

Treatment of textile wastewater by heterogeneous Fenton process using a new composite Fe₂O₃/carbon

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Abstract

This paper evaluates the treatment of textile wastewater using new composites as adsorbents and/or heterogeneous catalysts for Fenton oxidation. The efficiency of the process was explored as a function of the experimental parameters: pH, hydrogen peroxide concentration and iron oxides content. The composites with high iron oxides content were effective to adsorb contaminants in textile wastewater, and the adsorptive capacity increased with the superficial iron concentration. These solids were also used as heterogeneous Fenton catalysts and had the advantage of being effective at pH 3.0 with a consumption of hydrogen peroxide lower than required by the homogeneous Fenton process.

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1. Introduction

The textile industry produces large volumes of effluents that contain appreciable quantities of organic compounds which are not easily amenable to chemical or biological treatment. The non-biodegradability of textile wastewater is due to a high content of dyestuffs, surfactants and additives which generally are organic compounds of complex structures. These compounds can be removed by adsorption onto porous solids, but this process only transfers the contaminant from the liquid phase to the solid phase. Alternative solutions to the conventional treatment have been reported, including electrochemical treatment, ozonation and other advanced oxidation processes, such as heterogeneous photocatalysis or Fenton reagent. Advanced oxidation processes show potential as one of the technologies for treating refractory compounds in textile wastewaters.

The combination of hydrogen peroxide and a ferrous salt has been referred to as “Fenton’s reagent” [1,2]. The primary oxidant in Fenton’s reagent is the hydroxyl radical ($\cdot\text{OH}$) generated by the reaction of hydrogen peroxide with ferrous ion. However, despite the high efficiency, the process is limited by the acidic

pH required (pH 2–4) and the high amount of sludge in the coagulation step [3].

Catalytic wet oxidation (WCO) is a reaction involving an organic compound in water and oxygen over a catalyst. Heterogeneous oxidation involves intensive contacting of an organic compound in solution with oxygen over a solid catalyst. Although the use of the catalyst makes the reaction conditions milder than uncatalyzed wet oxidation, the catalytic process still requires moderate temperature and pressure [4,5]. The catalytic wet hydrogen peroxide oxidation (CWHPO) could be a more efficient process than WCO since the oxidative properties of hydrogen peroxide are stronger than those of molecular oxygen [6,7]. Both CWO and CWHPO have proved their efficiency [4–7], but for application in large scale, it is necessary to develop catalysts that are active and stable at room temperatures.

Iron oxides are effective catalysts for catalytic wet hydrogen peroxide oxidation [1,2,8,9] and this process is also called heterogeneous Fenton degradation. These heterogeneous processes are promising because homogeneous processes need a separation step of the iron sludge at the end of the reaction. However, only a few attempts have been made to evaluate the potential of heterogeneous Fenton process.

The activity of the catalyst depends on characteristics of the iron oxides, such as crystallinity [8,10,11] and surface area [12].

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However, it has been demonstrated that iron oxide catalysts lose their activity because of leaching effects of metallic catalysts in acidic medium [12,13]. The leaching and deactivation of the catalyst are still challenges for developing advantageous catalyst for oxidation of wastewaters.

Effective heterogeneous catalysts for Fenton oxidation are also suitable for adsorptive filtration [1,14]. The adsorptive filtration is an innovative approach for the removal of contaminants from the liquid phase where toxic compounds are attached to a thin layer of iron oxide that has been immobilized on the surface of an appropriate filter medium, such as sand grains [14]. The modification of the filtration matrix allows the simultaneous sorption of soluble contaminants, as well as the removal of particulate material for filtration.

In this work, we studied the treatment of textile wastewater by adsorption and simultaneous catalytic wet hydrogen peroxide oxidation using new composites Fe₂O₃/carbon, and evaluated the effects of the pH, H₂O₂ concentration and catalyst dosage on the efficiency of the treatment.

2. Experimental

2.1. Material

Two different adsorbent/catalysts were used – Carbotrat AP[®] and Carbotrat Premium[®] – and they were supplied by Carbonífera Criciúma S.A. (Criciúma, Santa Catarina State, Brazil). The solids are named in this work as CA1 and CA2, respectively. CA2 is produced by the controlled deposition of iron oxides on CA1 [15].

