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RESEARCH OF METHODS FOR THE PURIFICATION OF SURFACE SEWAGE WATERS FROM HIGHWAYS WITH THE USE OF MODERN FILTERING MATERIALS

ДОСЛІДЖЕННЯ МЕТОДІВ ОЧИЩЕННЯ ПОВЕРХНЕВИХ СТОКІВ З АВТОМОБІЛЬНИХ ДОРІГ З ВИКОРИСТАННЯМ СУЧАСНИХ ФІЛЬТРУЮЧИХ МАТЕРІАЛІВ

Ugnenko Yevheniia Borysivna, *Doctor of Technical Science, Professor, Ukrainian state university of railway transport, Head by Researches and Designing communications, geodesy and land management, e-mail: ugnenko.ievgenia@gmail.com, +30675713565,*

https://orcid.org/0000-0002-3945-788X

Sorochuk Nataliia Ihorivna, *Ukrainian state university of railway transport, assistant of the Department of Researches and Designing communications, geodesy and land management, e-mail: nat.sorochuk50@gmail.com, +30953265929,*

https://orcid.org/0000-0002-6042-2681

Tymchenko Olha Mykolaivna, *Candidate of Engineering Science (Ph.D.), Ukrainian state university of railway transport, associate professor of the Department of Researches and Designing communications, geodesy and land management, e-mail: oleka55@gmail.com, +30958307968,*

https://orcid.org/0000-0002-5391-0388

Petrovich VV, *Candidate of Technical Sciences, Professor, Senior Researcher, Professor of the Transportation Construction and Property Management Department, National Transport University. e-mail: petrovichvv60@ukr.net, tel. +3804428027338,*

https://orcid.org/0000-0003-0422-2535

Summary. The general properties of modern filtering materials of the new generation, such as natural zeolites, are considered. The aspects for the use of natural zeolites for the purification of surface sewage waters from highways are analyzed. It is determined that zeolites are an extremely promising natural raw material, which is characterized by high technological parameters and the absence of negative environmental consequences in their widespread use. Mathematical models of aerobic and anaerobic biological treatment of surface sewage waters are presented. One of the ways to increase the efficiency of biological treatment is the introduction of a biosorption method based on the joint biological and adsorption treatment of sewage waters in time and space. The simulation results made it possible to evaluate the adequacy of the mathematical models used to describe the dynamics of the purification of surface sewage waters from highways using natural zeolites in order to provide further recommendations and optimal control of sewage treatment plants during biological treatment. An improved mathematical model can be used to determine the quality of surface sewage waters from highways. As a result of experimental studies, the efficiency of using alternative filtering natural materials has been determined. The introduction of new cleaning methods with the use of natural zeolites solves the problem of improving the technical level of roads, traffic safety and environmental performance.

Key words: surface sewage waters from highways, natural zeolites, mathematical simulation, adsorption, concentration of pollutants

Introduction. In modern technologies of water purification one of the main places is filtering processes, and, accordingly, filtering materials. The progressive deterioration of the ecological situation of water objects requires a constant refurbishment of filtering elements, which are subject to increasingly high technological and environmental requirements. The new generation of modern filtering materials include zeolites.

Zeolites are a large group of minerals hydrated with aluminosilicates of alkaline elements (Fig. 1). During the heating of zeolites, water is released gradually, without breaking the crystal lattice. They are colorless or white, sometimes painted in yellow, red colour.

Figure 1 – Natural zeolite
Рисунок 1 – Природний цеоліт

Zeolites are natural and artificial, have selective, adsorption and ion exchange properties, are used in many branches of the economy such as in industry, agriculture and in the processes of water purification.

The absorption of material by zeolites occurs through channels or window-entrances that have certain sizes. Penetrating through these channels within the zeolite can only molecules whose size is smaller than the diameter of the channel. This makes possible the use of zeolites as molecular sieves. About 50 mineral species of natural zeolites are known. These are so-called boiling stones.

In industry, only artificially synthesized zeolites (permutites) are used, they are widely used in water treatment devices, such as adsorbents, ion exchangers, molecular sieves. Also, zeolites have been widely used as catalysts for many processes of petrochemicals and petroleum refining.

