Influence of Bentonite and MB4 on the Chemical Characteristics of an Oxisol

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Abstract

The growing concern with the quality of life and the environment, due to the degradation of natural resources and their contamination, mainly with agrochemicals, led to the emergence of a sustainable or alternative agriculture. The objective of this study was to evaluate the effect of the addition of increasing doses of bentonite and MB4 on the availability of nutrients to the soil. The experiment consisted of a 4 × 4 factorial, bentonite doses (0, 30, 60 and 90 t·ha⁻¹) and MB4 doses (0, 3, 6 and 9 t·ha⁻¹) with three replications. The soil mixtures with the treatments were conditioned in the plastic pots, incubated for 90 days in a greenhouse, and chemically analyzed. Data were submitted to analysis of variance and comparison of means by the Tukey test. Increasing doses of bentonite and MB4 promoted an increase in the calcium (Ca), magnesium (Mg) in the soil sample either alone or the mixture of two factors, except for the mixture of the Ca Mg doses. Increasing doses of bentonite increased the cation exchange capacity of the soil, favoring the availability of nutrients in the soil. The increasing doses of MB4 favored the increase of the pH values and, consequently, decreased the soil potential acidity values for the applied bentonite doses. On the other hand, these treatments decreased the cation exchange capacity of the soil.

Keywords

Soil Conditioner, Nutrients, Rock Dust

1. Introduction

The soil can lose its nutrients through several processes: plant uptake, erosion, volatilization and leaching. Leaching is probably the most important process of
nutrient loss in moist soils, but according to [1] is very difficult to avoid it.

The low productivity of crops cultivated in sandy soils is due to constant losses of the nutrients through the ease with which they allow the movement of nutrients from the superficial layers to deeper layers of the soil, far from the roots of the plants [2]. Therefore, the replacement of these nutrients, through elements and chemical compounds, is indispensable to the crop yields.

Considering the model of agricultural development adopted in Brazil, much of the demand for fertilizers for crops is supplied through the use of readily soluble fertilizers by NPK formulations, associated or not with the use of macro and micronutrients, to ensure satisfactory yields. Many farmers also use organic fertilizers as a source of nutrients, sometimes associated with mineral fertilizers. In organic agriculture, ground natural rocks have been used as a source of nutrients. The use of natural rocks in agriculture, as natural fertilizers, has grown greatly in recent years [3].

The minerals contained in the rocks are nutrient sources of slow release of to the soil and, depending on their mineralogical composition, can contribute with a varied and expressive amount of essential elements to the plants. The use of grounded rock silicate fertilizers is attractive as these types of fertilizers have the potential to supply soils with a large array of macro and micronutrients in comparison to commercially available soluble fertilizers, which commonly only supply the main macronutrients N, P and K, but not nutrients such as Ca, Mg and micronutrients [4]. Grounded rocks are increasingly being used due to the need to recover impoverished, unbalanced soils that have lost much of the nutrient reserve of their mineral constituents [5].

The effectiveness of rock powder as a source of nutrients to the soil is questioned because of the low solubility and the need to be applied in large amounts to the soil to obtain positive responses [6]. This depends on factors such as the chemical and mineralogical composition of the rock, the granulometry of the material, the reaction time, and soil factors such as pH and biological activity [7].

In Brazil, there are still few references to the use of grounded rocks in agriculture on a commercial scale. Mixtures of several grounded rocks have been commercialized, for example, by the company MIBASA of Arapiraca, State of Alagoas, whose main product is the MB4 rock meal. MB4 is a mixture of two rocks: biotitaxisto and serpentinite, in the ratio of 1:1 [8]. This product comes from the grinding of silicate rocks and has about 48% silica in its composition.

According to [9], MB4 has been tested in various soils and has proven to be an efficient recovering and improver of soils, because it has a wide variety of chemical elements, providing essential nutrients for plants.

Bentonite has also been investigated as a possibility for agronomic use, as soil conditioning or fertilizer material [2] [10]. Bentonites are predominantly composed of mineral clay from the smectite group, usually known as montmorillonite, and quartz impurities. In some varieties are also kaolinite and illite [11].
These are found in large deposits in the municipality of Boa Vista, Paraíba state, Brazil.

