



Catalytic ozonation of phenol in water with natural brucite and magnesia

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ABSTRACT

Natural brucite and magnesia were applied as catalysts in catalytic ozonation of phenol in this work. It was found that both brucite and magnesia had remarkable accelerations on degradation of phenol and removal of COD in water. On this basis, effective and feasible routes for catalytic ozonation of phenol in water were proposed. The influence of initial pH value, radical scavengers and reaction temperature were investigated. The results revealed that there were different ozonation mechanisms in two systems: molecular ozone direct oxidation mechanism was proved in catalytic ozonation with brucite, and hydroxyl radical mechanism was demonstrated to play a main role in catalytic ozonation with magnesia.

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1. Introduction

Recently, treatment of industrial wastewaters has attracted much attention of many countries' governments and lots of environmental experts. The pollution of wastewaters is mainly owed to the presence of organic contaminants such as PAH's, dyes, halogenated hydrocarbons, phenolic compounds, etc. [1,2]. Amongst these pollutants, phenols are widely used in petroleum, petrochemical, coal conversion, and pharmaceutical industries and confirmed as refractory pollutants by the US EPA for their highly toxic and carcinogenic properties [3–5].

To remove phenol and its compounds from water, kinds of methods are applied according to literatures appeared. They include: wet peroxide oxidation [1,6], catalytic wet air oxidation [7–9], adsorption [5], and ozonation [10,11]. Especially, ozonation is a widely used method to mineralize organic pollutants in water. However, phenols usually could not be oxidized efficiently in ozonation and their byproducts are always more toxic and resistant, such cases will lead to a low mineralization level [12]. To settle this problem, technologies of O₃/UV, O₃/H₂O₂ and catalytic ozonation, which are advanced oxidation processes (AOP), were proposed. In these processes, ozone could be decomposed to generate hydroxyl

radicals, which have higher reaction rate constants with phenols [13,14], but those agents such as UV and H₂O₂ always present some drawbacks: high costs, turbidity of water, etc. [15–17]. As another advanced oxidation process, catalytic ozonation could also achieve the same effects on phenols degradation. According to literatures, many catalysts have been used in catalytic ozonation, such as transition metal oxides [15,18,19], metals ions [20,21]. Assalin et al. [18] have studied the degradation of phenol in catalytic ozonation with Mn(II) and Cu(II), and he concluded that these two ions could apparently accelerate the phenol degradation rate. Okawa et al. [21] revealed that the presence of metal ions would lead to certain catalytic effects on decomposition of phenol with ozonation in acetic acid. However, it is well known that those transition metal ions may lead to a secondary pollution in water.

Recently Takehira et al. [22] has found that Cu/Fe/Al mixed oxide catalysts prepared by calcining hydrotalcite precursor showed high activity for the mineralization of both phenol and oxalic acid by ozone in aqueous solution. And as we know, just as hydrotalcite, natural brucite is also a kind of low-cost and environmental friendly alkali mineral with a moderate solubility in water [23]. Thus in consideration of Takehira's work and our former studies [24], natural mineral brucite and its calcined-product (magnesia) without any purification are introduced as catalysts in ozonation of phenol in this paper. It was found that both brucite and magnesia have prominent catalytic effects on the degradation of phenol and the removal of chemical oxygen demand (COD) in water. On this basis, economically feasible

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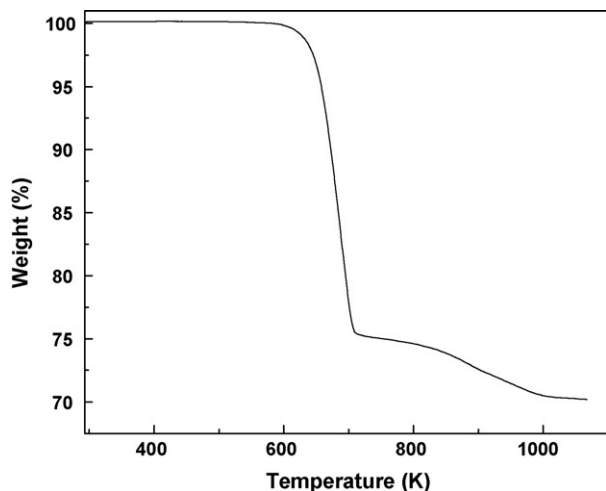


Fig. 1. Thermo-gravimetric curve of brucite.