Zeolite is an extremely perspective natural raw material, characterized by high technological parameters and the absence of negative environmental effects in their widespread use. They do not swell in water, they are easily machined with subsequent fractionation, have absorption, ion exchange and other properties, are safe for living organisms and therefore of great importance for use in the processes of surface runoff purification.

Materials and methods. Natural zeolites are a relatively new class of mineral raw materials used in the technological processes of purification and posttreatment of sewage waters. In connection with the development of adsorption methods for cleaning liquids more and more there is a lack of adsorbents that have high thermal stability and resistance in acidic surroundings. The acid resistance of natural zeolites can be used in such cases, in which the use of synthetic zeolites is virtually eliminated.

High mechanical strength of a natural mineral allows to exclude granulation of adsorbent. As a result, the cost of natural clinoptilolite, which is determined by the cost of extraction, grinding and dispersion, is several times lower than the cost of synthetic zeolites.

Sokirnitsky zeolite satisfies all the necessary requirements for filtering loads of water treatment plants and belongs to the list of materials that are allowed for use in the processes of purification and concentration of drinking water. According to the mineralogical composition, Sokirnitsky zeolite refers to clinoptilolite, the content of which in the rock is estimated at 75 per cent (this allows the use of this material without prior enrichment). According to the chemical composition klinoptilolit refers to sodium-potassium zeolites [1-3].

Advantages: it has strong sorbing properties, therefore, the more effective material than the filtering materials used in the treatment facilities (coal, sand, crushed anthracite, gravel, quartz, marble, ceramic crumb, metallurgical slag, polymer materials). Disadvantage of this material is washout from filter of a fine fraction of zeolite.

The use of zeolites for the purification of surface runoffs is regulated by technical specifications of TU U 14.5-00292540.001-2001.

The urgency of solving the problems associated with efficiency upgrading of treatment of surface runoff on the adjoining roads of the territories determines the relevance of the topic.

The aim of the work is to compare the efficiency of sorbent cleaning of surface wastewater from petroleum products using zeolite and gravel blend.

Results and Discussion. For a successful solution of problems related to forecasting, operational management and control over the quality of the process of water purification, a complex description of hydrodynamic, hydrochemical and hydrobiological processes is required. Such a description is currently being carried out using methods of system analysis and mathematical modeling. An important part of the system for the evaluation and management of the purification quality of surface sewage waters from highways is the automated monitoring system for wastewater treatment plants [4].

In most cases it is virtually impossible to determine the concentrations of organic substances contained in surface runoff separately. Therefore, when considering biological purification processes, the variation of the total concentration of the pollutant and the total biomass of microorganisms was studied. The process of aerobic biological treatment can be represented in the form of a formalized scheme (Fig. 2) [4-5]

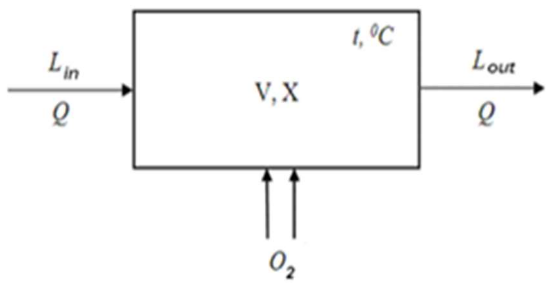

Figure 2 – Formalized scheme: L_{in} – the concentration of surface sewage waters, mg/l; L_{out} – the concentration of purified water, mg/l; V - volume, m^3; Q – runoff of entering sewage waters, m^3/h; X – the concentration of natural zeolite, g/l

Рисунок 2 – Формалізована схема: L_{in} – концентрація поверхневих стоків, що надходить, мг/л; L_{out} – концентрація очищеної води, мг/л; V - об'єм, м^3; Q - витрата, стічної води, що надходить, м^3/год; X – концентрація природного цеоліту, г/л

On the basis of a detailed analysis of existing waste water treatment systems, an adaptive model of the process of aerobic biological treatment of surface sewage waters from highways with the help of natural zeolite has been improved.