The adsorbent carbons were characterized through the determination of their specific BET area and iron oxide content. These solids have presented high capacity for removal of iron dissolved in water [15,16]. The morphologic analysis and mapping of the elementary composition of solids were determined by scanning electronic microscopy (SEM/EDAX Philips XL-30). Mass titration proposed by Noh and Schwarz [17], which is an alternative method to the conventional acid–base titration technique, was carried out to estimate the point of zero charge of the solids (PZC).

The textile wastewater was obtained from a textile industry from Santa Catarina State (Brazil) and it was characterized through the determination of the chemical oxygen demand (COD), biochemical oxygen demand (BOD₅), concentration of total and dissolved solids and the pH [18] (Table 1).

Table 1
Characterization of the textile wastewater

pH	9.0
COD (mg O ₂ L ⁻¹)	1000
BOD ₅ (mg O ₂ L ⁻¹)	300
Total solids (mg L ⁻¹)	2545
Total fixed solids (mg L ⁻¹)	1665
Total volatile solids (mg L ⁻¹)	880
Ammonia nitrogen (mg L ⁻¹)	57
Nitrate-nitrogen (mg L ⁻¹)	1.2

2.2. Methods

The capacity of adsorption of the solids was determined experimentally by contacting the wastewater with different dosages of solids, in the range 100–300 g L⁻¹, at different initial pHs. The flasks were shaken during 24 h at 25 °C. Afterwards, the liquid was drained for determination of the remaining BOD₅, COD, color and aromaticity (UV₂₅₄).

The adsorption and simultaneous heterogeneous Fenton oxidation were carried out using different dosages of solids, in the range 100–300 g L⁻¹, and hydrogen peroxide concentration in the range 500–1000 mg L⁻¹, at different initial pHs. Blank tests using only hydrogen peroxide were also performed and the results showed that a negligible degradation occurs by the oxidation with hydrogen peroxide only.

In a typical run, 400 mL of textile wastewater was added to the reactor together with the solids. The mixture was agitated during 10 min at 90 rpm and the pH was adjusted to the desired value using HCl (1 mol L⁻¹). Then, H₂O₂ was added to achieve the desired H₂O₂ concentration and the mixture was agitated at 90 rpm during 60 min. After treatment, the samples were centrifuged and the liquid was analyzed in order to determine the residual hydrogen peroxide concentration [19], COD [18,20], color and aromaticity (UV₂₅₄) [18], using a UV–vis spectrophotometer (UV 1650C, Shimadzu, Japan).

Leaching tests were carried out in order to establish whether small amounts of the dissolved iron were responsible for the observed catalytic activity. After the oxidation with hydrogen peroxide, the solids were removed by filtration and the total iron concentration in the liquid phase was measured. The iron concentration was determined by UV–vis spectrometry (UV1650-C, Shimadzu) using the absorption band of Fe(II)/1,10-phenantroline complex ($\epsilon = 11,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 505 nm) [18].

3. Results

3.1. Chemical and textural characterization of CA1 and CA2

The textural characteristics of CA1 and CA2 are summarized in Table 2. The solids present a small surface area with a wide pore sizes distribution (Table 2). The morphologic analysis of CA2 is shown in Fig. 1. The solid presents an irregular surface, and small particle aggregates are observed. The composition of these aggregates on the surface of CA2 is shown in Table 2.

It has been reported that the deposition of iron oxides on porous solids decreases the BET surface area [21] since the iron oxides have a relatively small surface area (~66 m²/g). However, CA2 presented nearly the same surface as CA1. The point of zero charge of CA2 is slightly higher than that of CA1 due to the characteristics of the aggregates containing iron oxides [22].