Table 1

XRF results of chemical composition for magnesia

MgO	86.15
SiO ₂	3.72
CaO	1.37
Fe ₂ O ₃	0.69
Al ₂ O ₃	0.28
Burn-off	7.72
Others	0.11
Total	100.04

2.2. Materials

Ozone was generated in a laboratory ozone generator from pure oxygen, and the flow rate of ozone was 0.36 mg/min. Methanol used as mobile phase in HPLC was chromatographically pure. Phenol used to preparing for the model solutions was analytical grade. All the other reagents such as *tert*-butanol, sodium hydroxide, borax and phosphate were analytical grades without further purification. The water used in this work was distilled water.

2.3. Ozonation experiments

Experiments were carried out in a semi-continuous flow mode. In a typical catalytic ozonation procedure, 0.5 g brucite or magnesia was mixed with 100 ml model aqueous solution (initial concentration of phenol and COD are 100 and 227.0 mg L⁻¹) in a flask under stirring and thermostatic control. Then the ozone flow was fed into the bottom of the flask with continuous stirring. At certain intervals, 5.0 mL of samples were got out and centrifuged for analytical determination of the phenol concentrations and COD in solutions.

The concentrations of phenol in solution were determined by HPLC (SHIMADZU LC-10AD). A COSMOSIL C-18-AR-II column (250 mm, 4.6 mm i.d.) was used. The mobile phase was an aqueous mixture (50% methanol and 50% water) with detection at 210 nm. The values of COD were obtained through oxidation with K₂Cr₂O₇ under acidic conditions and titrate analysis with (NH₄)₂Fe(SO₄)₂ aqueous solution according to the national criterion of PR China [25]. The pH values of solutions were recorded by pH analyzer (Lei Ci Instrument Plant, Shanghai, China). The mass velocity of ozone was measured by standard iodometry.

3. Results and discussion

3.1. Catalytic effects of catalysts

In order to test the effects of brucite and magnesia on phenol degradation and COD removal from water, series of ozonation experiments with and without catalysts were carried out at 25 °C. Fig. 3 shows the evolution of the residual concentration of phenol in ozonation experiments. It can be observed that both brucite and magnesia have acceleration effects on the degradation of phenol in some extent. For instance, at 15 min the decomposition rate of phenol has been enhanced by proportion of 55% in catalytic ozonation with brucite and 91% in catalytic ozonation with magnesia to that in single ozonation. As shown in Fig. 4, brucite and magnesia, especially magnesia, had remarkable catalysis on COD removal.

3.2. Adsorption

As it is well known, adsorption usually is an un-neglected factor in experiments. To describe adsorptions of phenol and its decomposed-products on catalysts, experiments as follows were carried out. In the first experiment, 0.5 g brucite and 0.5 g magnesia were added into 100 ml 100.0 mg L⁻¹ model solutions, respectively,

ozonation processes on degradation of phenol in water were proposed.

2. Experimental

2.1. Preparation and characterization of catalysts

Natural mineral brucite was exploited from Fengcheng of Liaoning province in China. Bulky brucite was crushed and sieved into 100 mesh size, and its main chemical composition is: Mg(OH)₂, 94.71%; SiO₂, 2.85%; others [24]. From the gravimetric curve of brucite (Fig. 1), it can be observed that the first dehydration of brucite completes at about 450 °C. Thus to obtain magnesia, 100-mesh brucite was calcined at 450 °C for 6 h. This powder sample was characterized by X-ray diffraction (XRD) (Fig. 2) on an X-ray diffractometer (ARL, Switzerland) and X-ray fluorescence spectrometry (XRF) (Table 1) on an X-ray fluorescence spectrometer (ARL, Switzerland). Fig. 2 shows that sharp and intense peaks at diffraction angles of 2θ = 37°, 43°, 62° should be mainly ascribed to diffraction by basal planes (1 1 1), (2 0 0), (2 2 0), respectively, which is in a good agreements with periclase (JCPD S4-0829). From the results presented in Table 1, it can be proved that the sample magnesia is mainly composed of MgO and most of the water has been burned off.