The choice of a mathematical model reflects the hydrodynamics in the existing models of purification processes. For traditional aerotanks, this approach is justified, since there are known dependencies between the length of the reactor and its hydrodynamic characteristics. The mathematical model of the process of purification of surface sewage waters in aerotanks is compiled in the form of a system of differential equations of the material balance, describing the dynamics of changes in pollution concentrations, zeolite and dissolved oxygen [4, 6, 7]:

$$\frac{dL^j_{out}}{dt}=\frac{Q_{liq}(1+R_i)}{V_i}(L^j_{out\,(i\text{-}1)}-L^j_{out\,(i)})+R^j_{Li} \tag{1}$$

where $L^j_{out\,(i)}$ and $L^j_{out\,(i\text{-}1)}$ – the concentration of the j-th component in the considered i-th test and in the previous one, mg/l;

$V_i = V_a/N_a$ – volume of i-th test, m³;

V_a – incoming flow rate, m³/hour;

R_i – coefficient of zeolite recycling;

R^j_{Li} – the speed of consumption of j-th substrate in the i-th test in accordance with an adequate model, mg/l·hour;

$$\frac{dX_i}{dt}=\frac{Q_{lig}(1+R_i)}{V_i}(X_{i\text{-}1}-X_i\ )+R_{X_i} \tag{2}$$

where $X_{i\text{-}1}$ and X_i – the concentration of zeolite in the considered i-th test and in the previous one, g/l;

R_{X_i} – the speed of accumulation of zeolite according to an adequate model, gX/l·hour;

$$\frac{dC_i}{dt}=\frac{Q_{lig}(1+R_i)}{V_i}(C_{i\text{-}1}-C_i)+KLa(C_a-C_i)+R_{C_i} \tag{3}$$

where $C_{i\text{-}1}$ and $C_{i\text{-}1}$ – the concentration of oxygen in the considered i-th test and in the previous one, mg/l;

KLa – coefficient of mass transfer of oxygen, hour⁻¹;

C_a – concentration of water saturation with oxygen at given temperatures and pressures, mg/l;

R_{C_i} – oxygen consumption speed, mgO_2/l·hour.

As the boundary conditions for the solution of equations (1) - (3) the parameters of the first cell are taken

$$X_{i\text{-}1}=\frac{X_r R_i}{(1+R_i)} \tag{4}$$

where X_r – the concentration of zeolite in the recirculation flow, g/l;

$$L^j_{out(i\text{-}1)}=\frac{L_{out}R_i+L_{in}\ )}{(1+R_i\ )} \tag{5}$$

where L_{in} – the concentration of j-th component in surface sewage waters, mg/l;

$$C_{i\text{-}1}=\frac{(C_{sv}+C_{vi}R_i)}{(1+R_i)} \tag{6}$$

where C_{sv}, C_{vi} – dissolved oxygen concentration in surface sewage waters and recirculation flow of zeolite, mg/l. They are usually taken $C_{vi}=0$ and in the absence of aeration $C_{sv}=0$.

The most appropriate biochemical kinetics model was chosen to determine the appropriate speeds of consumption of RL substrate, growth of RH biomass and consumption of oxygen in the RC. In the structure of the model, the module of biochemical kinetics is basic and offers a calculation of the purification process for a number of mathematical models of biochemical kinetics, conditionally divided into 2 groups: mono and fixed order. To identify the model constants and determine the most adequate biochemical kinetics model, the following generalized criterion was used:

$$S=\sum_{i=1}^{n}(X_i^{експ}-X_i^{розр})^2+\sum_{i=1}^{n}(L_i^{експ}-L_i^{розр}) \qquad (7)$$

In the world practice, powdered adsorbents are widely used in the processes of aerobic and anaerobic sewage treatment. It is believed that they not only adsorb organic matter, contributing to the biodegradation of pollutions but also create a buffering effect for the biological system against the toxicants contained in the treated wastewater. In this case natural zeolite was used.

Along with the petrochemical enterprises, the largest sources of pollution of the water environment with petroleum products to date are enterprises of the automobile and highway complex.

One of the ways to increase the efficiency of biological treatment is to introduce a method of biosorption based on a common in time and space biological and adsorption wastewater treatment.

A substrate is included in the structure of anaerobic silt in addition to microorganisms. It is a colloidal system, which consists of products of their vital activity. Treated sewage water includes multicomponent organic and inorganic impurities. For biological purification, the process is determined by the presence of three phases: biogas - liquid - flakes of anaerobic silt (conditionally solid phase), for the process of biosorption is the complication of the presence of another solid phase such as adsorbent. The efficiency of acts of biochemical renewal is largely determined by the hydrodynamic situation and the mass of the exchange characteristics of the apparatus [4, 8].