3.2. Textile wastewater adsorption onto CA1 and CA2

The contact of the effluent with the solids for 24 h at 25 °C, pH 9.0 and different dosages of solids showed that the COD

Table 2
Characterization of the solids CA1 and CA2

	CA1	CA2
BET surface area (m ² /g)	3.8	4.9
Micropore volume (cm ³ /g)	2.5 × 10 ⁻³	1.4 × 10 ⁻³
Micropore width (nm)	4.22	3.20
Pore size distribution (%)		
Micro	42.9	55.5
Meso	21.2	16.5
Macro	35.9	28.0
Point of zero charge	6.5–7.5	8.4
% Fe ₂ O ₃ (m/m)	0.46	1.36
Semiquantitative analysis ^a		
C	74.70	31.27
O	16.56	17.89
Al	3.20	8.25
Si	4.17	7.41
K	0.56	0.93
Ti	0.33	0.54
Fe	0.48	21.04
S	–	4.89
Ca	–	1.44
Na	–	4.81
Cl	–	1.53

^a Obtained by energy dispersive analysis X-ray (EDAX) in the point shown in Fig. 1.

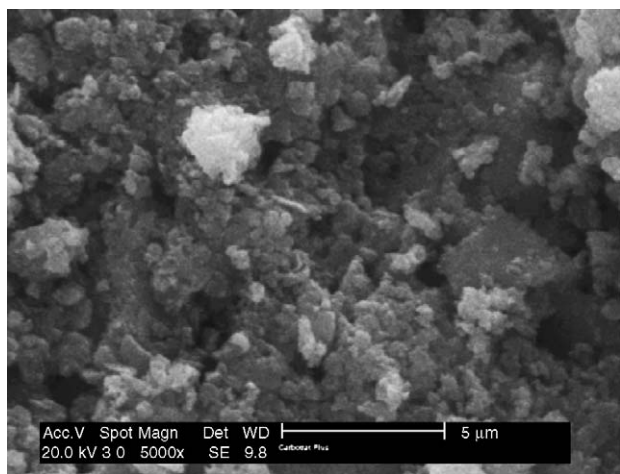


Fig. 1. Scanning electronic microscopy of CA2 (5000×) (semi-quantitative analysis was measured in the point inside the box).

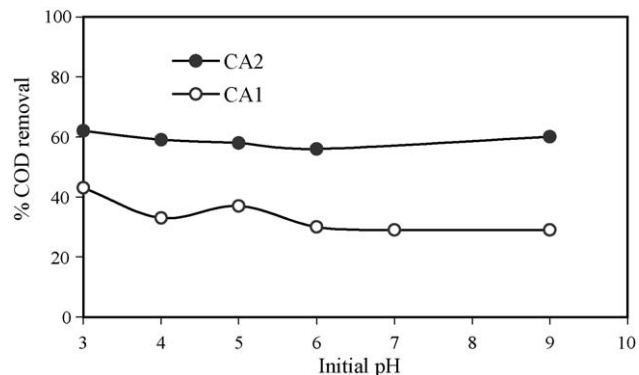


Fig. 3. Effect of the initial pH on the COD removal by adsorption (adsorbent dosage = 300 g L⁻¹; contact time = 24 h; T = 25 °C).

removal using CA2 is about twice as high as for CA1 (Fig. 2a). Aromatic compounds are preferably removed by adsorption on CA2 (Fig. 2b). At pH 9.0, the surface charge for both adsorbents should be negative since the point of zero charge is nearly neutral. Then, the difference of adsorption capacity does not relate to the electrostatic phenomena.

The adsorptive capacity of the solids CA1 and CA2 depends on the iron oxides content. Iron oxides aggregates have special characteristics in aqueous solution and are present as ferrihydrite in a gelatinous and insoluble coverage on the adsorbent carbon surface with high adsorptive capacity [22].

The effect of the pH on the adsorptive capacity of the solids was evaluated in the range 3–9 (Fig. 3). The COD removal is nearly independent of the initial pH and the capacity of adsorption of CA2 is almost twice as high as CA1.

3.3. Degradation of textile wastewater by heterogeneous Fenton oxidation

The concentration of iron in the liquid phase was measured during the reactions and the results showed that negligible amount of iron oxides was leached to the liquid phase. Then, no contribution of the homogeneous Fenton reaction during the degradation of textile wastewater by heterogeneous Fenton oxidation could be expected.