Chemical and mineralogical analyses showed that there are differences between clays of different colors. Green and chocolate clays, for example, generally contain high smectite content and few impurities, such as illite and kaolinite. These clays are also chemically different because they contain low silicon content and high aluminum content relative to other colors [11].

Both bentonite and MB4 were donated materials to be used in scientific research, so there was no cost to purchase them.

In this sense, the objective of this work was to evaluate the effect of the addition of increasing doses of bentonite and MB4 on the availability of nutrients to the soil.

2. Materials and Methods

This experiment was carried out in a greenhouse at the Agricultural Engineering Department, Federal University of Campina Grande, Paraíba, Brazil, using soil samples collected in the superficial layer (0 - 20 cm) of Eutrophic Red Latosol [12]. These samples were air-dried, crushed, sieved through a 2 mm sieve and chemically characterized according to [13], presenting the following attributes: pH (H2O) = 5.5; Ca = 2.14 cmolc∙kg⁻¹; Mg = 0.98 cmolc∙kg⁻¹; Na = 0.12 cmolc∙kg⁻¹; K = 0.18 cmolc∙kg⁻¹; H+ Al = 6.25 cmolc∙kg⁻¹; organic carbon = 8.13 g kg⁻¹; P = 8.0 mg kg⁻¹ and CTC = 9.67 cmolc∙kg⁻¹.

The bentonite clay samples were collected in the Primavera mine, Paraíba State, Brazil. These samples were air dried and sieved with 0.074 mm mesh in order to precede X-ray diffraction and X-ray florescence analysis. According to these analysis, bentonite samples presents picks of smectite clays, tridymite (a silicate mineral and polymorph of high temperature of quartz), and quartz (low quantity), also presenting the following composition: SiO2 = 76.784%; Al2O3 = 13.339%; Fe2O3 = 6.035%; MgO = 2.225%; CaO = 0.759% and other oxides = 0.545%. The cation exchange capacity was also determined by the methylene blue method [14], resulting in 48 meq/100g of dry clay and specific area: 375 m²/g.

The MB4 rock powder used in the experiment came from MIBASA company, located in Alagoas state, Brazil. This powder is a mixture of two rocks: biotite shale and serpentinite, in the proportion of 1:1 [8]. According to [15], MB4 is a rock mixture composed of: 39.73% SiO2; 17.82% MgO; 7.10% Al2O3; 6.86% Fe2O3; 5.90% CaO; 1.48% Na2O; 0.84% K2O; 0.18% of S; 0.075% P2O5; 0.074% Mn; 0.029% Cu; 0.029% Co and 0.03% Zn.

The experiment followed a completely randomized design, in a 4 × 4 factorial scheme: four doses of bentonite (B0 = 0, B30 = 30, B60 = 60 and B90 = 90 t∙ha⁻¹) and four doses of MB4 (M0 = 0; M3 = 3; M6 = 6 and M9 = 9 t∙ha⁻¹) with three replications, in a completely randomized design, totaling 48 experimental units.

Each experimental unit consisted of a plastic bucket with 14 kg of soil, pre-
viously dried, sieved and mixed with the doses of bentonite and MB4 corresponding to the treatments.

The soil mixtures with the treatments were conditioned in the plastic buckets and placed in field capacity with water supply, remaining incubated for 90 days. The moisture of these mixtures was maintained close to the field capacity.

After incubation, soil samples from each experimental unit were collected, air dried, sieved in a 2 mm mesh and chemically characterized, according to the methods adopted by [13].

The results were submitted to analysis of variance, using the SISVAR program [16].

3. Results and Discussion

The analysis of variance showed that the interaction between the bentonite and MB4 factors was significant at p < 0.01 for all elements, except for potassium and H + Al, which did not present significant effects. Bentonite doses influenced all analyzed parameters (p < 0.01), while MB4 doses had a significant effect for all parameters except for potassium (Table 1).