Since one of the elements of the system is an adsorbent, the mathematical model reflects the absorption of substrates by its surface. Thus the mathematical model taking into account adsorption is as follows:

$$\frac{dX}{dt}=\frac{\mu_m XL}{(K_L+L+\frac{L^2}{K_i}+\frac{Me^2}{K_{Me}})}-\beta X \qquad (8)$$

$$\frac{dL}{dt}=-K_X(L_c-L_c^*)-K_a(L-L_c^*) \qquad (9)$$

$$\frac{dL_C}{dt}=K_X(L_c-L_c^*)-\frac{1}{Y}\frac{\mu_m XL_c}{(K_L+L_C+\frac{L_C^2}{K_i})} \qquad (10)$$

$$\frac{dL_A}{dt}=K_A(L_c-L_c^*) \qquad (11)$$

$$L_c^*=L_c^*(L) \qquad (12)$$

$$L=L(L_A) \qquad (13)$$

where L_A – pollution concentration that adsorbed on the surface of the adsorbent, mg/l;

K_A – mass transfer coefficient of pollution to adsorbent, hour^{-1}.

In order to obtain the most complete mathematical model of the process in the biosorbir, it was supplemented for lotic regime with allowance for recirculation.

$$\frac{dX}{dt}=D(X_{вх}-X)+\frac{\mu_m XL_C}{(K_L+L_C+\frac{L_C^2}{K_i})}-\beta X \qquad (14)$$

$$\frac{dL}{dt}=D(L_{вх}-L)-K_X(L_c-L_c^*)-K_a(L-L_c^*) \qquad (15)$$

$$\frac{dL_C}{dt}=K_X(L_c-L_c^*)-\frac{1}{Y}\frac{\mu_m XL_C}{(K_L+L_C+\frac{L_C^2}{K_i})} \quad (16)$$

$$\frac{dL_A}{dt}=K_A(L_c-L_c^*) \quad (17)$$

$$L_c^*=L_c^*(L) \quad (18)$$

$$L=L(L_A) \quad (19)$$

$$X_{вх}=\frac{rX_r}{1+r} \quad (20)$$

$$L_{вх}=\frac{rL_f}{1+r}+\frac{rL}{1+r} \quad (21)$$

$$D=\frac{1}{t_{пр}} \quad (22)$$

$$t_{пр}=\frac{V}{\upsilon(1+r)} \quad (23)$$

Initial conditions:

$$t=0;L=L_O;L_C=L_{CO};\ L_A=L_{AO};L_f=L_O;\ L_{CO}^*=L_{CO};X=X_O;Xr=X_{rO} \quad (24)$$

where L_f – pollution concentration at the input to the system, mg/l;

$L_{вх}$ – pollution concentration at the input to the device, mg/l;

$X_{вх}$ – biomass concentration at the input (after recycling), mg/l;

X_r – pollution concentration at the input, mg/l;

D – wash speed, hour^{-1};

$t_{пр}$ – time of stay, hour;

r – recirculation factor;

υ – volume flow rate of sewage water, m^3/hour;

V – volume, m^3.

It is noted that biosorbent purification can self-stabilize when exposed to the system from the outside (for example, when volley discharges and change of time of stay) [4, 9].

Thus, the results of simulation modeling allowed to estimate the adequacy of the mathematical models used to describe the dynamics of surface runoff cleaning from highways with the help of natural zeolites with the aim of providing further recommendations and optimal management of sewage disposal plants in biological purification.

In the modern technologies of water purification, the processes of filtration and filtering materials occupy the main place. The progressive deterioration of the ecological situation of water objects requires a constant refurbishment of filtering elements, which are subject to higher technological and environmental requirements. The new generation of modern filtering materials include zeolites.

Experimental studies were carried out in laboratory conditions on model surface sewage waters such as emulsions of petroleum products [10, 11]. Model surface sewage waters was prepared by emulsifying diesel fuel in distilled water while stirring with a mechanical stirrer (3,000 revolutions per minute) for 6-7 min. (Fig. 3-4).

