

Behavior of polyvinyl alcohol in anaerobic environment after (pre)treatment with chemical oxidation

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Abstract:

This work focused on behavior of polyvinyl alcohol after chemical treatment with Fenton reagent in anaerobic environment. Polyvinyl alcohol anaerobic biodegradation reached only 7% in anaerobic tests using digestion sludge activated sludge from the municipal wastewater treatment. Fenton reaction was used for (pre)treatment of polyvinyl alcohol prior to biological treatment. Effect of pH, dosage reactants in Fenton process, time of reaction on the rate of polyvinyl alcohol degradation was studied. Test biodegradability showed that the oxidative products of polyvinyl alcohol after Fenton process were not toxic to anaerobic digested sludge. Fenton reaction may be an option for biodegradability improvement of polyvinyl alcohol in wastewater treatment.

Key-Words: - polyvinyl alcohol (PVA), chemical oxidation, anaerobic, biodegradation, wastewater treatment

1 Introduction

Polyvinyl alcohol (PVA) is commonly used as a sizing agent in the textile industry, in adhesives, emulsion paints, paper-coating, food and pharmaceutical industries. Polyvinyl alcohol is one of few synthetic polymers which at least slowly and low degree undergoes biodegradation.

Biodegradation of organic substances under anaerobic conditions occurs in many kinds of environment, for example, in wastewater treatment plants, in landfills of waste, natural sediments, in marshes and the like. It is hence a process without access of oxygen when by means of specific microorganisms more complex matter is gradually degrade to CH₄, CO₂, mineral substances and new biomass. Chiellini et al.[1] reported that high polyvinyl alcohol degradation level were observed in an aqueous environment containing adapted bacterial species often appearing in wastewaters and sewage sludge polluted with polyvinyl alcohol. Biodegradability of this polymer depends on its structure and molecular weight. The anaerobic biodegradability of polyvinyl alcohol was investigated in detail by Matsumura et al. [2], and the result showed that over 60% of polyvinyl alcohol was biodegraded as determined by total

organic carbon after 4 months of incubation. In contrast with the above investigations, polyvinyl alcohol was found to show only minor degradation, ranging between 0% and 12% in 77 d, in anaerobic tests using digestion sludge according to ISO and ASTM standard procedures [3, 4].

The rate and extent of polyvinyl alcohol biodegradation can be increased by including a chemical oxidative agent, such as Fenton's reagent which has been used in the treatment of aromatic hydrocarbons. The Fenton reaction is most often used either for the pretreatment or for mineralization of chemical oxygen demand prior to biological treatment or for the mineralization of toxic or only with difficulty degradable pollution [5-8]. The chemical and photo-chemical oxidation of polyvinyl alcohol in water has been increasingly studied [9, 10]. Giroto also showed that photo-Fenton degradation under optimal conditions could mineralize polyvinyl alcohol up 90 %. Lei LC et al. [11] studied the degradation of polyvinyl alcohol by using advanced oxidation process (AOP). Efficient degradation of polyvinyl alcohol was achieved by applying photochemical Fenton reactions.

Degradation of polyvinyl alcohol by using a combination of chemical treatment with Fenton's

reagent and biological degradation with the white rot fungus *Pycnoporus cinnabarinus* investigated by Larking et al [12]. Inclusion of the chemical pretreatment resulted in greater degradation of polyvinyl alcohol than the degradation observed when biological degradation alone was used. Biodegradation of polyvinyl alcohol by fungal *Phanerochaete chrysosporium* after pretreatment with Fenton reagent studied Huang et al. [13]. The overall degradation was 74.4 % as determined by chemical oxygen demand analysis.

Appropriate molar ratio of Fenton reagents and initial pH are the two most important factors to achieve maximum COD removal performance.

This study was conducted to assess the removal of polyvinyl alcohol from an aqueous solution using of oxidative degradation and biodegradation in an anaerobic sludge from the municipal wastewater treatment plant.

