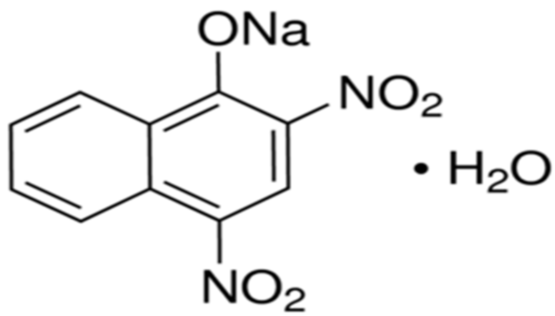
2) *METHODS:* Investigation were carried out by mixing 75 mg of activated MLSH with 50mL of AY 24 solution (100 mg/litre) and solution of adsorbate and adsorbent was stirred using mechanical shocker for determined interval of time. Fixed aliquots of solution after adsorption were withdrawn and analyzed with UV-visible spectrometer at wavelength λ = 420 nm.

Reusability of carbonized hull i.e. desorption study was checked by stirring dye loaded adsorbent and 50 mL of distilled water maintained at range of pH for 80 minutes. Interpretation of studies was accomplished by plotting the respective graphs.

The percentage amount of dye adsorbed was calculated using the equation[8]:

$q_e = \frac{(C_o - C_e)V}{W}$ x 100 where q_e is the amount adsorbed per gram of adsorbent, C_e is the equilibrium concentration of dye (mg/L), W is mass of adsorbent (g) and V is volume of solutions.

3) *Characterization of Adsorbent*



The various properties and characteristics of adsorbent for the present work is given in the table

Common Name	Martius Yellow, 2,4-Dinitronaphthol
IUPAC Name	2,4-Dinitronaphthalen-1-ol
Chemical formula	$C_{10}H_5N_2NaO_5$
Molecular weight	256.15
Type of dye	Nitro dye
Maximum Wavelength(nm)	420
Moisture Content (%)	18.75
Ash Content(%)	5.15
Volatile Content (gm)	3.75
Bulk density(gm/ml)	0.804
Surface area(m^2/gm)	1205.3
Size of adsorbent(nm)	195.5

III. BATCH ADSORPTION STUDIES:

1) *Adsorption Experiments:* The adsorption studies were carried out in a batch system. 75 mg of MLSH carbon was mixed with 50 mL of synthetic or textile dye AY24 of concentration (100 mg/liter) for further studies. The effects of all parameters were investigated at room temperature.
2) *Effect Of Contact Time:* Contact time is required to know the time needed for establishing uptake equilibrium between adsorbate and adsorbent. The study was performed at the dyes natural pH maintained at 180 rpm.
3) *Effect Of Adsorbent Dose:* Initial concentration of adsorbent has critical role in the studies to determine the required driving force to overcome the repulsive forces to the mass transfer of dye between the aqueous and the solid phases. Effective adsorbent dose was determined by stirring 50 ml of aqueous solution of AY 24 (100 mg/ml) with varying doses of adsorbent i.e. 0.01-2.5g at its normal pH and 180 rpm above time needed for equilibrium between dye and carbon[9].
4) *Effect of PH:* Uptake equilibrium of dye is influenced by pH of the solution. Hence study was forwarded for effect of pH by attaining acidic and basic medium maintained with 0.1 M HCl and 0.1 M NaOH respectively between 2 to 12.

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5) *Desorption Study:* Recyclability and reusability of the adsorbent after the adsorption process was performed by desorption of the dye loaded carbon. 75 mg of adsorbent laded with AY 24 was stirred with 50 ml of aqueous solution for greater than uptake equilibrium time at 180 rpm at various pH.

IV. RESULTS AND DISCUSSION

1) *Effect Of Contact Time:* It is evident from the graph (Fig 1) that uptake of the dye increased rapidly and attained saturation after about one hour. Saturation basically may be due to adsorption of active site of the adsorbent by the adsorbate and not permitting further uptake leading to saturation of the process[10,11,12].

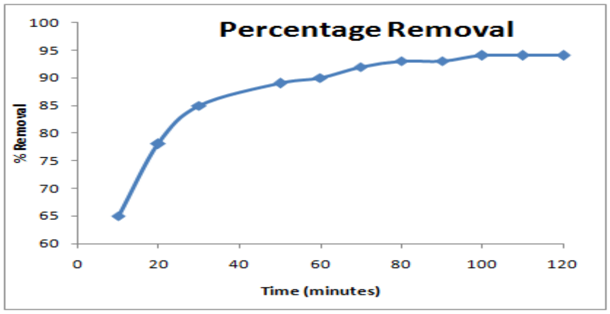

Fig. 1 Percentage removal Vs Time (minutes)

MLSH removed maximum up to 94% of the dye from water at dose of 75 mg.