Figure 3 – Use of zeolite samples of different fractions for simulation of surface runoff
Рисунок 3 – Використання зразків цеолітів різних фракцій для моделювання поверхневих стоків

Figure 4 – Simulation of surface sewage waters by emulsifying diesel fuel in distilled water by mixing with a mechanical stirrer
Рисунок 4 – Моделювання поверхневих стоків шляхом емульгування дизельного палива в дистильованій воді при перемішуванні механічною мішалкою

The effectiveness of adsorption purification from petroleum products was investigated in 5 variants of adsorbents. Four zeolite fractions (≤1, 1-3, 3-5, ≥5 mm) and a gravel mixture (3-5 mm) were used as adsorbents for the purification of the model run, which is used in a known method of treatment of washing-off from highways.

The concentration of petroleum products was created in the model sewage waters that typical for rain washing-off from highways, which are formed in the first 10-20 minutes of rain (5-10 mm of precipitation), when the concentration of pollution has the highest value and the outflow from the rain should be cleaned in full [12, 13].

The effect of purification was calculated according to the formula

$$E = (C_{in} - C_{con})/C_{in} \cdot 100 \quad (25)$$

where E – purification efficiency, %;

C_{con} – the concentration of petroleum products in water after purification;

C_{in} – the concentration of petroleum products in water for purification.

The concentration of petroleum products was determined by gravimetric method in accordance with the methodology recommended by the normative documents. The gravimetric method is based on the extraction of petroleum products from the aqueous medium by chloroform, evaporation and removal of the solvent, dissolution of the butts in hexane, separation of the polar compounds on a column with aluminum oxide, removal of the solvent and gravimetric measurement of the residual mass.

The speed of purification increases when the size of the zeolite fraction is reduced, which is typical of the sorption processing methods (Fig. 5-6).

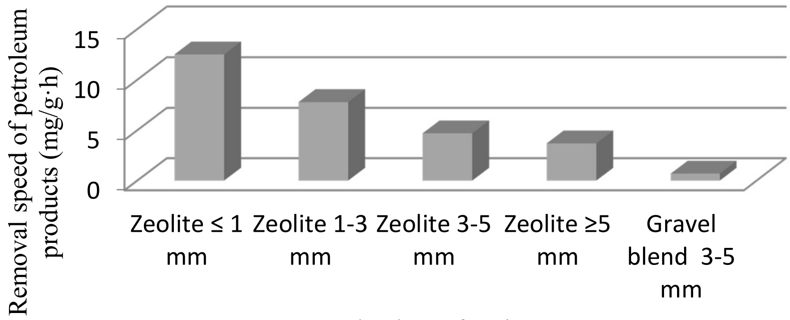

Figure 5 – Removal speed of petroleum products (mg/g·h) with a processing time of 10 minutes
Рисунок 5 – Швидкість видалення нафтопродуктів (мг/г·год) при тривалості обробки 10 хвилин

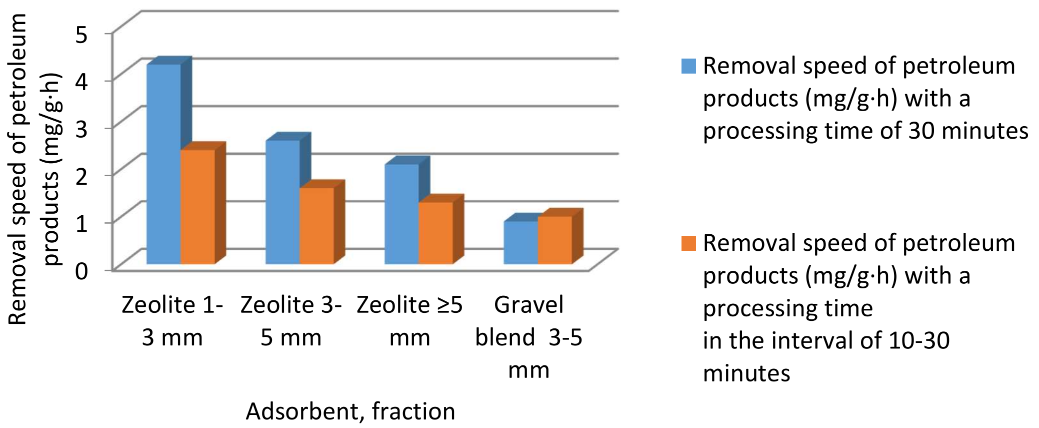

Figure 6 – Removal speed of petroleum products (mg/g·h) with a processing time of 30 minutes and in the interval of 10-30 minutes
Рисунок 6 – Швидкість видалення нафтопродуктів (мг/г·год) при тривалості обробки 30 хвилин та в інтервалі 10-30 хвилин

