

Hydrothermal Transformation of Natural Zeolite from Ende-NTT and Its Application as Adsorbent of Cationic Dye

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ABSTRACT

A synthetic zeolite was produced from natural zeolite from Ende-Nusa Tenggara Timur (NTT) by hydrothermal method. This study aims to produce synthetic zeolite from Ende natural zeolite to remove cation dye through the adsorption process. Temperature of crystal formation (ageing) was performed at 60 °C for 6 h and hydrothermal process was at 100 °C for 24 h. The natural zeolite produced synthetic NaP1 and synthetic Faujasite. Based on the research results, the synthesis of zeolite by the hydrothermal method can enhance the adsorption capacity and Cation Exchange Capacity (CEC). The adsorption capacity in the natural zeolites of type ZG, ZL and ZC before the hydrothermal process were 17.289, 17.276, and 16.483 mg/g, respectively, and after hydrothermal they increased to 37.398, 37.369 and 37.362 mg/g, respectively. In addition, the CEC increased from 84.154, 81.042, and 77.474 cmol/kg, respectively, to 244.063, 216.354, and 211.432 cmol/kg, respectively. The Langmuir model most closely matched the isothermal adsorption equilibrium process.

Keywords: zeolite; hydrothermal; adsorption; methylene blue

ABSTRAK

Telah dilakukan sintesis zeolit dari zeolit alam Ende-Nusa Tenggara Timur (NTT) dengan metode hidrotermal. Penelitian ini bertujuan untuk menghasilkan zeolit sintetis dari zeolit alam Ende yang digunakan untuk menghilangkan pewarna kation melalui proses adsorpsi. Suhu pembentukan kristal (ageing) dilakukan pada 60 °C selama 6 jam dan proses hidrotermal pada 100 °C selama 24 jam. Zeolit alam yang telah disintesis merupakan jenis NaP1 dan Faujasite. Berdasarkan hasil penelitian, sintesis zeolit dengan metode hidrotermal dapat meningkatkan kapasitas adsorpsi dan Kapasitas Tukar Kation (KTK). Nilai kapasitas adsorpsi zeolit alam jenis ZG, ZL, dan ZC sebelum hidrotermal berturut-turut sebesar 18,305, 18,271, dan 17,096 mg/g dan setelah hidrotermal meningkat menjadi 37,394, 37,365, dan 37,360 mg/g. Selain itu, nilai KTK optimum zeolit sebelum dan sesudah hidrotermal berturut-turut sebesar 84,15, 81,04, dan 77,47 cmol/kg meningkat menjadi 244,06, 216,35, dan 211,43 cmol/kg. Model Langmuir lebih sesuai untuk proses kesetimbangan adsorpsi isothermal.

Kata Kunci: zeolit; hidrotermal; adsorpsi; metilen biru

INTRODUCTION

Research on natural zeolite in Indonesia has been done recently primarily on zeolites derived from Bayah, Cikalong, and Lampung, but zeolites of different origin do not have the same characteristics [1]. Therefore, this study was done on the natural zeolites from the district of Ende, Nusa Tenggara Timur (NTT) to enrich the data on the natural zeolites of Indonesia.

Data in 2008 from Geological Agency, Ministry of Energy and Mineral Resources stipulates that Ende-NTT has reserves of around 6,115,000 tons natural zeolite. Although the natural zeolite resource in the area is quite large, its use is not maximized. Efforts to increase the potential of the natural zeolites should be developed with the goal that the use of resources will be more varied

and profitable focuses in the fields of environment, industry, and agriculture [2].

Zeolite utilization continues to grow and the ability of zeolites to exchange ions has attracted significant attention among scientists. Based on International Standards, natural zeolites considered of good quality if it has a Cation Exchange Capacity (CEC) value after activation of above 150 cmol/kg [3]. The determination of CEC values of the zeolites in different regions of Indonesia, especially in the district of Ende, needs to be done to determine the quality of the zeolites.

Natural zeolites have good thermal stability properties, but crystallinity and catalytic activity is low. In addition, some natural zeolites contain metal oxides and have non-uniform pore size. Synthetic zeolites contain minimum quantities of metal oxides and have high crystallinity which gives them much better catalytic

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activity than natural zeolites [4]. Based on this fact, one opportunity for research is to increase the crystallinity of zeolite through activation and synthesis of zeolite using natural zeolite as a source of Si and Al by the hydrothermal method.