2) *Effect of Adsorbent Dose:* As a function of adsorption, adsorption dose varied between 0.05 to 2.5 g was used for the study of dye removal. The response was found to increase initially with increasing concentration for the adsorption of AY24. If adsorbent dose is increased further more than most favorable dose i.e. 75 mg, increase in adsorption is practically constant making the whole process cost ineffective.

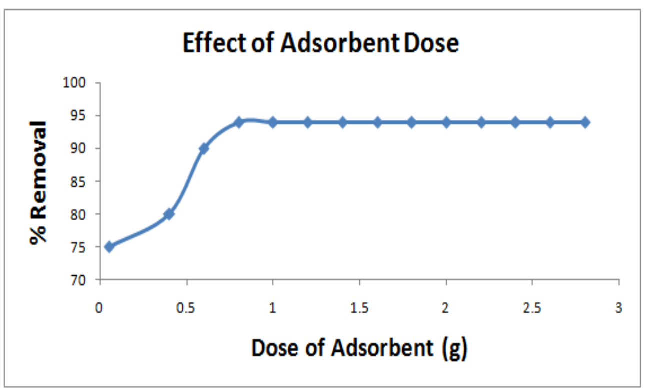

Fig.2 Percentage removal Vs Dose adsorbent

3) *Effect of PH:* pH of the solution significantly influence the adsorption process. Here we found that adsorption decreases with increase in pH of the solution (figure 3). Suitable pH range obtained was between 2 to 4.

Decrease may be due to developing of repulsive forces between adsorbate and adsorbent with increasing pH[13-15].

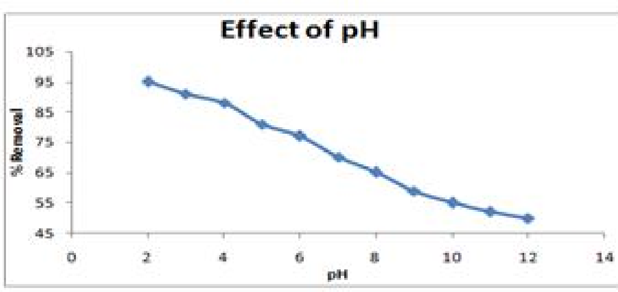

Fig. 3 Percentage removal Vs pH

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4) *Desorption Study*: Recyclability of the adsorbent makes the process further inexpensive, though used MLSH is cheap. Percentage of desorption decreased from 48 to 22 as pH increased from 2 to 12 in figure 4.

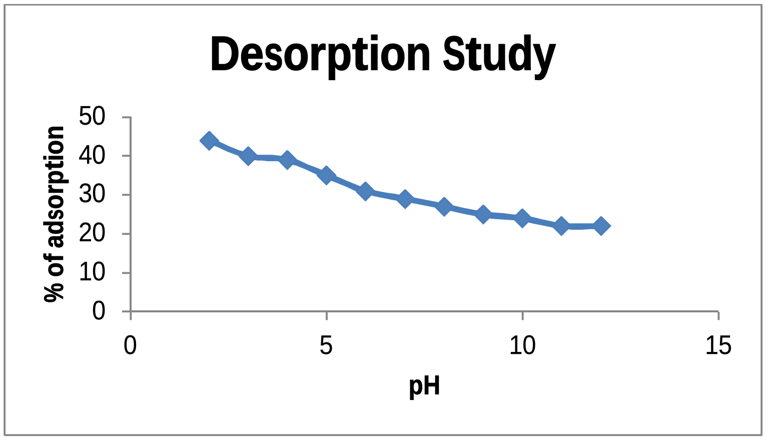

Fig. 4 percentage of Adsorption Vs pH

5) *Adsorption Isotherms:* Adsorption studies were examined using linear form of Freundlich and Langmuir isotherm. Freunlich isotherms models[16] are known for explaining the isotherms and represented as $\log Q_e = \log K_f + \frac{1}{n}\log C_e$ where Q_e is amount of dye absorbed (mg/g), C_e is the equilibrium concentration of dye (mg/l), K_f and n are coefficients of adsorption capacity and intensity respectively.

From the Freundlich isotherm figure 5, values of K_f and n were found to be 14.98 and 2.47 respectively showed high competency for uptake of dye on MLSH.

Adsorption in multilayer form might have taken on the active sites of MLSH.