The kinetics of COD removal by heterogeneous Fenton oxidation was studied using 300 g L⁻¹ of CA1 or CA2 at initial pH 3.0 (Fig. 4a). The kinetics can be divided in two steps: a fast first

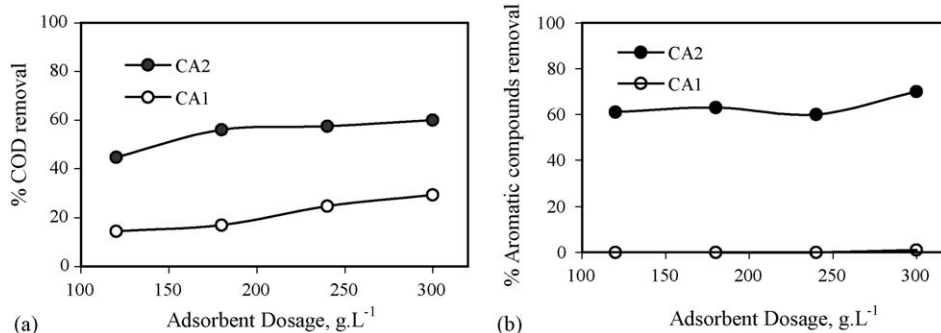


Fig. 2. Effect of the dosage using CA1 and CA2 as adsorbents: (a) COD removal and (b) aromatic compounds removal (contact time = 24 h, pH 9.0; T = 25 °C).

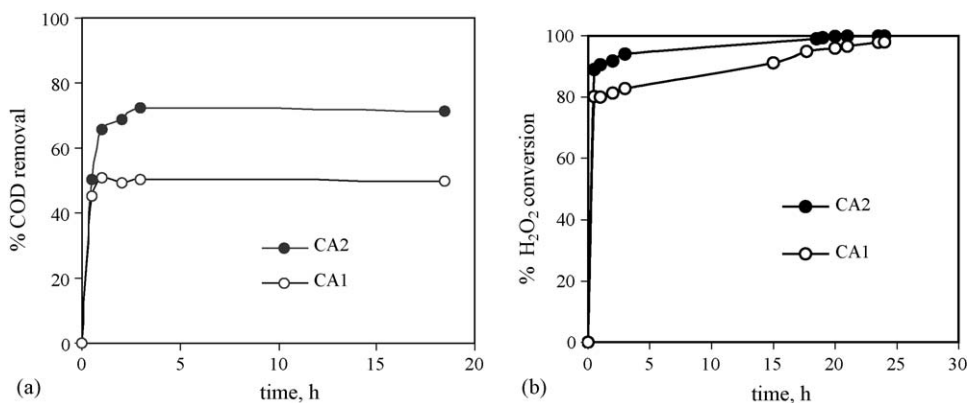
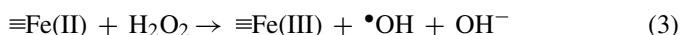
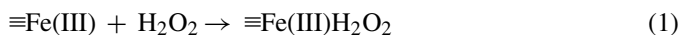


Fig. 4. Kinetics of COD removal (a) and hydrogen peroxide decompositions (b) by heterogeneous Fenton reaction using CA1 and CA2 as catalysts (solid dosage = 300 g L⁻¹; [H₂O₂]₀ = 500 mg L⁻¹; pH 3.0; T = 25 °C).

stage followed by a slow stage. This behavior was also observed in the homogeneous Fenton [23] and can be explained considering that hydrogen peroxide reacts quickly with iron oxide on the solid's surface to produce a great quantity of hydroxyl radicals. The hydroxyl radicals produced can react rapidly with the organic matter. The oxidized iron on the solid's surface produced in the first stage could react with hydrogen peroxide to produce hydroperoxyl radicals and regenerating the catalyst on the solid's surface. As the hydroperoxyl radical is less oxidative than the hydroxyl radicals [3], a slow second stage occurs.

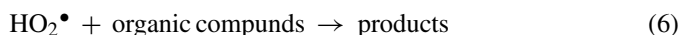
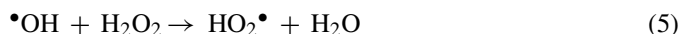
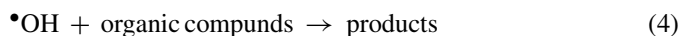
The kinetics of hydrogen peroxide disappearance was also evaluated during the wastewater degradation (Fig. 4b) and the decomposition rate of hydrogen peroxide is faster using CA2 than CA1.