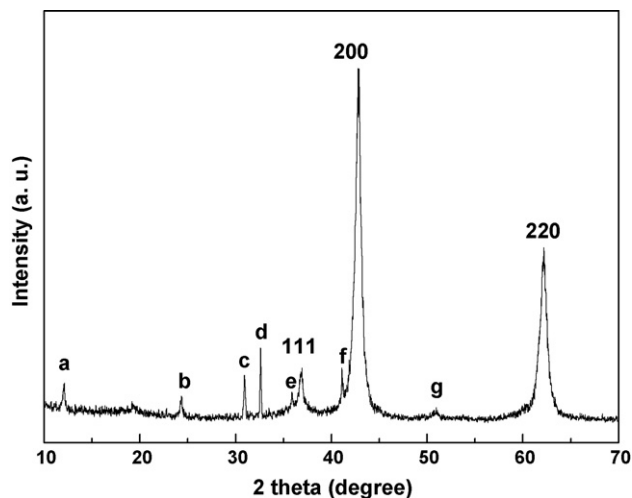


Fig. 2. XRD pattern of magnesia.

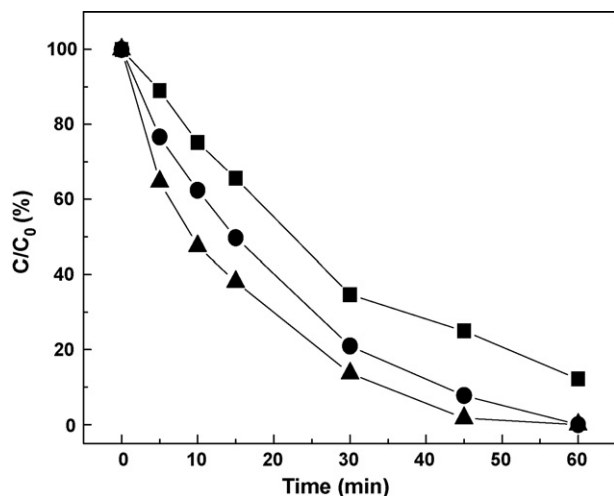


Fig. 3. Degradation of phenol under single ozonation (■), catalytic ozonation with brucite (●) and catalytic ozonation with magnesia (▲). C_0 : initial concentration; C : residual concentration. *Conditions:* Initial phenol concentration, 100 mg L^{-1} ; catalyst concentration, 5 g L^{-1} ; flow rate, 5 mL min^{-1} ; ozone concentration, 0.36 mg min^{-1} ; initial pH, 6.35 (single), 10.18 (brucite), 10.80 (magnesia); temperature, 25°C .

and then the solutions were stirred for 60 min. The phenol concentrations of solutions gained were determined to be 98.8 and 98.7 mg L^{-1} , respectively. This result indicates that phenol was hardly adsorbed on brucite and magnesia. In the second experiment, firstly two flasks of $100 \text{ ml } 100.0 \text{ mg L}^{-1}$ phenol solutions were reacted under single ozonation for 60 min, then 0.5 g brucite and 0.5 g magnesia were added into those solutions, respectively, with stirring for 60 min. The COD values of solutions in two flasks were detected to be 135.2 and 112.3 mg L^{-1} correspondingly. From Fig. 4, it can be seen that COD at 60 min of single ozonation is 141.0 mg L^{-1} . The results indicate that abatements of COD by adsorption on brucite and magnesia were 5.8 and 28.7 mg L^{-1} . The removals of COD at 60 min of brucite and magnesia catalytic ozonation are higher than that of single ozonation for 45.2 and 119.6 mg L^{-1} , respectively. Therefore, it can be demonstrated that adsorption of decomposed-products of phenol by two alkaline minerals contributes little to the removal of COD.