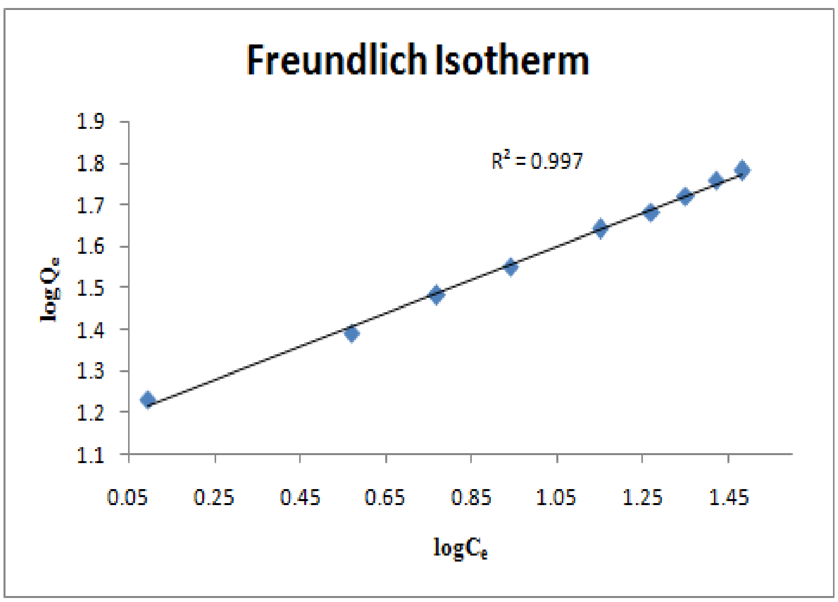

Fig. 5 Freundlich Adsorption Isotherm

Langmuir isotherms[17,18] assume monolayer adsorption and uniform energies as MLSH has identical active sites. Isotherm in linear form is represented as: $\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}$ where C_e is equilibrium concentration (mg/l), Q_e is the amount adsorbed (mg/g) and Q_m and b are Langmuir constants for adsorption efficiency and adsorption energy respectively. From the isotherms figure 6, values of Q_m and b were found to be 117.06 and 0.079 respectively showing adaptability majorly for monolayer uptake of AY 24 on MLSH.

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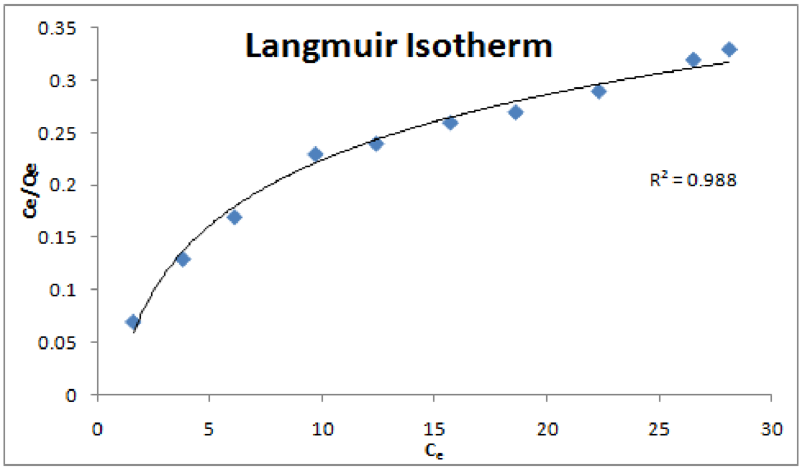

Fig.6 Langmuir Adsorption isotherm

If R^2 values were compared then it is concluded that Freundlich adsorption isotherm model will best fitting model.

6) KINETICS: To determine best kinetic model, second order model was tested using following equation[19]:

$\frac{t}{Q_t} = \frac{1}{K_2 * q_e{}^2} + \frac{t}{Q_e}$ where q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and at time t respectively. K_2 is the rate constant (g mg^{-1} min^{-1}).

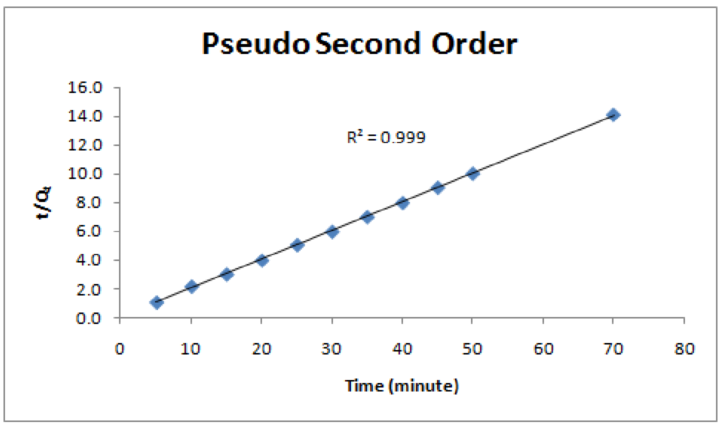

Fig. 7 Plot of t/q_t

Plot of t/q_t with time figure 7, gave intercept value 0.083 and slope value 0.199. A high value of R^2value 0.999 from linear plot is suggestive of pseudo second order mechanism and the chemical adsorption process controls the adsorption rate.