2 Experimental study

2.1 Material

Materials MOWIOL 5–88 (PVA), viscosity 5.5 ± 0.5 mPas, hydrolysis degree – 88 mol %, molecular weight 37 000 g/mol, produced by Kuraray, Japan. The polyvinyl alcohol solutions were prepared by gradually dissolving small amounts of solid commercial polyvinyl alcohol in a beaker with magnetic stirring, at about 50°C, in order to prevent foam formation. The solution was then diluted in water, in order to obtain the certain concentration of polyvinyl alcohol.

The following analytical reagents were used: pent hydrated ferrous sulfate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, hydrogen peroxide H_2O_2 (30,84%, w/w, in water), H_2O_2 concentration was determined by iodometric method sodium hydroxide, sulfuric acid

Inoculum always used was partly digested activated sludge from anaerobic stabilization of the municipal wastewater treatment plant Zlín-Malenovice, CZ. Before use, it was disposed of coarse impurities, centrifuged at 3,000g for 10 minutes at 15 °C. Anaerobic sludge was diluted with mineral medium mentioned below to required dry matter concentration.

Preparation of solutions and all dilutions utilized a mineral medium prepared as follows: Quantity of following solutions is used for 1L of mineral medium (filled to 1 L with distilled water):

40 mL phosphate buffer (8.5 g/L KH_2PO_4 ; 21.75 g/L K_2HPO_4 ; 44.7 g/L $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$), 50 mL $(\text{NH}_4)_2\text{SO}_4$ (10 g/L), 1 mL CaCl_2 (7.5 g/L), 1 mL $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.25 g/L), 1 mL $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (22.5 g/L), 1 mL solution of trace elements (0.75 g/L H_3BO_3 ; 3 g/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; 0.1 g/L $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$; 0.5 g/L $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$; 0.05 g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; 0.05 g/L $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 0.1813 g/L $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$.

pH were measured by a pH meter OP 208 (Radelkis, Hungary)

Gas chromatography - Agilent 7890, column filled with Porapack Q, length 3.6 meter, diameter 3 mm, detector - TCD, temperature 250°C, Carrier gas: helium 99.999%, flow rate 30 ml / min, Termostat: 50°C, injector: 200°C

Calibration: mixed gas 4.05% CH_4 , 0.798% CO_2 , 95,152% N_2 – Linde Technoplyn a.s., CR

2.2 Experimental procedure

2.2.1 Assessment of anaerobic analysis - Method by measurement of the biogas production

Biodegradability of polyvinyl alcohol and oxidative products of PVA after Fenton process in an aqueous anaerobic environment was studied in the presence of a mixed microbial culture supplied in the form of partly digested sludge from anaerobic stabilization of residual activated sludge from the municipal wastewater treatment plant.

Tested samples of polyvinyl alcohol (approx. 20 mg organic carbon) or 100 ml oxidative products of PVA after Fenton process were dosed into test bottles of 250-ml volume for each bottle to contain sample in 100 ml liquid phase. Starting concentration of anaerobic sludge dry matter was 3-4 g/L. Filled bottles were bubbled through with nitrogen for approx. 5 min, than sealed gastight and immersed in hot water tempered to $35 \pm 1^\circ\text{C}$. Contents of bottle were continuously stirred during test. Anaerobic biodegradability was examined through produced CO_2 and CH_4 . Both produced gases were subjected to final analysis employing gas chromatography with TCD. Analysis of actual samples mostly used 0.2-ml quantities of gas phase withdrawn at determined time intervals.

Endogenous respiration was investigated at the some time. Sodium acetate (NaAc) was used as a standard substance. Actual degradation test were performed threefold in parallel at neutral pH level. Characteristics finally determined were dry matter, pH and content of organic and inorganic carbon (TOC and IC).

At the end of each test, a concentration of inorganic carbon (IC) was determined in liquid phase using an automatic TOC analyzer (Shimadzu 5000A). The final level of sample biodegradation was evaluated by the relation of the amount of carbon released in the form of both gas products (CH_4 and CO_2) and liquid compounds (IC), corrected by a blank, to a theoretical amount of carbon in the sample, and expressed in terms of percent mineralization.