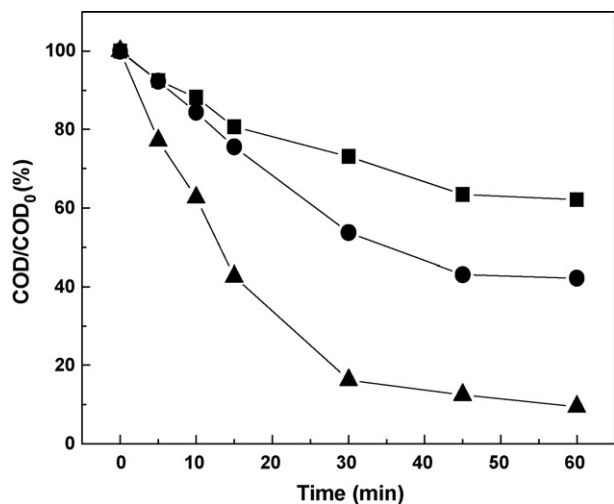


Fig. 4. Removal of COD under single ozonation (■), catalytic ozonation with brucite (●) and catalytic ozonation with magnesia (▲). COD_0 : initial value; COD: residual value. *Conditions:* Initial phenol concentration, 100 mg L^{-1} ; catalyst concentration, 5 g L^{-1} ; flow rate, 5 mL min^{-1} ; ozone concentration, 0.36 mg min^{-1} ; initial pH, 6.35 (single), 10.18 (brucite), 10.80 (magnesia); temperature, 25°C .

Table 2

Evolution of pH values during single ozonation and catalytic ozonation

	Time (min)						
	0	5	10	15	30	45	60
Single ozonation	6.35	3.90	3.29	3.69	3.18	2.75	2.76
Brucite	10.18	9.77	9.45	9.11	8.91	8.74	8.52
Magnesia	10.80	10.78	10.80	10.83	10.82	10.92	10.83

3.3. Evolution of pH value

It is well known that pH value is usually considered as an important factor in ozonation. As natural alkaline mineral, brucite and its calcined-product magnesia will alter the pH value in water [26,27]. To describe the influences on pH value by two catalysts, pH values in the processes of single ozonation and catalytic ozonation were determined, respectively. And the results are summarized in Table 2. It can be seen that pH value varies from 6.35 to 2.76 in single ozonation and ascends a lot with the presence of both the catalysts. In the process of catalytic ozonation with brucite, the pH value is 10.18 at the beginning, and then presents an obvious descent from 10.18 to 8.52. While in magnesia system, pH value maintains nearly 10.80.

3.4. Control experiments

To study the influence of initial pH value on degradation rate of phenol in ozonation, experiments as follows were carried out at 25°C . Six 100 mg L^{-1} model phenol solutions (Nos. 1–6) with different initial pH values were prepared as samples, and then ozonation experiments with these samples were processed for 15 min. The number and corresponding materials of the samples are shown in Table 3, and the initial pH and the pH after reactions are also presented in the table. Residual phenol concentrations of these samples are shown in Fig. 5. It can be observed that, there is a positive relationship between the decomposition rate and the initial pH value, which is in agreement with former study in a literature [28].

On the basis of experiments above, alkaline environment provided by the catalysts was considered as the main factor which accelerates the degradation rate of phenol in this paper.

3.5. Influence of radical scavengers

In traditional opinion, catalysis in ozonation usually processes in two main routes: ozone direct oxidation and free radical reactions. And it is well known that, when adding radical scavengers in catalytic ozonation, the phenomenon of inhibition on catalytic effect should suggest a radical type reaction, otherwise ozone direct reaction should be more possible [13,14,29].

To clarify whether generation of hydroxyl radicals had been accelerated by brucite and magnesia, the influence of radical scavengers was investigated. Here *tert*-butanol which has the reac-

Table 3

Corresponding pH values before and after reactions of the samples

Samples	a	b
1 (free)	6.35	3.69
2 (mixed phosphate)	6.86	6.82
3 (borax)	9.18	9.18
4 (brucite)	10.18	9.11
5 (NaOH)	10.50	6.86
6 (magnesia)	10.80	10.83

a, initial pH values and b, pH values after reactions. Initial concentrations of samples: 2 (mixed phosphate), 6.8 g L^{-1} ; 3 (borax), 3.6 g L^{-1} ; 4 (brucite), 5 g L^{-1} ; 5 (NaOH), 0.04 g L^{-1} ; 6 (magnesia), 5 g L^{-1} .