In the treatments without MB4, represented by the curve M0 (Figure 1(a)), Ca is released by bentonite, and the results were better adjusted to the quadratic regression model, where its peak occurred in 1.3 cmol·kg⁻¹, then decreasing with increasing doses. However, even with this decrease, bentonite promoted an increase of 13.6% when the dose of 90 t·ha⁻¹ is compared to control. On the other hand, the M3, M6 and M9 t·ha⁻¹ curve of MB4, behaved inversely to the M0 (0 t·ha⁻¹) curve, whose initial values (0 t·ha⁻¹ of bentonite) were 1.43; 1.33 and 1.43 cmol·kg⁻¹, respectively, greater than 1.058 cmol·kg⁻¹ (M0); decreasing with the increase of the doses of bentonite until the minimum point 0.96; 1.06 and 1.11 cmol·kg⁻¹ for M3, M6 and M9, respectively.

The Ca contained in MB4 interacted with the bentonite providing a reduction of the available Ca (Figure 1(a)). This occurred, possibly, to the adsorption of Ca by bentonite. According to [17], this is due to the higher specific surface area of the bentonites and, consequently, higher cation adsorption capacity. However, from the minimum point, the levels of Ca available in the soil increased in the M3, M6 and M9 curves, probably because of the saturation of the clay exchange sites, i.e., it exceeded the maximum adsorption capacity of the bentonite.

Magnesium (Figure 1(b)) presented the opposite effect compared to Ca, i.e., increasing doses of bentonite without MB4 (M0) had lower Mg values than those with bentonite and MB4 (M3, M6 and M9). However, in the M0 curve it can be observed an increase of 158.9% in the available Mg in the soil, when comparing the 90 t·ha⁻¹ dose with the 0 t·ha⁻¹ dose of bentonite, showing that there was release of Mg by bentonite. Also in Figure 1(b), it was found that the doses of MB4 within the increasing doses of bentonite had a linear trend of the Mg available in the soil, promoting an increase of 306.9; 144.6% and 141.6% when comparing the highest bentonite dose (90 t·ha⁻¹) with the control (0 t·ha⁻¹) for
Table 1. Analysis of variance of soil parameters: calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), potential acidity (H + Al), cation exchange capacity (CEC) and pH after incubation with the treatments.