The mechanism of H₂O₂ decomposition on iron oxides and hydroxides was recently reported by Kwan [9], and can be described according to Eqs. (1)–(3). The controlling step would be the surface reaction between hydrogen peroxide adsorbed on the solid's surface and the iron oxides. Then, the rate of formation of hydroxyl radicals (\bullet OH) depends on the iron oxide content and could explain why CA2 is more active than CA1.



The site ($\equiv\text{Fe(III)}$) represented in Eq. (1) is regenerated through Eq. (3) and it has been suggested that the adsorption of hydrogen peroxide (Eq. (1)) is much faster than that of the others [9].

The hydroxyl radicals (\bullet OH) formed in Eq. (3) could oxidize organic compounds present in the textile wastewater (Eq. (4)) or react with hydrogen peroxide in the liquid phase to form hydroperoxyl radicals (Eq. (5)) [3], that react slowly with organic compounds (Eq. (6)).



The COD removal increased as the catalyst dosage increased (Fig. 5), as expected, due to the increasing of amount of active sites for H₂O₂ decomposition and organic compounds adsorption.

The color removal and aromatic compounds removal by adsorption and reaction using CA1 and CA2 at different initial pHs are shown in Fig. 6. The removal of color and aromatic compounds by adsorption decreases as the pH increases, but the heterogeneous Fenton reaction is much less sensitive to pH than the homogeneous Fenton reaction [23].

Some authors have reported that the catalytic wet hydrogen peroxide oxidation depends on the pH when the leaching of iron varies with the pH [1,7], but leaching effects were not important in this study. Additional tests proved that the decomposition rate of hydrogen peroxide on CA2 is also nearly independent on the pH [24].

3.4. Effect of hydrogen peroxide concentration on the degradation of textile wastewater by heterogeneous Fenton reaction

It was previously reported [23] that the enhancement in the hydrogen peroxide concentration from 500 to 1000 mg L⁻¹

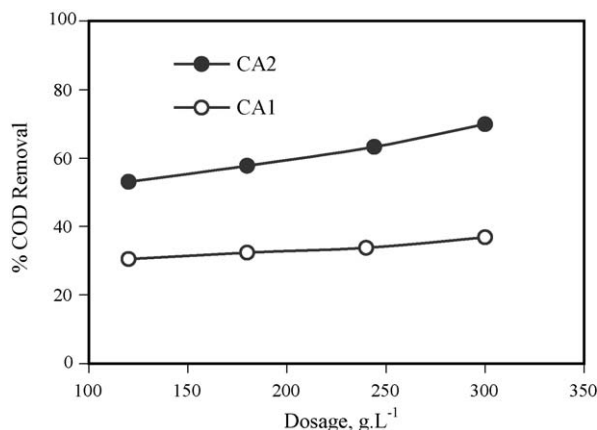


Fig. 5. Effect of catalyst dosage on the COD removal by heterogeneous Fenton oxidation ([H₂O₂]₀ = 500 mg L⁻¹; pH 3.0; reaction time = 1 h; T = 25 °C).

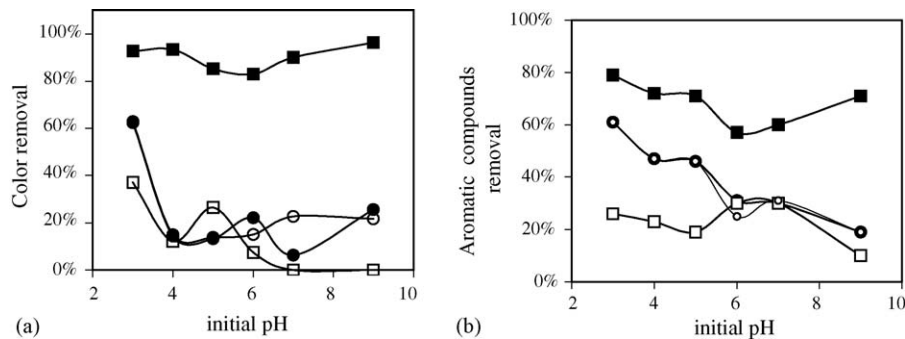


Fig. 6. Effect of pH on (a) removal of color and (b) removal of aromatic compounds by heterogeneous Fenton oxidation (catalyst dosage = 300 g L⁻¹; contact time = 1 h). (Open symbols) CA1; (closed symbols) CA2; (circles) adsorption; (squares) reaction ([H₂O₂]₀ = 500 mg L⁻¹).

increases the COD removal by homogeneous Fenton oxidation from 58 to 69%. However, no increase in the COD removal by heterogeneous Fenton oxidation using CA1 or CA2 (Fig. 7) was observed, and low H₂O₂ concentration was necessary to achieve 71% of COD removal using CA2.