Percentage of biologically removed polyvinyl alcohol – D_T (%) was evaluated through produced carbon dioxide and methane in gas phase and quantity of CO_2 in liquid phase.

$$D_t = \frac{(CO_2)_t - (CO_2)_b + (CH_4)_t - (CH_4)_b + T_{IC}}{Th_C} \cdot 100$$

where

$(CO_2)_t$ is quantity of CO_2 released in bottle (mmol),
 $(CO_2)_b$ is average quantity of CO_2 released in bottle during endogenous respiration (mmol),

$(CH_4)_t$ is quantity of methane released in bottle (mmol),

$(CH_4)_b$ is average quantity of methane released in bottle during endogenous respiration (mmol),

Th_C is quantity of total (theoretical) carbon in dry matter of tested sample (mmol),

T_{IC} is quantity of CO_2 in liquid phase (mmol),).

2.2.2 Chemical oxidation of polyvinyl alcohol by Fenton reaction

Chemical oxidation of water solution of PVA was carried out at ambient temperature according to the following sequential steps.

100 ml of polyvinyl alcohol solution was placed in Erlenmeyer flasks (250 mL). The pH has been adjusted to the initial value of 4 by a sulfuric acid. The total amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in the PVA solution before an aliquot of 30.84 % H_2O_2 was added to reach a molar ration ($\text{PVA}/\text{Fe}^{2+}/\text{H}_2\text{O}_2$). The reaction mixture was stirred rapidly for 120 minute. Samples for analysis were collected during the reaction time. At selected time intervals (10, 20, 30, 60, 90, 120 min.). 10 mL sample collected from each triplicate Erlenmeyer flask.

The measurement of the polyvinyl alcohol degradation as a function of oxidation condition depends strongly on the ability to stop the oxidation reaction at a chosen reaction time. Fenton reaction will continue as long as H_2O_2 prevails in the reaction system, even at lower temperatures. Therefore a reductive a precipitation agent (solution of $0.1 \text{ mol.L}^{-1} \text{ Na}_3\text{PO}_4$, $0.1 \text{ mol.L}^{-1} \text{ KI}$ and 0.1

$\text{mol.L}^{-1} \text{ Na}_2\text{SO}_3$) was added in order to reduce all residual H_2O_2 . Ferric and ferrous ions precipitated in the presence of basic phosphate solution or $1 \text{ mol.L}^{-1} \text{ NaOH}$. Precipitate was removed by filtration or centrifugation using Rotanta 460 R (Hettich Zentrifugen, SRN).

The samples (filtrate) were taken to a Total organic carbon TOC analyzer (Shimadzu 5000A). Fenton process was monitored by analyzing the dissolved organic carbon concentration (DOC) and concentration of residual polyvinyl alcohol.

2.2.3 Determination of concentration of residual polyvinyl alcohol

In Fenton's experiments, the residual polyvinyl alcohol concentrations were performed at 660 nm using a UV-VIS spectrophotometer Sunrise (Tecan, Switzerland). The method is based on the blue color produced by reaction of polyvinyl alcohol with iodine in the presence of boric acid [15].

2.2.4 Dissolved organic carbon (DOC) analysis

The analysis of the DOC (dissolved organic carbon) has been carried out using a TOC (total organic carbon) 5000 analyzer ($T = 690 \text{ }^\circ\text{C}$) from Shimadzu Corp., Austria.

3 Results and discussion

3.1 Oxidative degradation of polyvinyl alcohol by Fenton Process

First, optimal conditions were studied for the most efficient degradation of polyvinyl alcohol (Mowiol 5-88) by chemical oxidation. Optimal reaction conditions in terms of cost and treatment efficiency are required to be established to improve the overall process performance.

3.1.1 Effect of pH on polyvinyl alcohol removal by Fenton process

pH value is one of the major factors influencing the rate of degradation of polyvinyl alcohol. Figure 1 showed the DOC removal at different pH. pH control in the Fenton process was carried out by using sulphuric acid and sodium hydroxide solution. The effect of pH was significant, and the degradation of polyvinyl alcohol was favorable at lower pH. Optimum pH value was 2 for (24 time of reaction) 3-4 (reaction for 120 minutes). pH lower than optimum affects the PVA removal by producing less hydroxyl radicals. During Fenton process pH was kept in the range 4 - 4.2.