| Source   | DF | Mean Square          | Ca   | Mg   | Na   | K    | H + Al$^1$ | CEC  | pH    |
|----------|----|----------------------|------|------|------|------|------------|------|-------|
| Bent (B) | 3  | 0.09** 2.250** 3.338** | 0.011** | 0.015** | 13.532** | 1.328** |
| Linear   | 1  | - - - 0.006* 0.034** | -    | -    | -    | -    | -          | -    | -     |
| Quad     | 1  | - - - 0.022** 0.003ns | -    | -    | -    | -    | -          | -    | -     |
| Deviation| 2  | - - - 0.005* 0.007* | -    | -    | -    | -    | -          | -    | -     |
| MB4 (M)  | 3  | 0.022* 0.432** 0.253** | 0.002ns | 0.414** | 5.862** | 1.924** |
| Linear   | 1  | - - - - 1.231** | -    | -    | -    | -    | -          | -    | -     |
| Quad     | 1  | - - - - 0.005ns | -    | -    | -    | -    | -          | -    | -     |
| Deviation| 2  | - - - - 0.006ns | -    | -    | -    | -    | -          | -    | -     |
| B x M    | 9  | 0.066** 0.099** 0.352** | 0.001ns | 0.004ns | 0.416** | 0.767** |
| Linear   | 1  | 0.002ns 0.922** 1.176** | -    | -    | -    | -    | 10.786** 0.213** |
| Quad     | 1  | 0.128** 0.258** 0.004ns | -    | -    | -    | -    | 0.276ns 1.888** |
| Deviation| 1  | 0.019ns 0.142* 0.028ns | -    | -    | -    | -    | 0.001ns 3.192** |
| Linear   | 1  | 0.105** 2.424** 3.137** | -    | -    | -    | -    | 12.060** 0.006ns |
| Quad     | 1  | 0.252** 0.006ns 0.112* | -    | -    | -    | -    | 0.396ns 0.019ns |
| Deviation| 1  | 0.003ns 0.038ns 0.005ns | -    | -    | -    | -    | 0.006ns 0.001ns |
| Linear   | 1  | 4.2e-5 ns 1.542** 1.830** | -    | -    | -    | -    | 9.322** 0.002ns |
| B/M0     | 1  | 0.185** 1.0e-6ns 0.282** | -    | -    | -    | -    | 0.001ns 0.015ns |
| Quad     | 1  | 0.015ns 0.022ns 2.464** | -    | -    | -    | -    | 1.855** 8.2e-3ns |
| Deviation| 1  | 0.027* 1.980** 1.473** | -    | -    | -    | -    | 6.195** 3.973** |
| Linear   | 1  | 0.147** 0.030ns 0.388** | -    | -    | -    | -    | 0.456* 1.280** |
| Quad     | 1  | 0.008ns 0.280** 2.281** | -    | -    | -    | -    | 2.930** 0.291** |
| Deviation| 1  | 0.156** 0.004ns 0.054ns | -    | -    | -    | -    | 5.563** 0.105* |
| Linear   | 1  | 0.064** 0.103* 0.026* | -    | -    | -    | -    | 0.516* 1.817** |
| Quad     | 1  | 0.082** 0.141* 0.001ns | -    | -    | -    | -    | 0.001ns 0.405** |
| Deviation| 1  | 0.11ns 1.291** 2.412** | -    | -    | -    | -    | 0.177ns 0.018ns |
| Linear   | 1  | 0.10** 0.005ns 0.057ns | -    | -    | -    | -    | 0.907** 1.248** |
| Quad     | 1  | 0.027* 0.033ns 1.090** | -    | -    | -    | -    | 0.218ns 0.425** |
| Deviation| 1  | 0.022ns 0.191** 0.022ns | -    | -    | -    | -    | 6.753** 4.014** |
| Linear   | 1  | 0.063** 0.001ns 0.004ns | -    | -    | -    | -    | 0.550* 0.013ns |
| Quad     | 1  | 0.012ns 0.000ns 0.028ns | -    | -    | -    | -    | 0.002ns 0.003ns |
| Deviation| 1  | 0.096** 0.403** 0.105** | -    | -    | -    | -    | 6.593** 4.609** |
| Linear   | 1  | 0.007ns 1.5e-7ns 0.124* | -    | -    | -    | -    | 0.052ns 0.011ns |
| Quad     | 1  | 0.017ns 0.021ns 0.001ns | -    | -    | -    | -    | 0.001ns 2.0e-7ns |
| Residue  | 32 | 0.005 0.024 0.016 0.001 0.002 0.108 0.018 | 6.20 14.26 12.61 10.63 11.81 5.50 2.41 |
| CV (%)   |    | 6.20 14.26 12.61 10.63 11.81 5.50 2.41 |
| MG      |    | 1.20 1.08 1.01 0.30 0.35 2.39 5.56 |

* and **: significant (0.05 ≤ p) and (0.01 ≤ p) probability of error, ns: not significant; $^1$Transformed into log x.
Figure 1. Calcium (a), magnesium (b), sodium (c) and potassium (d) contents determined in the soil after application and incubation of the treatments, increasing doses of bentonite (0, 30, 60, 90 t·ha⁻¹).

the curves M3, M6 and M9, respectively. Both bentonite and MB4 have MgO composition (2.22% and 7.10%, respectively) which was released into the soil as Mg²⁺. Nichelle et al. [18], evaluating the potential of basalt powder as a source of nutrient release to bean, verified an increase of Ca and Mg contents in soil.

Regarding sodium (Na), the increasing doses of bentonite, without MB4, in-
creased sodium by 176.6% when comparing the 90 t∙ha⁻¹ dose with the control (Figure 1(c)). When the lower dose of MB4 (M3) is added, the Na values are lower when compared to M0, up to the 60 t∙ha⁻¹ dose of bentonite, which may be probably due to the adsorption power of the bentonite, increasing up to 90t∙ha⁻¹, probably by exceeding its cation adsorption capacity. On the other hand, with the incorporation of the doses 6 and 9 t∙ha⁻¹ of MB4, there was an increase of Na; however, the two curves were overlapped, showing that there was no difference between these two treatments.

Potassium (K) was significant only with the effect of increasing doses of bentonite (Table 1), showing a better fit in the quadratic form (Figure 1(d)). A decrease of potassium was observed when the dose of 30 t∙ha⁻¹ of bentonite was incorporated, until reaching the minimum point (0.268 cmolc∙kg⁻¹), corresponding to 52.32 t∙ha⁻¹ of bentonite.

