

# Plasma-induced degradation of diphenylamine in aqueous solution

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## Abstract

The liquid-phase degradation induced by a gaseous plasma was investigated. The plasma was generated between an electrolytic solution and an anode tip by means of contact glow discharge electrolysis (CGDE). Aqueous diphenylamine was smoothly oxidized and eventually degraded to inorganic carbon. Results indicated that the degradation rate can be considerably raised by prolonging the discharge time and the optimum pH value was 6.0 for diphenylamine degradation.  $\text{Fe}^{2+}$  shows an evident accelerated effect on the diphenylamine elimination, meanwhile the presence of  $\text{H}_2\text{O}_2$  benefited the degradation but the presence of *n*-butanol inhibited the degradation, demonstrating that the hydroxyl radicals were the most responsible oxidants in the diphenylamine degradation. The major intermediate products resulted from the degradation were identified by an HPLC analysis and a degradation path way was proposed.

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**Keywords:** Plasma; Glow discharge electrolysis; Diphenylamine; Oxidation

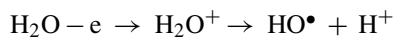
## 1. Introduction

By far the most common method for removal of the biodegradable fraction of the chemical oxygen demand (COD) of toxic substances is biodegradation, well-established and relatively cheap. But unfortunately not all toxic organic substances which are responsible for COD are easily biodegradable [1]. Several advanced oxidation process (AOP), e.g., ultraviolet photolysis, direct ozonation, electron beam, and various combinations of radiation are currently under development [2]. In this process, attention has been focused on hydroxyl radical, since the most powerful oxidizing species are in fact the hydroxyl radical. The hydroxyl radical reacts strongly with all organic substances usually by hydrogen abstraction.

In recent years, the application of glow discharge electrolysis to the water treatment has attracted much attention of the environmental researchers, because of its high efficiency, high amenability to automation and environmental compatibility in which high energy of plasmas, especially the hydroxyl radicals, were directly produced by the water discharge and were mostly utilized for the destruction of hazardous organics in the aqueous solution. In this process,  $\text{HO}^\bullet$  radical are

produced electrochemically in an anodic reaction directly from water.

Earlier studies have shown that most contaminants can be degraded by means of contact glow discharge electrolysis (CGDE). These results suggested that CGDE was an efficient process for the degradation of toxic substances especially for those that are difficultly treated by the biological way. In this process,  $\text{HO}^\bullet$  radicals are produced electrochemically in an anodic reaction directly from water, which has to be treated as follows:



By using the electrochemical production of hydroxyl radicals, no addition of chemical substances is necessary and the process can be performed at affordable costs and determined mainly by the power required for driving the electrochemical process and without the common AOP drawbacks. Most of the researches focus on dissolved easily and low toxic substances, some of them attempted to design complex apparatus including costly diamond anodes for the COD removal from several industrial wastewaters [3–9].

In the present investigation, an exhaustive degradation of diphenylamine dissolved in a potassium sulfate solution by means of glow discharge electrolysis under water was described, focusing on the reaction kinetics. The mechanism of producing

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plasmas in this process has been studied by M.A. Malik and co-workers [10–16]. Recently, there were several reports [17–20] on the degradation of certain organic target compounds dissolved in water by use of contact glow discharge. All these investigations confirm that contact glow discharge plasma was a prospective process for the degradation of toxic substances.

## 2. Experimental

The experimental apparatus consists of a reaction cell and a high voltage power supply as showed in Fig. 1. The anode from which the glow discharges emitted was a pointed platinum wire (I.D. 0.5 mm) encased in a glass tube located in the bottom center of a cylinder reactor, with the needle tip protruding 1 mm from the glass tube. The cathode was a stainless steel rod placed in the opposite position of the anode (5 cm from the anode). A positive high voltage was applied to the needle anode by a WYJ-1000V2A dc power supply produced by Shanghai Changjiang Eletron Instrument Company providing voltage of 0–1000 V and current output of 0–2 A. In addition, the reaction cell was coated by a water jacket, in which the temperature was controlled at the room temperature. When the glow discharge electrolysis began, a lot of heat was produced, which can convert the solution automatically. Therefore, no other system was employed to stir the solution.