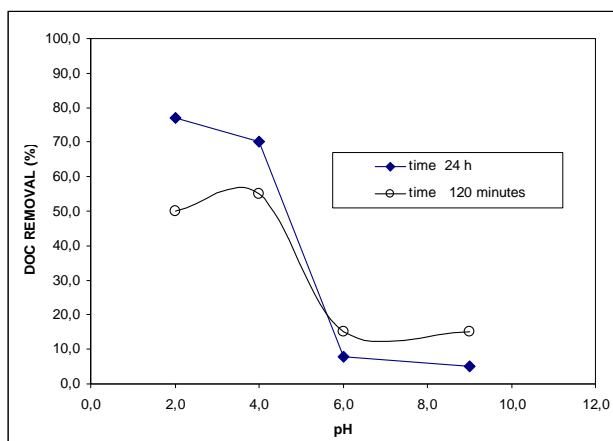


Fig.1. The effect of pH on DOC removal by Fenton reaction (experimental condition: PVA 200 mg.L⁻¹, molar ratio PVA/ H₂O₂/Fe²⁺ (1 : 4,4 : 0,05)

3.1.2 Effect of Fe²⁺ concentration on oxidative degradation polyvinyl alcohol

The iron concentration is important for the reaction kinetics. The effect of dosage of Fe²⁺ on oxidative degradation of polyvinyl alcohol by Fenton process is shown in Fig. 2

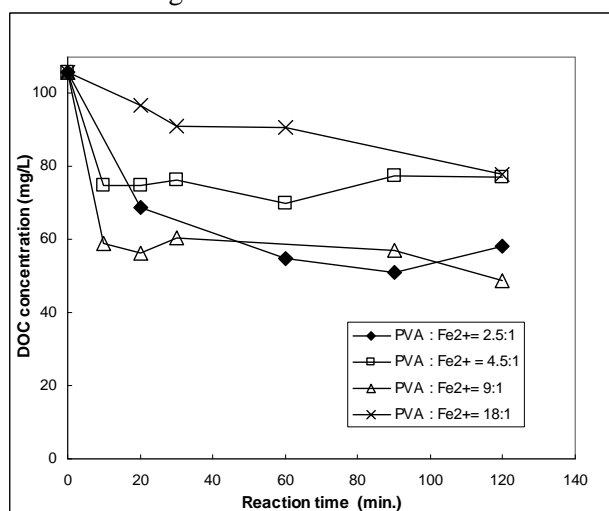


Fig. 2 Change in dissolved organic carbon (DOC) concentrations during oxidation of PVA - various doses of Fe²⁺ (experimental condition: initial PVA concentration 200 mg.L⁻¹, H₂O₂ 0,2 ml, pH=4)

Optimal efficiency of polyvinyl alcohol removal was achieved at a ratio of PVA: Fe (II) 9:1.

3.1.3 Effect of Fenton reagent dosage on oxidative degradation polyvinyl alcohol

The molar ratio of H₂O₂ and Fe²⁺ is very important in terms of overall cost and removal efficiency of the process. The peroxide dose is important in order to obtain better degradation efficiency. A decreased dosage of H₂O₂ does not

generate enough hydroxyl radicals to achieve complete mineralization. Fig. 3 shows the removal of PVA concentration at different H₂O₂ dosage and molar ratio H₂O₂/Fe²⁺ 10:1. We can see that increasing the dose of peroxide significantly accelerates the reaction rate.