The textile industry uses a lot of dye waste that becomes an environmental pollutant. Cation dye waste is a problem that requires proper handling. The adsorption method for this problem is attractive because it is a simple and effective process [5].

The interaction of methylene blue with water will produce positively charged methylene blue ions. The adsorption process involves an effective adsorbent that can immobilize the cation dye from the waste. The adsorbents used must meet necessary criteria such as it must have a different charge from the solute, it has a great capacity to absorb the solute, it has a large surface area, and it does not dissolve in adsorbed liquid water. These criteria exist in natural zeolites [6].

Characterization and utilization of natural zeolite of Ende as a source of Si and Al for the synthesis of zeolite by hydrothermal method has never before been studied. Therefore, this study will be carried out to test the method of hydrothermal synthesis of zeolite and it is used as an adsorbent for cation dye (methylene blue).

EXPERIMENTAL SECTION

Materials

Materials used in this study were three types of natural zeolite from Ende-NTT, NaOH (Merck), AgNO₃ (Merck), CaCl₂ (Merck), NH₄Cl (Merck), HCl (p.a), ethanol 80% (p.a), and methylene blue (Merck). The three types of Ende natural zeolite were zeolite from mountain location (ZG), marine zeolite (ZL), and brown colored zeolite (ZC).

Instrumentation

The natural zeolites and synthetic zeolites were characterized by using X-Ray Diffraction (XRD) D4 Bruker and Scanning Electron Microscopy (SEM) Carl-Zeiss Bruker EVO MA10. Zeolite adsorption capacity was measured using a UV-Vis spectrophotometer Shimadzu 1700. The value of the Cation Exchange Capacity (CEC) was measured with an Atomic Absorption Spectrophotometer (AAS) Shimadzu AA-7000.

Procedure

Preparation of natural zeolite

Each natural zeolite type was first ground to a 200 mesh powder before being physically and

chemically activated. Physical activation was done by through zeolite calcination at 600 °C for 4 h. Chemical activation was done by mixing the zeolite in solutions of HCl and NaOH at concentrations of 0.5, 1.5, and 3 M. The unactivated and activated zeolites were characterized using XRD and SEM.

Zeolite synthesis from natural zeolite by hydrothermal method

A sample of natural zeolite with a total weight of 5.0 g was added to 25 mL of 3 M solution of NaOH. The mixture was heated at a temperature of 60 °C for 6 h, which is known as the aging process. Next, it was heated at a temperature of 100 °C for 24 h. After this hydrothermal treatment, the resulting solid crystals were characterized by XRD and SEM.

The methylene blue adsorption

Zeolite sample of 0.2 g was mixed with 15 mL of 400 mg/L methylene blue solution and agitated using a shaker and then centrifuged at a speed of 3500 rpm for 15 min. The filtrate was then measured by UV-Vis spectrophotometer at the maximum wavelength.

Determination of Cation Exchange Capacity (CEC)

Zeolite of 0.1 g was added to solution of 0.5 M CaCl₂ 10 mL and saturated over 24 h. The solution was separated by centrifuged at a speed of 3500 rpm for 10-15 min. The supernatant was discarded and the pellet was then washed using 80% ethanol until it was free of chloride.

The pellet which was free of chloride was subsequently processed to extract the adsorbed calcium from the zeolite sample. Extraction was done by using 10 mL of 1 M NH₄Cl for 1 h. The extraction process was repeated 5 times. Extract from the 5 extractions was added with 1 M NH₄Cl up to a volume of 100 mL. Calcium measurements were done with AAS.

Adsorption isotherm

Natural zeolite of 0.2 g was added into 15 mL of methylene blue solutions with a concentration of 250, 500, 750, 1000, and 1250 mg/L which was then saturated over 24 h and centrifuged at a speed of 3500 rpm for 15 min. The filtrate then was measured by UV-Vis spectrophotometer. The results were analyzed to determine the adsorption isotherms using Langmuir and Freundlich models.