Results and Discussion. The obtained data have been confirmed by the adsorption mechanism for the removal of petroleum products. As a result of experimental researches, efficiency of the use of alternative natural materials such as zeolites has been determined [14].

Implementation of the newest methods of purification with the use of natural zeolites solves the problem of raising the technical level of highways, traffic safety and ecological functioning.

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ДОСЛІДЖЕННЯ МЕТОДІВ ОЧИЩЕННЯ ПОВЕРХНЕВИХ СТОКІВ З АВТОМОБІЛЬНИХ ДОРІГ З ВИКОРИСТАННЯМ СУЧАСНИХ ФІЛЬТРУЮЧИХ МАТЕРІАЛІВ

Угненко Євгенія Борисівна, доктор технічних наук, професор, Український державний університет залізничного транспорту, завідувач кафедри вишукувань та проектування шляхів сполучення, геодезії та землеустрою, e-mail: ugnenko.ievgenia@gmail.com, тел. +30675713565. Україна, 61050, м. Харків, майдан Фейєрбаха, 7, к. 1.300. https://orcid.org/0000-0002-3945-788X

Сорочук Наталія Ігорівна, Український державний університет залізничного транспорту, асистент кафедри вишукувань та проектування шляхів сполучення, геодезії та землеустрою, e-mail: nat.sorochuk50@gmail.com, тел. +30953265929. Україна, 61050, м. Харків, майдан Фейєрбаха, 7, к. 1.300. https://orcid.org/0000-0002-6042-2681 .

Тимченко Ольга Миколаївна, кандидат технічних наук, Український державний університет залізничного транспорту, доцент кафедри вишукувань та проектування шляхів сполучення, геодезії та землеустрою, e-mail: oleka55@gmail.com, тел. +30958307968, Україна, 61050, м. Харків, майдан Фейєрбаха, 7, к. 1.205. https://orcid.org/0000-0002-5391-0388

Петрович Володимир Васильович, кандидат технічних наук, професор, старший науковий співробітник, професор кафедри транспортного будівництва та управління майном Національного транспортного університету**.** e-mail: petrovichvv60@ukr.net, тел. +3804428027338, Україна, 01010, м. Київ, вул. М. Омеляновича-Павленка, 1, к. 138., https://orcid.org/0000-0003-0422-2535

Анотація. Розглянуто загальні властивості сучасних фільтруючих матеріалів нового покоління, таких як природні цеоліти. Проаналізовані перспективи застосування природних цеолітів для очищення стоків з поверхні автомобільних доріг. Визначено, що цеоліти є надзвичайно перспективною природною сировиною, яка характеризується високими технологічними параметрами і відсутністю негативних екологічних наслідків при їх широкомасштабному застосуванні. Представлені математичні моделі аеробної та анаеробної біологічної очистки поверхневих стоків. Одним із способів підвищення ефективності біологічної очистки є впровадження методу біосорбції, заснованого на спільній у часі та просторі біологічної та адсорбційної очистки стоків. Результати імітаційного моделювання дозволили оцінити адекватність використаних математичних моделей для опису динаміки очищення поверхневих стоків з автомобільних доріг за допомогою природних цеолітів з метою надання подальших рекомендацій та оптимального управління очисними спорудами при біологічній очистці. Удосконалена математична модель може бути використана для визначення якості поверхневих стоків з автомобільних доріг. В результаті експериментальних досліджень визначено ефективність використання альтернативних фільтруючих природних матеріалів - цеолітів. Впровадження новітніх методів очистки із застосуванням природних цеолітів вирішує завдання підвищення технічного рівня автомобільних доріг, безпеки руху та екологічного функціонування.

Ключові слова: поверхневі стоки з автомобільних доріг, природні цеоліти, математичне моделювання, адсорбція, концентрація забруднюючих речовин

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