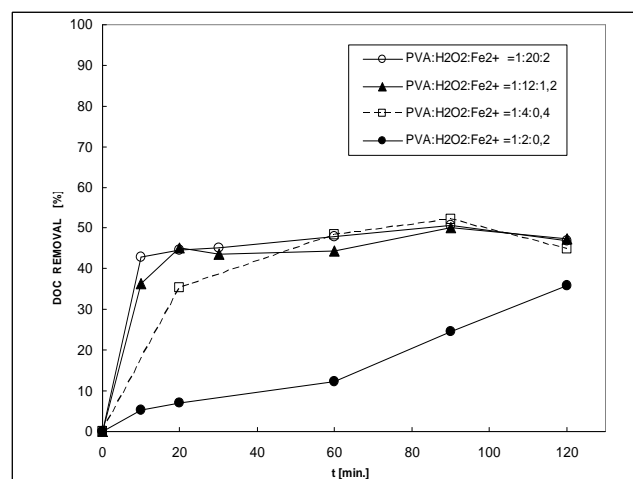


Fig.3. The effect of H₂O₂ dosage on DOC removal by Fenton reaction (initial concentration PVA 200 mg.L⁻¹, pH=4, molar ratio H₂O₂/Fe²⁺ was 10:1)

3.1.4 Effect of the initial concentration of polyvinyl alcohol

The Fenton reaction was carried out with water solutions of polyvinyl alcohol of concentrations: 200, 300, 400, 500, 5,000 and 15,000 mg.L⁻¹. Effect if initial concentration of polyvinyl alcohol on degradation rate is shown in Tab.1. It was observed, that the removal of DOC increased with increasing initial PVA concentration for same amount of reagents used.

Tab.1 The degradation of polyvinyl alcohol at different initial concentration PVA (experimental condition: molar ratio of PVA/ H₂O₂/ Fe²⁺ (1:3.6 : 0.36), time 120 minutes, pH 4)

C _{PVA} [mg.L ⁻¹]	V _{H₂O₂} [ml]	m _{FeSO₄ · 7 H₂O} [mg]	Removal DOC [%]	SD
200	0.16	44.48	60.23	1.91
300	0.24	66.72	60.07	4.64
400	0.32	88.97	65.66	1.95
500	0.4	111.2	68.29	1.07
5000	4	157	63.42	3.28
15000	12	473	68.72	1,52

3.2.6 Mineralization of polyvinyl alcohol

The mineralization of polyvinyl alcohol had been investigated by the time-dependent measurement of the DOC and IC concentration in filtrates. In Tab. 2 we can see that the concentration of IC was increased during Fenton process. Thus it can be assumed that part of the PVA could be mineralized to CO_2 , which remained in solution in the form of CO_2 , HCO_3^- and CO_3^{2-} .

Tab.2 Concentration of total carbon (TC), dissolved organic carbon (DOC) and an inorganic carbon (IC) in Fenton reaction (experimental condition: initial concentration PVA 200 mg.L^{-1} , molar ratio of $\text{PVA}/\text{Fe}^{2+}$ (9:1), $V_{\text{H}_2\text{O}_2} = 0,2 \text{ ml}$, pH 4)

Time [h]	TC [mg.L^{-1}]	DOC [mg.L^{-1}]	IC [mg.L^{-1}]
0	111.1	108	3,1
2	102.9	95.0	7.8
5	90,1	49.1	41.0
23	39.4	32.32	7.1

3.2.7 Pretreatment of PVA

Based on previous experiments were used condition with less ferrous ions and hydrogen peroxide. The solutions of polyvinyl alcohol concentration 5 g.L^{-1} and 15 g.L^{-1} were treated by Fenton process at experimental conditions: molar ratio of $\text{PVA}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$ 1:3,6:0,36, pH 4, temperature 25 °C, time 120 minutes. The solid particles created during degradation reaction were separated by filtration. More than 63 % of PVA was removed by this process (Tab.I.). The residual products were tested in the digested sludge from anaerobic stabilization of residual activated sludge from the municipal wastewater treatment plant.

3.3 Biodegradation of polyvinyl alcohol (Mowiol 5-88) and of oxidative products of Fenton process under an anaerobic condition

Firstly, the biodegradability of polyvinyl alcohol under the anaerobic conditions was observed. Percentage of biologically removed polyvinyl alcohol – D_T (%) was evaluated through produced carbon dioxide and methane in gas phase and produced carbon dioxide in liquid phase. Methane

content in the biogas varied from 60% to 72% and the remaining was assumed as carbon dioxide. Percentage of biologically removed polyvinyl alcohol - D_C (%) through produced carbon dioxide and methane in gas phase we can see in figure 4. Polyvinyl alcohol decomposition process under anaerobic conditions was very slow and only 7% was removed within 45 days.