The potential acidity values were significant at p < 0.01 only for the isolated effect of increasing doses of bentonite and MB4 (Table 1). The incorporation of bentonite to the soil incubated for 90 days favored the linear increase of the potential acidity (Figure 2(a)), causing an increase of 23.2% when comparing the 90 t∙ha⁻¹ dose of bentonite to control. This fact can be justified due to the high content of Al₂O₃ (13.34%) presented in the bentonite composition used in this study.

Although bentonite retains exchangeable cations, it is generally found that increasing doses of bentonite favored cation exchange capacity (CEC), especially without the presence of MB4 (M0) (Figure 2(a)), corroborating [19]. Clays have high micro porosity and greater specific surface, increasing the number of available sites for the bonds, thus favoring a greater CEC. According to [17], fine soil aggregates and clay minerals have a greater capacity to retain heavy metals due to their larger surface area, corroborating [20]. It can be inferred that the bentonite was favorable to the release of exchangeable cations to the soil, showing an increase of 44.8% when compared to the higher dose (90 t∙ha⁻¹) in relation to the control in the absence of MB4. When increasing doses of bentonite mixed with the doses of MB4 (Figure 2(b)), there was a decrease in CEC values in relation to the M0 curve, which may be due to competition from exchange sites. However, even with the reduction of CEC in the curves M3, M6 and M9, increasing doses of bentonite raised the CTC in 57.8; 53.8% and 43.5%, respectively, when comparing the 90 t∙ha⁻¹ dose of bentonite with the control.

It is observed that in M0 there were practically no differences in pH values with the addition of bentonite doses (Figure 2(c)), varying only 0.9% between the highest and the lowest dose of bentonite, despite the pH value of this clay being around 8.5. Increasing doses of bentonite within M3 and M6 raised the pH from 4.7 to 5.86 (Figure 2(c)), although these results were not statistically significant. However, when increasing doses of bentonite were mixed at a higher dose of MB4 (M9), there were variations in pH, promoting an increase of 29.3% when comparing the 90 t∙ha⁻¹ dose with the 0 t∙ha⁻¹ dose. The maximum point of
neutralization occurred in 69.19 t·ha⁻¹ of bentonite, corresponding to a pH value of 6.6.

According to the regression equation for Ca in the soil without bentonite (B0), there is an increasing quadratic behavior for the MB4 doses, ranging from 1.08 (0 t·ha⁻¹ MB4) to 1.39 (9 t·ha⁻¹ of MB4), corresponding to a 28.7% increase in the highest dose comparing to the control (Figure 3a). It can be verified that in spite of the curve B0 within the increasing doses of MB4 present higher values of Ca, the increment between the highest dose and the control was relatively small, agreeing [21]. These authors evaluated the effect of increasing doses of grounded basalt on an acid Yellow Latosol for a period of 180 days, which showed that the increases in the concentration of calcium and magnesium were relatively low, indicating that these elements must be present in minerals of low solubility. Similar results were found by [22].
Figure 3. Calcium (a), magnesium (b) and sodium (c) values determined on soil after application and incubation of treatments, increasing doses of MB4 (0, 3, 6, 9 t·ha\(^{-1}\)).

Toscani & Campos [23] working with grounded rock during one year, verified that Ca was the element that increased more sharply, varying from 1 to 2.6 cmol/dm\(^3\). Von Wilpert and Lukes [24] observed positive effects of the use of silicate rock powder on forest soils in Germany, since increased Ca, K and pH levels were observed as a function of the application of 6 t·ha\(^{-1}\) of rock dust. In the present study, when mixing MB4 with bentonite (B30, B60 and B90), Ca values were lower than those shown in curve B0. Probably, Ca was retained in bentonite due to competition for the exchange sites, which is in accordance with [25] who claim that the levels and types of clay influence the reactions of adsorption/desorption.

Increasing doses of MB4 without bentonite (B0), increased Mg content in the soil only 2.3% when comparing to the highest MB4 dose (9 t·ha\(^{-1}\)) (Figure 3(b)), probably due to the MB4 low releasing of nutrients, corroborating [21]. However-
er, [3] evaluated the potential use of volcanic rock powder in a sandy soil and found increases in Ca, Mg, P and K in the soil. Similarly [26] observed increases in Mg levels in the soil with increasing doses of basalt powder, with no significant difference with the highest dose (10 t·ha⁻¹).