RESULT AND DISCUSSION

Results of Natural Zeolite Sample Preparation

Three natural zeolite samples from Ende-NTT were used in this study: mountain zeolite (ZG), marine

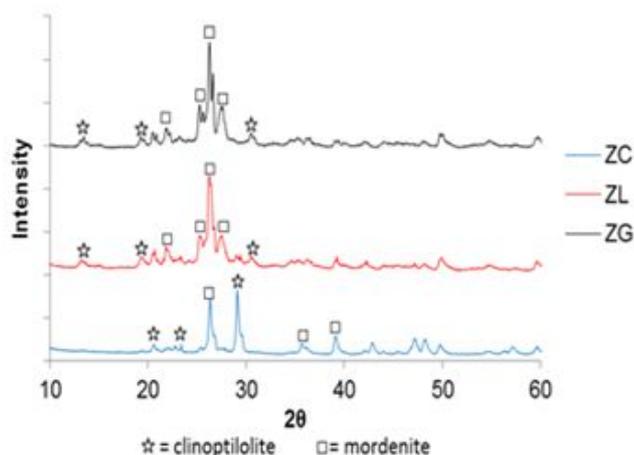


Fig 1. XRD diffractogram of natural zeolites from Ende are from mountain (ZG), marine (ZL), and brown zeolites (ZC)

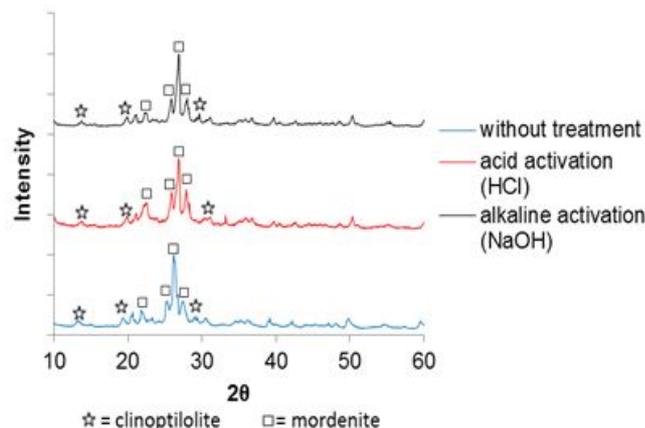


Fig 2. Diffractogram natural zeolite from mountain (a) without treatment; (b) with acid activation (HCl); (c) with alkaline activation (NaOH)

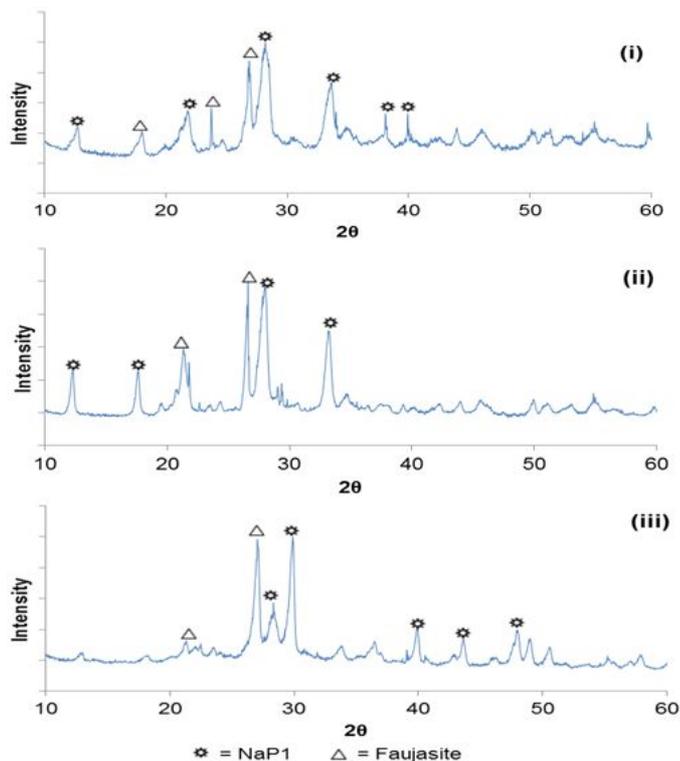


Fig 3. Diffractogram of natural zeolite types ZG (i), ZL (ii), ZC (iii) transformed by hydrothermal method

zeolite (ZL), and brown-colored zeolite (ZC). These zeolites were cleaned from nonzeolite impurities and resized to pass a 200 mesh sieve. Changing the size was intended to homogenize the size and increase the contact surface so that the adsorption capacity was maximized [7]. Characterization of the ZG, ZL, and ZC natural zeolites from Ende are shown by XRD diffractogram in Fig. 1.