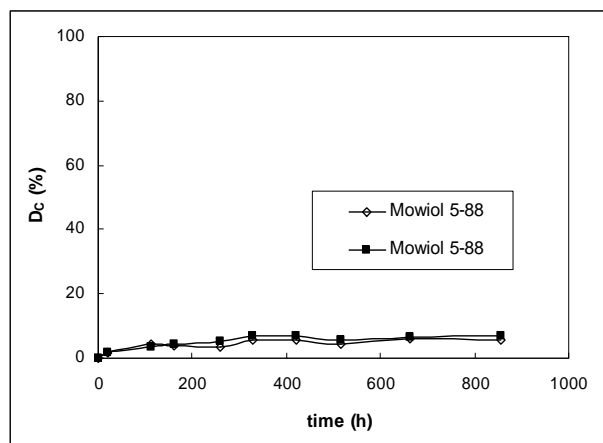


Fig. 4 Test biodegradability of polyvinyl alcohol (Mowiol 5-88) under an anaerobic condition

In the Fig. 5 we can see biogas (CH_4 and CO_2) production from residual samples of polyvinyl alcohol after degradation by Fenton reagent. Endogenous respiration (blank) was investigated at the same time.

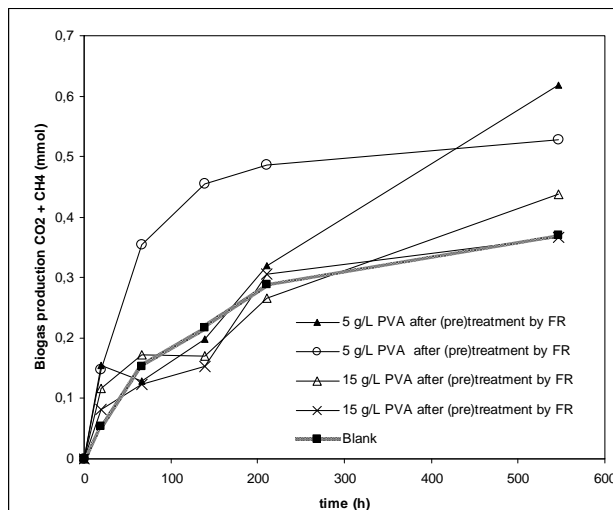


Fig.5. Course of biogas production from samples of polyvinyl alcohol after pretreatment by Fenton reaction

During the three weeks were the detected only small amounts of CH_4 in biogases produced from samples of PVA after Fenton reaction. Biogas compositions were mostly carbon dioxide and small quantities of

methane. Occasionally one sample (5g/L) produced more methane than the blank. It can be assumed that the products of Fenton process would be better decomposed in aerobic conditions. On the other hand, anaerobic sludge is continuously produced CO₂ and CH₄ after adding the PVA solution after pre-Fenton oxidation, so the oxidative products of polyvinyl alcohol were not toxic to anaerobic microorganism. These results suggest that Fenton reaction may be an effective pretreatment to enhance biodegradability of polyvinyl alcohol in wastewater industry.

4 Conclusion

In this work behavior of polyvinyl alcohol and oxidative products of polyvinyl alcohol in anaerobic condition was investigated. Biodegradability of polyvinyl alcohol and oxidative products of PVA after Fenton process in an aqueous anaerobic environment was studied in the presence of a mixed microbial culture supplied in the form of partly digested sludge from anaerobic stabilization of residual activated sludge from the municipal wastewater treatment plant. Only about 7% degradation of PVA within 45 days under anaerobic conditions was achieved.

A series of experiments were performed in order to investigate the performances and the behaviors chemical oxidation of PVA using Fenton reagent. At about 60% of the initial dissolved organic carbon was removed within 120 min under the optimal experimental conditions applied.

Test biodegradability under anaerobic condition showed that the oxidative products of polyvinyl alcohol after Fenton process were not toxic to anaerobic digested sludge. Fenton reaction may be an option for biodegradability improvement of polyvinyl alcohol in wastewater treatment.

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