The addition of bentonite with the MB4 treatments caused a linear increase of the Mg content in soil (Figure 3(b)) due to the increasing doses of bentonite. There were increases of 175.0; 33.5 and 35.8% of Mg when comparing the doses 0 t·ha⁻¹ to 9 t·ha⁻¹ of MB4, respectively with treatments B30, B60 and B90.

The lowest values of Na were observed in the soil without bentonite (B0) (Figure 3(c)) and these values decreased as a function of the increasing doses of MB4, providing a reduction of 45% of the control in relation to the highest dose of MB4. Probably it is due to the Na content present in the bentonite, around 6 cmol·kg⁻¹ [19]. At the 90 t·ha⁻¹ dose (B90), this increase was quadratic and the maximum point was 1.73 cmol·kg⁻¹ decreasing until the dose 9 t·ha⁻¹ of MB4, reaching 1.61 cmol·kg⁻¹, i.e., a reduction of 7.15%.

In relation to the increasing doses of MB4 (Figure 4(a)), it was verified a linear reduction of 76.6% in H⁺ + Al comparing the higher dose with the control. This shows that MB4 did not release Al³⁺ exchangeable in the reaction of the rock powder with the soil solution. Besides, MB4 present the liming potential with increasing application rates according to [28]. Melo et al. [21], in an incubation experiment with different doses of grounded basalt, observed that the addition of these doses presented greater efficiency for the neutralization of the potential acidity.

Increasing doses of MB4 reduced CEC, especially in the absence of bentonite (B0). Possibly, this rock powder reacted in some way with the available cations in the soil solution were unavailable (Figure 4(b)). The opposite result was verified by [29]; the incubation of 36 months in weathered soils treated with equivalent doses up to 300 t·ha⁻¹ of basalt powder indicated an increase in CEC. Gillman et al. [30] also observed an increase in CEC of seven soils of Queensland, Australia, incubated with increasing doses of basalt powder (0, 1, 5, 25 and 50 t·ha⁻¹). It is interesting to note that CEC, like soil fertility, depends directly on the chemical quality of the parent rock which, when milled, can release mineral nutrients to the soil.

According to [31], the application of rock powders to the soil does not replace chemical fertilizers, but rather leads to a change of conception on the management of agroecosystem fertility.
In relation to the effect of MB4 on soil pH (Figure 4(c)), it can be observed that without bentonite (B0) the pH followed a quadratic equation, with an increase in pH to the point of maximum neutralization of the acidity with 4.82 t·ha⁻¹ of MB4, equivalent to pH 5.62, representing an increase of around 22%, decreasing again with 9 t·ha⁻¹. However, even with this reduction, a 5.5% increase in pH occurred in the highest dose in relation to the control. This increase in pH with increasing doses of MB4 was possibly due to the high percentages of MgO and CaO contained in MB4, such pH value is around 8.3. Theodorou & Leonardos [3] verified that the application of volcanic rock powder in a sandy soil significantly increased the pH, which can be explained by the lower buffer power of the studied soil, corroborating [30]. On the other hand, [18] did not observe significant pH differences between treatments in a similar soil.
Although the use of grounded rocks as fertilizers is attractive, since they have the potential to supply soils with a large array of macro and micronutrients in comparison to commercially available soluble fertilizers, some disadvantages can be pointed out, such as the very slow solubility that can negatively affect the agronomic effectiveness of short term crops [4].

In this sense, it can be figured out that the incubation time of MB4 and bentonite doses in the soil during the experimental period of the current study was not long enough to allow releasing expressive amount of nutrients in the soil. Therefore, it is recommended that further studies with MB4 and bentonite doses be conducted over a longer period of time in order to evaluate the release of nutrients to the soil by these materials over time.

4. Conclusions

The increasing doses of bentonite increased the cation exchange capacity of the soil, favoring the availability of nutrients in the soil.

The increasing doses of MB4 favored the increase of the pH values and, consequently, decreased the soil potential acidity values for the applied bentonite doses. On the other hand, these treatments decreased the cation exchange capacity of the soil.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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