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Struvite Crystallization for Anaerobic Digested Supernatants: Influence on the Ammonia Efficiency of the Process Variables and the Chemicals Dosage Modality

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The treatment or recovery of nutrients (N and P) from anaerobically digested supernatants is now a central topic, related both to the zootechnical wastewaters and the supernatants from the sludge lines of urban wastewater treatment plants (WWTP), applying codigestion of excess sludge and organic fraction of municipal solid waste (OFMSW). In both cases, the crystallization and precipitation of Struvite (Magnesium Ammonium Phosphate) is a hypothetical solution to reduce the high concentrations of ammonia nitrogen and to reuse the final product. This study shows the effects of the main variables of Struvite crystallization (pH, reaction time and dosage modality) applied in bench scale to anaerobic zootechnical and codigested urban supernatants. The matrices with initial concentrations of NH_4-N from 1000 to 2000 mgL^{-1}, were added to phosphoric acid (source of P) and magnesium oxide (source of Mg), pure and of industrial origin, to achieve the correct molar ratios. Adjustment of the pH at 8.5 was provided through NaOH dosage. The experimental tests, at increasing ratios (Mg:N:P) from 1:1:1 to 2:1:1, have been carried out at reaction times from 0 to 60 minutes and at two distinct dosage modalities. Indeed, the dosing tests were firstly provided by direct addition of the different reagents and next by indirect addition, with the prior dilution of the magnesium source in the phosphoric acid. The results defined as the different sequence of reagents addition modifies the percentage of struvite formation and, consequently, the ammonia decrease. Specifically, compared to the obtained efficiencies range between 50 % and 70 % with direct dosage, the tests with indirect dosage allow the recovery of nitrogen greater than 20 %, at the same molar ratios and reaction times. The time factor does not affect the precipitation more than 10 %, regardless of the dosage carried out. Further, the use of a thermodynamic model allowed to assess and justify the transformation of other ions in solution (K^+ and Ca^{++}) highlighting the formation of other secondary compounds (k-struvite, hydroxyapatite).

1. Introduction

Anaerobic digested sludge represents an important resource in agricultural applications, defining a possible recycle of nutrients by soils assimilation. Indeed, the digestate spreading can enhance the land fertility, improving the contents of organic matter and microelements. Moreover there is increasing concern about the excessive manure spreading, which is related to the nutrients release in waterbodies and the consequent degradation of the water quality. Therefore, both the usage of sustainable and non-invasive agricultural and breeding techniques and the application of effective and feasible farming wastewater treatments are required. Concerning the last diffusion of the anaerobic digestion process, codigestion of waste activated sludge and the organic fraction of municipal solid waste (OFMSW) has been widely applied (Bolzonella et al., 2006) as alternative to the disposal and for the production of good quality compost. Onsite treatment could represent a reliable solution to cope with the agroindustrial productivity with the reduction of the nutrients pollution, as offsite handling is often economically unsustainable (Wang et al., 2005). In this scenario, the application of technologies to favour the energy production from

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zootechnical wastes and to enhance the fertilizers obtainment from digestate could be valuable for farming producers.

The phosphorous (P) recovery through struvite (MAP-$MgNH_4PO_4$) precipitation represents, among the different P recovery techniques, a reliable method to supply to the demand of this limited and almost consumed resource and to remove both ammonia (NH_4) and phosphate (PO_4) (Zeng et Li, 2006). Struvite precipitates has white orthorhombic crystals, which internal structure is composed by regular tetrahedrons of PO_4^{3-}, distorted octahedrons of $Mg(H_2O)_6^{2+}$ and NH_4 groups, linked together through hydrogen bonds. The phases of nucleation and crystal growth have been deeply studied to determine the optimization of the solution conditions and the relations with the type of crystal formation. According to Battistoni et al. (2005), both the nucleation and growth occur simultaneously when the fines contents are scarce, while with higher particles concentrations the crystal accretion is the dominant phase. The increasing struvite precipitation is related to the pH trend: each formation phase corresponds to the decrease of the pH values and to the enhancement of the phosphate solubility, with increment in P removal at greater pH. On the other hand, struvite solubility increases with pH values higher than 9. Another predominant factor is represented by the method of reagents dosage to allow the precipitation. Experiments showed how the different addition of Mg^{2+} and PO_4^{3-} sources determined different percentages of struvite formation and hence the ammonia reduction (Harrison et al., 2011).