As shown in Eqs. (1)–(6), the heterogeneous oxidation of the organic matter occurs after the adsorption and decomposition of hydrogen peroxide on the solid's surface. The reaction represented in Eq. (1) is fast and reaches pseudoequilibrium according to the Langmuir model (Eq. (7)) [9,24].

$$[\equiv\text{Fe}^{\text{III}}\text{H}_2\text{O}_2] = [\equiv\text{Fe}^{\text{III}}]_T \frac{K_a[\text{H}_2\text{O}_2]}{1 + K_a[\text{H}_2\text{O}_2]} \quad (7)$$

The equilibrium constant for the adsorption of hydrogen peroxide on the solid's surface is defined by Eq. (8).

$$K_a = \frac{[\equiv\text{Fe}^{\text{III}}\text{H}_2\text{O}_2]}{[\equiv\text{Fe}^{\text{III}}][\text{H}_2\text{O}_2]} \quad (8)$$

and the concentration of iron sites (free or occupied) is given by Eq. (9).

$$[\equiv\text{Fe}^{\text{III}}]_T = [\equiv\text{Fe}^{\text{III}}\text{H}_2\text{O}_2] + [\equiv\text{Fe}^{\text{III}}] \quad (9)$$

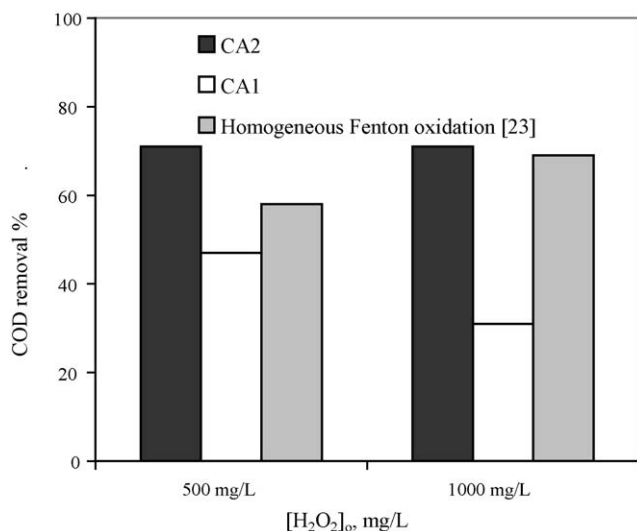


Fig. 7. Effect of the hydrogen peroxide concentration on the removal of COD during heterogeneous Fenton (catalyst dosage = 300 g L⁻¹; pH 3; reaction time = 1 h; T = 25 °C).

When the iron sites are saturated with hydrogen peroxide, further increase of the hydrogen peroxide in the aqueous phase does not increase the formation of hydroxyl radicals, and consequently, it does not increase the oxidation of organic compounds in the wastewater.

The maximum COD removal achieved in the treatment of the same textile wastewater by homogeneous Fenton oxidation is nearly 70% using H₂O₂ concentration higher than 1000 mg L⁻¹ at pH 3.0 [23]. The heterogeneous Fenton oxidation using CA2 as catalyst achieved 71% COD removal at room temperature using H₂O₂ concentration lower than 1000 mg L⁻¹, and presented the additional advantage of being less sensitive to pH than the homogeneous process.

4. Conclusions

Composites of iron oxides/carbon can be used in the treatment of textile wastewater as heterogeneous catalysts in the Fenton reaction. The adsorptive capacity of these solids increases as the superficial iron oxide content increases. The treatment of textile wastewater using these heterogeneous catalysts can be carried out at initial pH above 3.0 and lower hydrogen peroxide consumption than in the homogeneous Fenton process is needed. No iron was leached to the aqueous phase indicating that the homogeneous Fenton reaction was not important and the catalyst is quite stable.

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