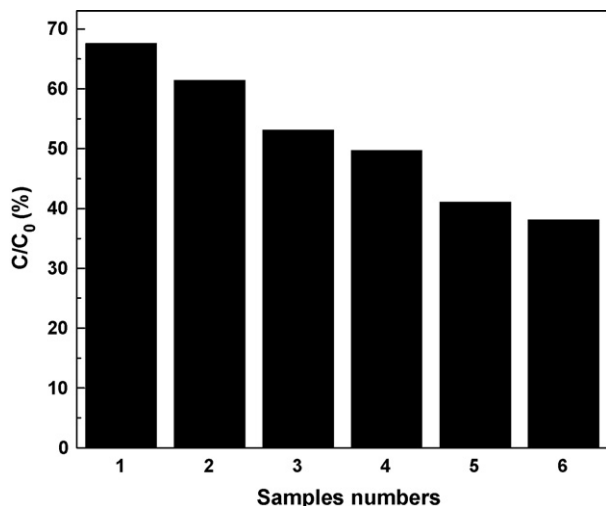


Fig. 5. Effect of initial pH value variation to the degradation rate of phenol. Conditions: Initial phenol concentration, 100 mg L⁻¹; flow rate, 5 mL min⁻¹; ozone concentration, 0.36 mg min⁻¹; temperature, 25 °C.

tion rate constants of $6 \times 10^8 \text{ M}^{-1} \text{ S}^{-1}$ with hydroxyl radicals [30] and $3 \times 10^{-3} \text{ M}^{-1} \text{ S}^{-1}$ with ozone [31] was introduced as scavengers. *tert*-Butanol (0.3 g) were added to 100 ml reaction solutions. Fig. 6(a) shows the influence of *tert*-butanol on the degradation of phenol in catalytic ozonation with brucite. Not a decrease of phenol degradation rate but a slight increase is observed. Therefore, it can be demonstrated that catalytic ozonation with brucite probably proceed according to direct oxidation by ozone molecule. While a distinct result can be observed in Fig. 6(b), the presences of *tert*-butanol obviously block the degradation rate of phenol in catalytic ozonation with magnesia. This result should demonstrate that hydroxyl radicals play an important role in magnesia system.

According to former investigation, pH value in water can determine the decomposition of ozone in water. When pH is higher than 10, ozone is able to decompose to generate a high concentration of hydroxyl radicals in water [17,29,33]. From Table 2, it can be observed that pH value in magnesia system maintains nearly 10.80, thus lots of hydroxyl radicals may be generated in this process. While in process of catalytic ozonation with brucite, although the initial pH value is 10.18, it quickly descends below 10, in this case the assumption that the generation of hydroxyl radicals are hardly accelerated by brucite should be in all probability. These assumptions were in agreement with the conclusions deduced from the results shown in radical scavenger experiments.

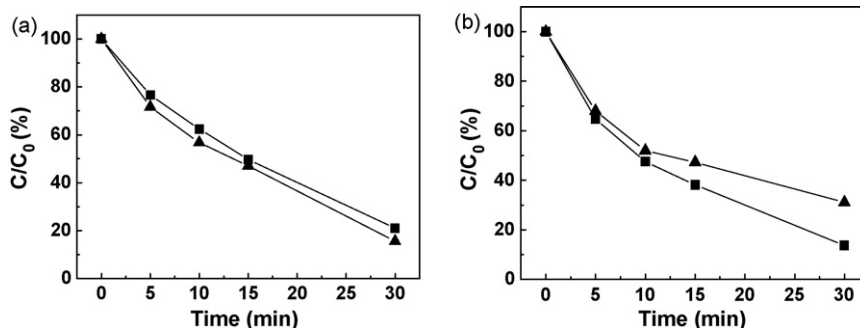


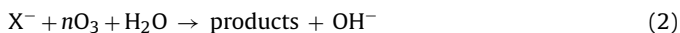
Fig. 6. Influence of *tert*-butanol on degradation of phenol. (a) Catalytic ozonation with brucite; (b) catalytic ozonation with magnesia. Without *tert*-butanol (■); with *tert*-butanol addition (▲). Conditions: Initial phenol concentration, 100 mg L⁻¹; *tert*-butanol concentration, 3 g L⁻¹; flow rate, 5 mL min⁻¹; ozone concentration, 0.36 mg min⁻¹; initial pH, 10.18 (brucite), 10.80 (magnesia); temperature, 25 °C.