In this study, batch tests for the struvite precipitation were conducted on two different anaerobic supernatants, from the digestion of zootechnical manure and the codigestion of the OFMSW and urban sludge, by varying the Mg^{2+} and PO_4^{3-} fonts and the Mg:N:P molar ratios, the dosage modality and the reaction time, to evaluate P and N removal. The objective of this paper is to provide an overview on impacts in struvite precipitation and nutrient recovery at different operative conditions, aiming at obtaining products with agronomic properties.

2. Materials and Methods

Tests at laboratory scale were performed on two different anaerobic digested supernatants. The substrates derived from a full scale digester of an urban wastewater treatment plant, applying codigestion of the excess sludge and the organic fraction of municipal solid waste (A), and from the digestion of cattle manure and agroindustrial residuals (B). Batch tests to evaluate the precipitation of struvite were developed using a 1 L reactor, equipped with mixing and thermal conditioning systems. The pH and temperature values were monitored through online probes. Samples of 50 mL were collected and analyzed at the beginning and consequently after 2, 5, 15, 30 and 60 min, once filtered at 20 µm and 0.45 µm. Optimal precipitation conditions were reached through the addition of pure and industrial magnesium oxide MgO (purity w/w 85 %), phosphoric acid H_3PO_4 (purity w/w 75 %) and sodium hydroxide NaOH (solution 30 %w/w) to maintain the pH at 8.5, by varying the molar ratios of Mg:N:P at 1:1:1, 1.5:1:1 and 2:1:1. Direct and indirect reagent dosage was achieved in the first case by adding MgO followed by H_3PO_4 and, in the second modality, by mixing MgO in the phosphoric acid before the dosage. All the testing conditions and parameters, for both the supernatants, are summarized in Table 1.

Table 1: Testing conditions for the struvite precipitation

$MgO-H_3PO_4$ Dosage	Supernatants	Molar ratios	MgO_{pure}	$MgO_{industrial}$	H_3PO_4	NaOH
		Mg:N:P	g	g	mL	mL
Direct	A	1:1:1	0.303	0.357	0.659	1.70
		1.5:1:1	0.463	0.545	0.659	1.70
		2:1:1	0.623	0.733	0.659	1.60
	B	1:1:1	0.498	1.200	1.014	1.75
		1.5:1:1	0.749	1.810	1.014	1.50
		2:1:1	2.000	2.400	2.040	3.50
Indirect	A	1:1:1	0.303	0.357	0.659	1.75
		1.5:1:1	0.463	0.659	0.659	1.40
		2:1:1	0.623	0.733	0.659	1.30
	B	1:1:1	1.140	0.578	2.330	5.00
		1.5:1:1	1.710	0.879	2.330	3.00
		2:1:1	2.000	1.177	2.340	2.05

The characterization of the influent matrices and the samples, collected at different reaction times, was carried out according to Standard Methods (APHA, 2005). Through the use of the thermodynamic model Visual Minteq ver. 3.0, the estimation of struvite precipitation and other compounds formation was assessed.

3. Results and Discussion

3.1 Characterisation of the anaerobic supernatants

Through the characterisation of the two liquid fractions from the digestate dewatering, an estimation of the main parameters for the reagent dosage was conducted (Table 2). The first matrix A, from the codigestion of the excess sludge of an urban WWTP and the OFMSW, was characterised by average values of pH and alkalinity equal to 8.01 and 5811 mgL^{-1}. The supernatants B, from the digestion of cattle manure and agroindustrial residuals, is characterized by higher values of pH and alkalinity, equal to 8.57 and 8929 mgL^{-1} respectively. The main parameter for the evaluation of struvite precipitation is the ammonia nitrogen NH_4-N, which amounts were of 1119 mgL^{-1} (A) and 1797 mgL^{-1} (B), while the concentration of Mg resulted higher in A (99 mgL^{-1}) rather than in B (mgL^{-1}). The PO_4-P amount was almost absent for the first supernatants, with an average concentration of 8.6 mgL^{-1}, while in B it assessed at a medium value of 61 mgL^{-1}. Considering the sodium and calcium concentrations, the values were almost comparable for both the supernatants, equal to 684 mgL^{-1} (A) and 867 mgL^{-1} (B) for Na^+ and to 215 mgL^{-1} (A) and 220 mgL^{-1} (B) for Ca^{++}, while a net difference was appreciable for the potassium. Indeed, the K^+ amount in A was equal to 457 mgL^{-1} while in B the average values was of 1757 mgK$^+$L $^{-1}$.