V. CONCLUSION

The present paper focuses on investigation of adsorption of Acid yellow 24 dye using MLSH and optimizing of the operative parameters such as pH, adsorbent dose etc. The studies opened that the MLSH cannot remove 100 % textile dye from industrial effluent. Adsorption attempts revealed the sorptive process to be chemo selective and multilayer. Ease of availability, low cost, clean adsorption process and its recyclability makes the MLSH a substitute to other expensive bio adsorbent.

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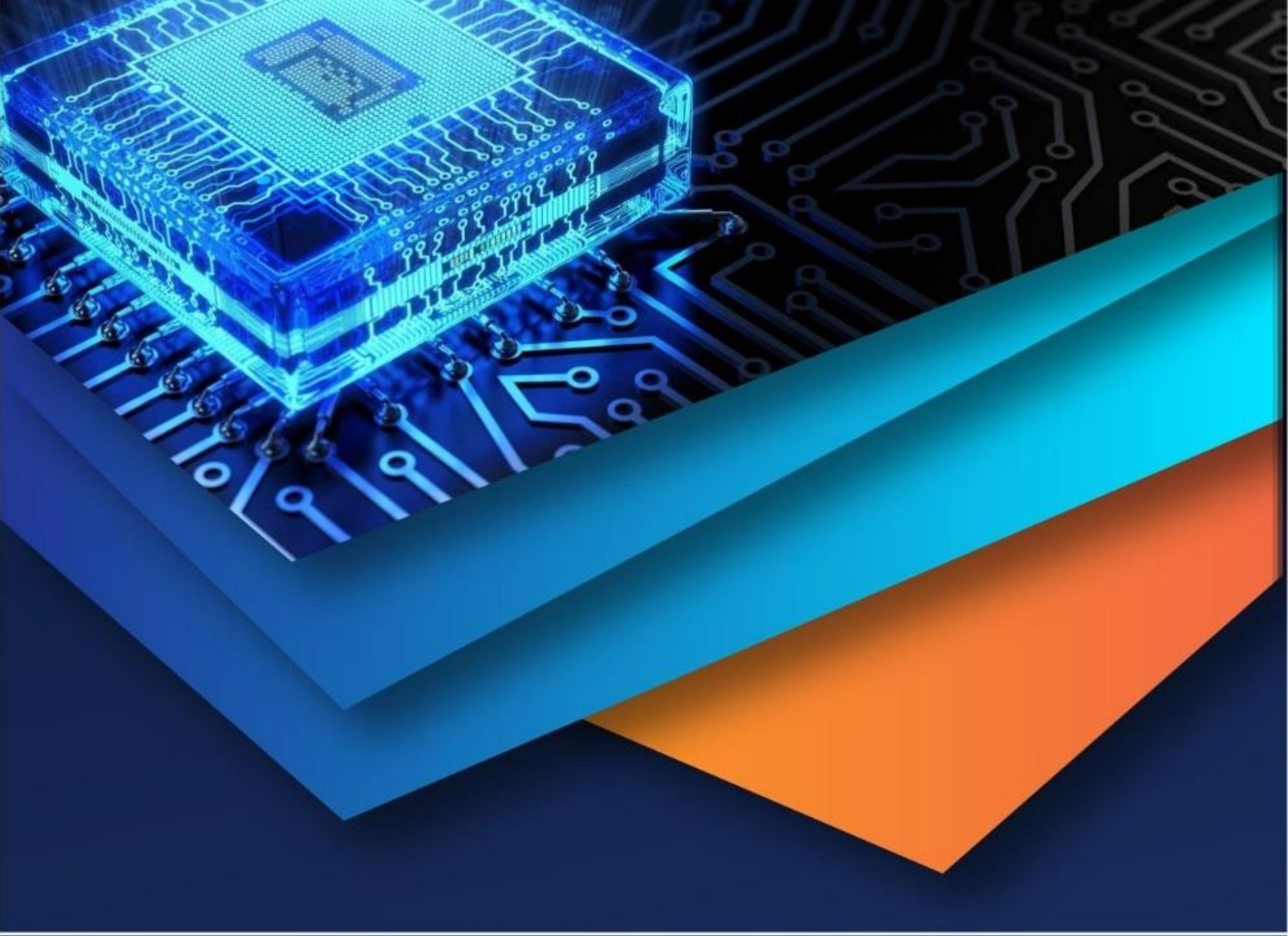

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