Analysis of the XRD diffractograms show that the Ende zeolites had 2θ peaks associated with mordenite and clinoptilolite type zeolites as confirmed in the JCPDS database. The quality of natural zeolites can be improved by activation treatment. Physical activation was carried out by calcination of the natural zeolites at a temperature of $600\text{ }^{\circ}\text{C}$. This treatment aimed to remove water vapor and metal oxides adsorbed in the zeolites. The release of water vapor and metal oxides from the zeolite creates spaces and pores and thus increases the zeolite reactivity [8].

Chemical activation was done with solutions of HCl and NaOH to remove adsorbed impurities to uncover the surface of zeolite in order to increase the porosity and contact area [9]. Characterization of the natural zeolites without treatment and with activation treatments are shown with XRD diffractograms in Fig. 2.

Activation treatment by HCl and NaOH at a concentration of 3 M did not change the diffractogram peaks significantly. Natural zeolites are relatively stable due to metal oxides that play a role in strengthening the natural zeolite structures.

Transformation of Natural Zeolite by Hydrothermal Method

Sodium hydroxide that is reacted with natural zeolite acts as an activator that dissolves Si and Al in the form of silicate and aluminate salt that are contained in the zeolite so that the Si/Al ratio changes. Cation Na^+ also plays as an important role in zeolitisation in which the production of sodium silicate dissolved in water increases so that the crystallization process in the formation of the synthetic zeolites became faster. The heating process in the hydrothermal

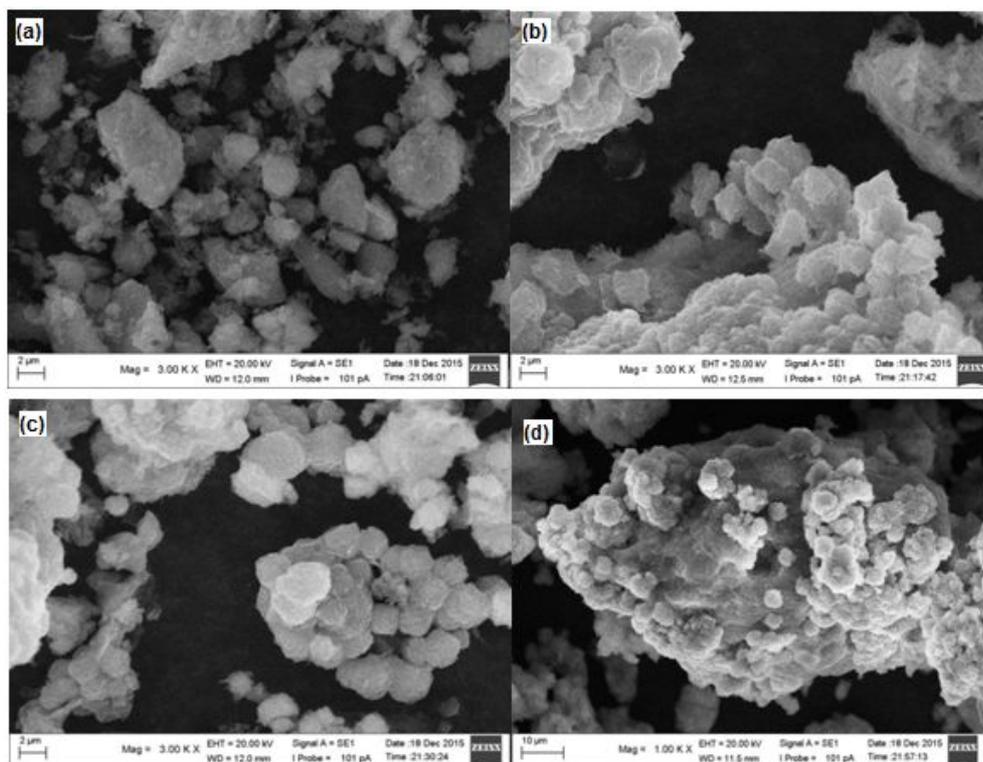


Fig 4. Surface morphology of Ende natural zeolite (a) without treatment; (b) hydrothermally transformed type ZG Ende natural zeolite, (c) hydrothermally transformed type ZL Ende natural zeolite; and (d) hydrothermally transformed type ZC Ende natural zeolite

method aims to accelerate the formation of the zeolite crystal cores in order to produce more perfectly formed zeolites [10]. Diffractograms of the natural zeolites transformed by the hydrothermal method are shown in Fig. 3.