Table 2: Supernatants characterization - excess sludge and OFMSW (A) and cattle manure (B)

Supernatants	pH	Alk	COD	NH_4-N	P-PO_4	Na	K	Mg	Ca
		mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}	mgL^{-1}
A	8.08	5811	12653	1119	8.57	684	457	99	215
B	8.57	8929	8907	1797	61	867	1757	19	220

3.2 Effects of increasing molar ratios and reagents dosage on removal performances

In this section, an evaluation of the dosage modality of H_3PO_4 and MgO, both pure and of industrial origin, on the two different kind of supernatants is given. Further, this effect is linked with the performances due to the molar ratio Mg:N:P increase, from minimum values of 1:1:1 to the maximum of 2:1:1. In particular, figure 1 shows the NH_4-N removal at the end of the precipitation test, after 1 h, by varying the molar ratios and the dosage of pure MgO. Concerning the sample A added with MgO and next with H_3PO_4, a slight increase in NH_4-N removal from 40 to 49 % corresponds to a greater dosage of Mg source, from 1:1:1 to 2:1:1. Indeed, when the molar ratio is 1.5:1:1, the increment in NH_4-N reduction (Δ=5 %) has almost reached a constant value, determining a partial increment when increasing the MgO dosage until 2:1:1 (removal different of 4 %). The same trend is appreciable when testing B, which increment in NH_4-N removal from the first and second molar ratios conditions (from 1:1:1 to 1.5:1:1) is equal to 9 %, while a further MgO addition reveals only in 3 % of increment in NH_4-N reduction (total removal of 12 %). This suggests that the reagent dosage is effective at initial condition (1:1:1), without increasing the molar ratios.

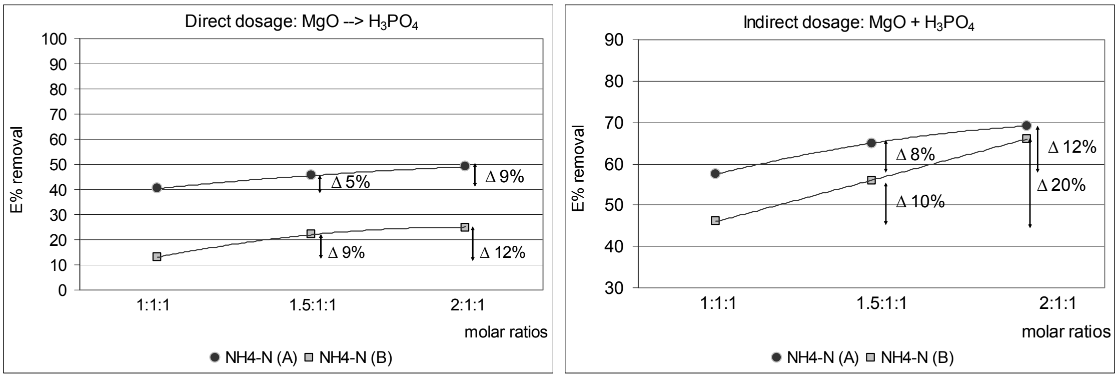

Figure 1: NH_4-N removal with pure MgO – direct and indirect dosage

Indeed the Mg value reached the almost complete removal at initial testing condition, with a reduction of 99 % at 1:1:1 molar ratio both for A and B, determining the saturation condition both for A and B. On the other hand, when adding MgO and H_3PO_4 mixed together, the increase in molar ratio determined a greater increment in NH_4-N removal in B, with an average reduction of 20 % at maximum molar ratio of 2:1:1, compared to the 10 % decrease obtained at intermediate dosage of Mg:N:P equal to 1.5:1:1. Concerning the precipitation test carried out on the sample A, as previously evaluated, an increase in Mg source dosage corresponded to a modest NH_4-N reduction percentage, varying from 57 % to 69 % as removal efficiencies. This aspect could be correlated to the presence of competitive salts, as calcium, dissolved in the matrix.