3.6. Influence of temperature

As another important factor which can influence the decomposition rate of ozone in water, the increase of temperature could impel ozone to decompose to generate more free radicals [27,34]. In this experiment, catalytic ozonations with brucite and magnesia were carried out at 25, 35 and 45 °C, respectively. Fig. 7(a) indicates the influence of temperature on the degradation of phenol in catalytic ozonation with brucite. It can be found that the variation of temperature almost did not affect the degradation rate. This result further attests the assumption made in 3.5. While as to the catalytic ozonation with magnesia shown in Fig. 7(b), the decomposition rate of phenol presents a prominent enhancement with the increase of temperature, that is to say catalysis in this system should be mainly attributed to the generation of free radicals. The conclusion drawn from the temperature experiments further confirms that ozone direct oxidation should play a main role in catalytic ozonation with brucite, and free radical mechanism should control the catalytic effects in catalytic ozonation with magnesia.

3.7. Mechanism of catalytic ozonation

From the discussion above, it can be concluded that, in the catalytic ozonation with brucite, hydroxyl radicals in solutions may be not much enough to play an important role, and phenol should be mainly oxidated by molecular ozone. It is well known that, phenol and its decomposed-products (saturated and unsaturated acids) are neutral form in neutral and acidic solution, and would become base form with negative charge in alkali solution [35]. At the same time molecular ozone possesses a strong electrophilic reactivity. In alkaline environments such as brucite solution or borax buffer solution, ozone shows higher reactivity towards phenol and its decomposed-products due to its electrophilic characteristics [11,14,23]. Therefore, the reactions between ozone molecules and phenol and its decomposed-products were accelerated. The catalytic mechanism in catalytic ozonation with brucite can be described as follows:



In the reaction, X-H denotes phenol and its intermediates.

While in catalytic system with brucite, although above-mentioned reactions also exist, free radical mechanism should play a dominant role.

At the same time, considering the environment friendly viewpoint, brucite and magnesia are advantageous which would not lead to a secondary pollution. A feasible choice for catalytic ozonation of phenol in wastewater was supplied.

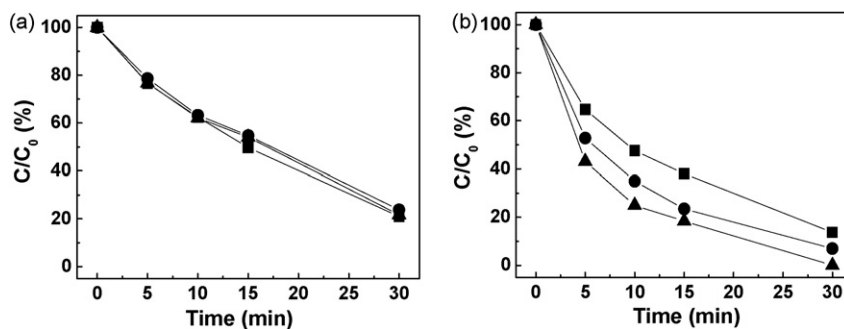


Fig. 7. Influence of temperature on the degradation of phenol. (a) Catalytic ozonation with brucite; (b) catalytic ozonation with magnesia: 25 °C (■), 35 °C (●), 45 °C (▲). Conditions: Initial phenol concentration, 100 mg L⁻¹; catalyst concentration, 5 g L⁻¹; flow rate, 5 mL min⁻¹; ozone concentration, 0.36 mg min⁻¹; initial pH, 10.18 (brucite), 10.80 (magnesia).

4. Conclusions

Main conclusions gained in this paper are presented as following:

- Natural minerals brucite and magnesia have remarkable catalysis on the degradation of phenol and removal of COD.
- Neither phenol nor its decomposed-products are adsorbed much by brucite and magnesia during ozonation.
- pH values of water are alkali in catalytic ozonation process with brucite and magnesia, and the alkaline environment is the main factor leading to the catalysis.
- Two catalytic systems have different catalytic mechanisms: in catalytic ozonation with magnesia, free hydroxyl radical mechanism is proved to play the dominant role; while in catalytic system with brucite, the direct ozone oxidation should contribute much more.
- Natural mineral brucite and its calcined-product magnesia have a promising application in treatment of phenol in wastewater by catalytic ozonation.

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