XRD results of the transformed natural zeolites ZG, ZL, and the ZC show that the transformed zeolites were a mixture of NaP1 and faujasite zeolites. Each sample was analyzed by comparing its 2θ peaks with the 2θ peaks in the JCPDS. Transformation of natural zeolite into types NaP1 and Faujasite produced substitutions of Si(IV) and Al(III) in the zeolite structure which as a result became more negative. The more negative nature of the transformed zeolite would thus work towards removing the cation dye (methylene blue) through the adsorption process. Solid particle morphology of the transformed zeolites synthesized from the Ende natural zeolites by the hydrothermal method was observed by SEM as shown in Fig. 4.

Generally, SEM images of the natural zeolite particles synthesized by the hydrothermal method showed that all syntheses looked crystalline and differed in particle shape with the untransformed natural zeolites. Orthorhombic shaped crystals appeared more dominant than any other form of particle shape which is indicative of NaP1 zeolite particles in agreement with the XRD

results [11]. Faujasite formation through the hydrothermal processes could be seen in the XRD peaks but was not clearly detected with SEM because of the small amount of faujasite produced.

Determination of Adsorption Capacity and Cation Exchange Capacity (CEC)

The determination of adsorption capacity was conducted to determine the ability of the Ende natural zeolites to adsorb methylene blue dye. The value of the Ende natural zeolite adsorption capacity increased after activation and after transformation by the hydrothermal method (Table 1).

The uses of natural zeolite derived from Bayah (BYH) and Cikalong (CKL) in this study were for comparative data because both types of zeolite have been researched in many studies. The NaP1 and faujasite type zeolites which were the results of the transformation of the Ende natural zeolites had higher adsorption capacity compared to the natural zeolites. This showed that the synthetic transformed zeolites were very good as dye adsorbents. Comparison in the adsorption capacity of Ende natural zeolite and the natural zeolites from several countries for methylene blue is shown in Table 2.

Table 1. Adsorption capacity of natural zeolite

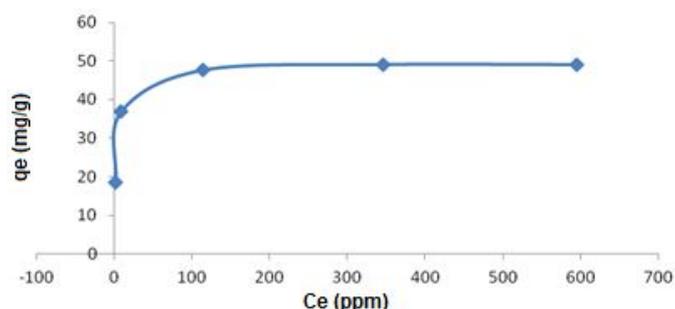
Types zeolite	Adsorption capacity (mg/g)		
	Without treatment	With activation NaOH 3 M	With transformation by hydrothermal
ZG	17.289	19.938	37.398
ZL	17.276	19.103	37.369
ZC	16.483	18.676	37.362
BYH	17.257	19.354	Unresearched
CKL	17.241	19.093	Unresearched

Table 2. Adsorption capacity of natural zeolites from Ende and several countries and the transformed Ende zeolite

Zeolite origin	Types zeolite	Adsorption capacity (mg/g)	Literature
Ende	Mordenite + Clinoptilolite	19.938	This study
Australia	Mordenite + Clinoptilolite	20.152	[12]
China	Clinoptilolite	19.943	[13]
Iran	Clinoptilolite	20.214	[14]
Hydrothermal	NaP1 + faujasite	37.398	This study