Precipitation test conducted by using the industrial magnesium oxide, which final removal performances are shown in Figure 2, highlighted greater overall NH_4-N reduction. Significant increases were detected when testing the supernatants B, at rising molar ratio conditions. Indeed, under direct reagent dosage, the removal efficiencies enhanced from 30 % (1:1:1) to 47 % (2:1:1). Similarly, the indirect dosage determined a variation in reduction percentage equal to 10 % for B. The MgO addition until reaching the molar condition of 2:1:1 had no effect in NH_4-N removal, as the best condition was reached with direct reagents dosage at intermediate molar ratio of 1.5:1:1, highlighting a general performance of 87 % (A). The indirect dosage for A revealed how the minor molar ratio condition was enough to obtain a NH_4-N removal of 78 %. The use of industrial magnesium oxide permitted to obtain an immediate reaction between chemicals, determining higher removal percentages if compared to the results related to the pure MgO dosage. Also, the effect linked to the indirect dosage was appreciable in this case (B), resulting in higher reduction percentages if compared with the results obtained when directly dosing the reagents.

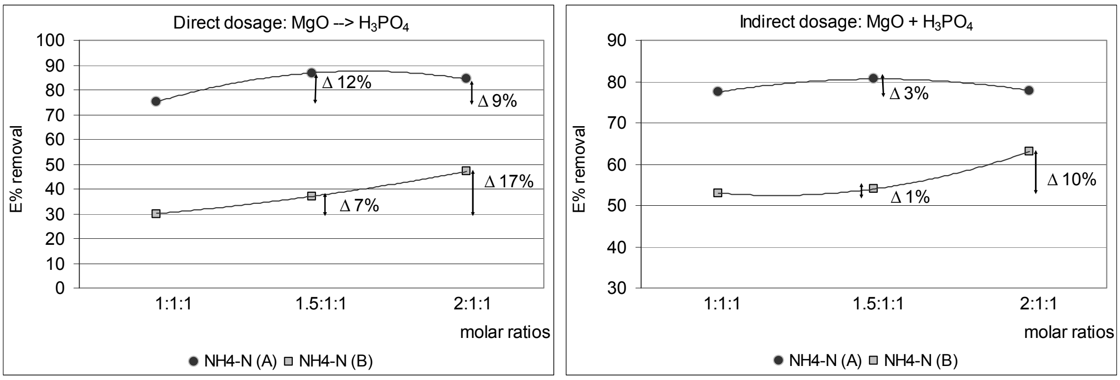

Figure 2: NH_4-N removal with industrial MgO – direct and indirect dosage

3.3 Ammonia removal at increasing reaction time

Struvite precipitation tests were developed on supernatant A, to evaluate the effect of the reaction time. Experimentals were carried out using both the pure and industrial magnesium oxide, and the results are shown in Figure 3 and Figure 4 respectively. Samples collected at different intervals highlighted the elevated performances during the first minutes of the investigation. When dosing pure MgO and H_3PO_4 separately, after 2 minutes the NH_4-N concentration assessed at values on the average equal to 720 mgL^{-1} with a removal of about 35 %. The increase in reaction time determined a further reduction of NH_4-N only at increasing the molar ratios. Indeed, when Mg:N:P was equal to 1:1:1 , the reduction percentages reached values equal to 38 % and 39 % after 5 and 15 min, remaining constant and equal to 40 % at the end of the test (1 h). When increasing the MgO addition, the NH_4-N concentrations decreased of 40 % (1.5:1:1) and 46 % (2:1:1) after 30 min, reaching further small reduction of 45 % (1.5:1:1) and 49 % (2:1:1) after 1 hour (Figure 2). The effect related to short reaction times efficacy was more estimable when indirectly dosing the reagents. Indeed, after 5 min, the NH_4-N removal percentages reached values equal to 56 % (1:1:1) and 69 % (2:1:1) and no significant reduction was obtained at the end of the experimental. The same trend was evaluated when the molar ration was equal to 1.5:1:1, with the only difference that the asymptote condition was reached after 15 min, with a percentage of removal of 62 %. The NH_4-N concentrations after 1 h were equal to 476 mgL^{-1} (1:1:1), 392 mgL^{-1} (1.5:1:1) and 345 mgL^{-1} (2:1:1).