Table 3. Cation Exchange Capacity (CEC) of natural zeolite

Types zeolite	Cation exchange capacity (cmol/kg)		
	Without treatment	NaOH 3 M activation	Hydrothermal transformation
ZG	84.154	205.026	244.063
ZL	81.042	168.906	216.354
ZC	77.474	165.286	211.432

**Fig 5.** Adsorption isotherms of methylene blue dye by Ende-NTT natural zeolites at room temperature (29 °C), initial adsorbate concentration: 250, 500, 750, 1000, and 1250 mg/L, 0.2 g adsorbent weight and contact time 24 h

One common indicator to determine the quality of zeolites is by measuring the Cation Exchange Capacity (CEC). CEC measurement results showed that the activation treatment and transformation by hydrothermal method increased the value CEC of the Ende natural zeolites (Table 3).

The increase in the value of adsorption capacity and CEC through the chemical activation process and the hydrothermal method was probably the result of clearing the zeolite pores of from water molecules and metal oxides along with the production of zeolite with high crystallinity so that the capacity increased [15]. Under normal circumstances, the spaces within the zeolite crystals are filled by water molecules and metal oxides that are regarded as impurities. The existence of

empty spaces on the surface of the zeolites can enlarge the active surface so that the adsorption capacity becomes larger [16].

Hydrothermal treatment resulted in more active zeolites. The zeolite surface produced through the hydrothermal process was more negative so that it had a greater ability to exchange cations. The hydrothermal method was apparently able to remove metal oxides that cover exchange site on the surface of the zeolites and enlarge the pore size. The hydrothermal method is able to transform the natural zeolites into synthetic zeolites with of increased quality [17].

Adsorption Isotherm for Methylene Blue

Determination of the adsorption isotherm was conducted to determine the relationship between the adsorbate, concentration and adsorbent surface absorption rates. The results in Fig. 5 show that as the initial concentration of methylene blue increases the amount adsorbed by the zeolite adsorbent also increases. This demonstrated that the adsorption capacity of the zeolite increased in line with the increase of initial concentration of methylene blue.

The experimental data for the adsorption Isothermal of methylene blue with the Ende natural zeolite was analyzed with two models, namely Langmuir and Freundlich. The Langmuir isotherm is based on monolayer adsorption in the homogeneous active side of the adsorbent. On the other hand, the Freundlich isotherm based on multilayer adsorption

Table 4. Parameters of Langmuir isotherm and Freundlich isotherm of methylene blue by natural zeolite

Ende-NTT natural zeolite	Langmuir				Freundlich		
	Qm	: b	: R ²	: RL	: Kf	: R ²	: n
	49.501	: 0.388	: 0.999	: 0.012	: 21.570	: 0.805	: 0.142

on the surface (heterogeneous) of the adsorbent with a uniform adsorption energy. Based on the equation of the Langmuir and Freundlich isotherms, the parameter values of the isothermal, qm, Kf, n, and R², could be determined from the slope and interception. Calculated isothermal parameter values are presented in Table 4.

The adsorption of methylene blue by the Ende natural zeolite had a greater correlation with the Langmuir model than the Freundlich model. It showed that the adsorption process was dominated by monolayer adsorption (homogeneous). Langmuir isotherm describes chemical adsorption on the active side where once the molecules occupy an active side then there will be no a further adsorption [18].

Another parameter that can be used to determine the adsorption process is the RL value, which is an equilibrium parameter or the dimension of an adsorption. When the RL value is >1, the adsorption is unfavorable, mean while when RL=1 it means the adsorption process is linear. When the value is 0<RL<1, the adsorption is favorable, and when RL=0 the adsorption process is irreversible [19]. In Table 4, the value of RL for the Ende natural zeolite was in the range of 0<RL<1 showing that the process of adsorption of the methylene blue was favorable therefore it can be used as an adsorbent.

CONCLUSION

Based on the results of the analysis, the natural zeolites from the district of Ende, East Nusa Tenggara, are of the mordenite and clinoptilolite types. Synthesis of zeolite by the hydrothermal method from three sources of natural zeolite (mountain (ZG), marine (ZL), and brown colored zeolite (ZC)) produced a NaP1 and faujasite synthetic zeolite. The synthetic zeolites showed a higher value of adsorption capacity and Cation Exchange Capacity (CEC) than the natural zeolites. The methylene blue dye adsorption by the zeolites followed the Langmuir isotherm.

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