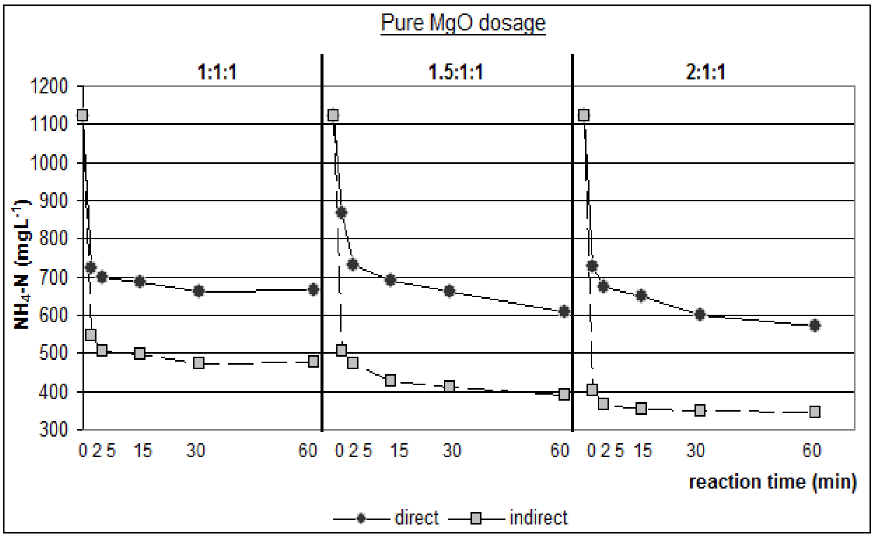

Figure 3: NH_4-N trends over reaction time – direct and indirect dosages using pure MgO

Results on the ammonia removal performances at different reaction times and molar ratios, when directly and indirectly adding MgO in industrial origin are shown in Figure 4. The performances achieved with this type of magnesium oxide, already highlighted above, were confirmed in the experimental. Indeed, concerning the separate reagents addition, the removal percentages of NH_4-N after 2 min of testing were equal to 67 % (1:1:1), 76 % (1.5:1:1) and 74 % (2:1:1), with corresponding concentrations of 366 mgL^{-1}, 269 mgL^{-1} and 286 mgL^{-1}. A further average reduction of 10 % was overall obtained when monitoring the ammonia amounts at the end of the tests. For the unitary molar ratio, the ammonia reduced to 279 mgL^{-1} after 1 h, with a removal of 75 %. When increasing the Mg contents, the reduction percentages reached values of 87 % and 84 % at 1.5:1:1 and 2:1:1 after 30 min, with minimum concentration of 150 mgL^{-1} and 180 mgL^{-1} and no consistent decrease was observed at the end of the tests. The same trend was appreciable when indirectly dosing the reagents. The variation in removal percentages was on the average equal to 10 %, between 2 and 60 min reaction times, with the main difference that the higher reduction values were reached after few minutes testing. Indeed, the removal after 15 minutes was equal to 75 % (1:1:1), 77 % (1.5:1:1) and 75 % (2:1:1) while at the end of the tests the obtained values were of 77 %, 80 % and 78 % respectively. Hence the effect related to the reaction time increase was, in the last case, negligible, irrespective of the dosage modality.

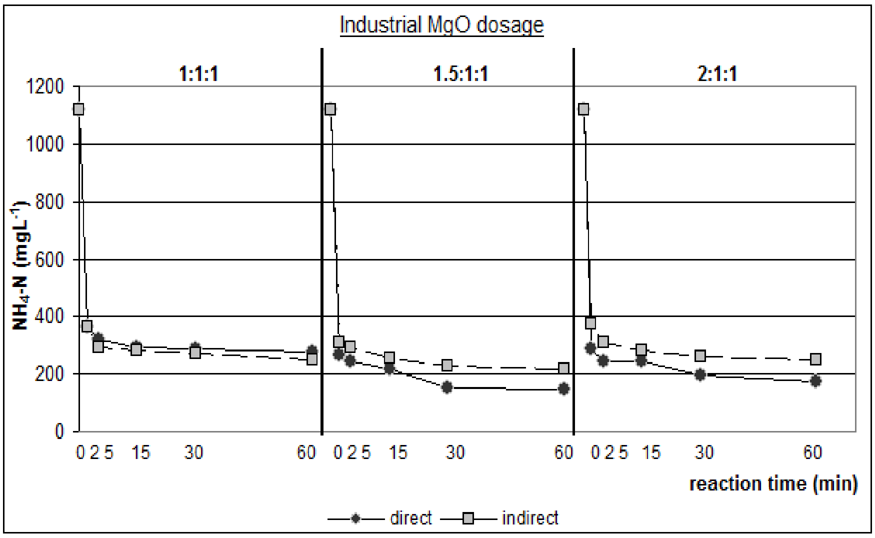

Figure 4: NH_4-N trends over reaction time – direct and indirect dosages using industrial MgO

3.4 Simulation of the struvite, k-struvite and hydroxyapatite formation

An evaluation of the possible precipitation of possible compounds on the supernatants B was carried out at pH=9, using the software Visual Minteq. Ions in solution, according to the above characterisation, suggested the possibility of other precipitation products over struvite. Indeed, the presence of Ca^{++} and K^{+} can determine the formation of hydroxyapatite $Ca_5(PO_4)_3OH$ or HAP (LogK -44.33), dicalcium phosphate $CaHPO_4 \cdot 2H_2O$ (LogK -19.27) or k-struvite $KMgPO_4 \cdot 6H_2O$ (LogK -10.61), besides the struvite (LogK -13.27) formation. The simulations were carried out by varying the Mg content and maintaining the N and P moles equal to 1: Mg moles were then defined equal to 0.01, 0.1, 0.2, 0.5, 1, 1.5 and 2. As expected, the k-struvite formation occurred. The HAP precipitation took place, instead of the other possible Ca^{++} compounds, due to its greater thermodynamic stability. The percentage of MAP on the total precipitated compounds reached up values of 98 % at molar ratio of 0.2:1:1, while 100 % MAP formation occurred when Mg:N:P was equal to 1:1:1. The higher HAP and k-struvite precipitation was reached at ratios of 0.01:1:1, with percentages of HAP and k-struvite moles on the total moles equal to 76 % and 24 % respectively. The k-struvite presence was null at increasing ratios, while the HAP progressively decreased.

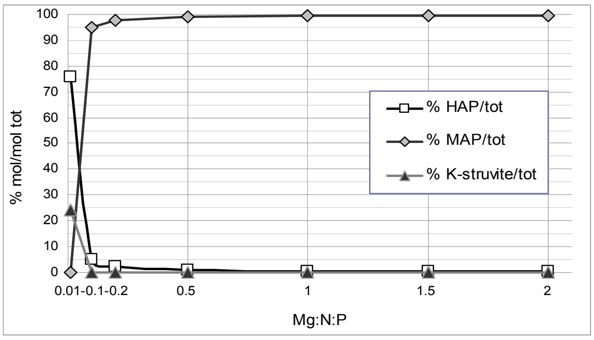

Figure 5: Visual Minteq simulation: precipitation of secondary compounds

4. Conclusions

Tests on anaerobic supernatants from the digestion of excess sludge plus the OFMSW and cattle manure with agroindustrial residuals were developed, by directly and indirectly adding pure and industrial MgO and H_3PO_4 and evaluating the effects of molar ratios and reaction time increases. The results highlighted how the indirect industrial MgO addition determined greater NH_4-N removals at the same molar ratios, when compared with the performances obtained at direct dosage. The indirect dosage of pure and industrial MgO resulted in a general improvement of 20 % of NH_4-N reduction, except when the presence of other ions in solution was consistent. The time factor determined differences in precipitation within 10 %, regardless of the dosage mode, as struvite precipitation occurred within the first minutes. Also, HAP and k-struvite formation was determined through the use of a thermodynamic model, defining amounts on the total precipitate compounds of 76 % and 24 % respectively at molar ratio lower than 1:1:1.

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