Diphenylamine was dissolved in an aqueous potassium sulfate solution (4 g/L). The pH of the solution was adjusted with dilute sodium hydroxylate and dilute sulfuric acid to the expected value. During the reaction process, a small portion of the solution (about 0.025 ml) was periodically sampled out from the sampling port with a finnpipette made by Thermo Electron Corporation to measure the reduction of diphenylamine immediately by a high performance liquid chromatography (LC-10AT vp) produced by Shimidzu Company with a UV detector at a wavelength of 254 nm (mobile phase: CH<sub>3</sub>OH/phosphate suffer (20 mmol/L) = 30:70 (V/V), flow rate: 0.8 ml/min).

The experimental conditions usually employed were: electrolyte, 150 ml; voltage, 600 V; temperature, 298 K. These are referred as the “standard conditions” or otherwise specified.

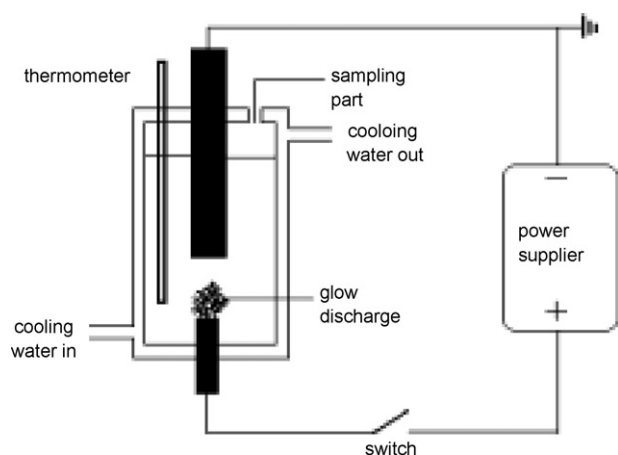


Fig. 1. Scheme of the experimental apparatus.

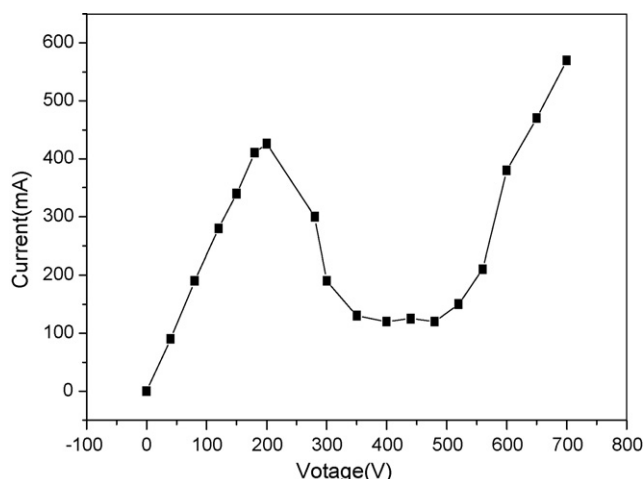


Fig. 2. The characteristic curve of current vs. voltage ( $c_0=100$  mg/L,  $V=150$  ml, pH 6.98,  $T=298$  K).

## 3. Results and discussion

### 3.1. The characteristic curve of current versus voltage

Experiments are run to reveal the relation of current versus voltage in the degradation process. Fig. 2 presents the characteristic curve of current versus voltage for the glow discharge electrolysis underwater. A 150 ml solution containing 100 mg/L diphenylamine was used for degradation under different voltage. From the curve, it can be found that the curve can be divided into three parts. In the first part (0–200 V), the current increased almost proportionately with the increase of the applied voltage, suggesting that the electrolysis observe the Ohm’s law in this stage. The reaction was mainly attributed to the oxidation of water at the anode and reduction at the cathode. And the current intensity was very stable in this stage. In the second part (200–480 V), some sparks were observed and the current became very unstable. This can be explained by the fact that a lot of heat was produced near the tip of the anode, making the water surrounding the anode vaporization and the current abruptly decreased because the water vapor is dielectric. Because the normal electrolysis still exists, the current cannot be zero. When the applied voltage is over 480 V, the current increases with the increasing of the voltage again, this is due to the full breakdown of the water vapor, and the normal electrolysis spontaneously switches to the glow discharge electrolysis and stable plasma is sustained. From the experiment, it was found that there is almost no signs of the melting of the anode even if the applied voltage was increased to 700 V, this proves that the glow discharge electrolysis under water can widen the applied voltage range.

### 3.2. Removal of the diphenylamine

Fig. 3 exhibits the time profile of diphenylamine removal under 600 V. Here, the initial concentration ( $c_0$ ) of diphenylamine was 100 mg/L. It can be seen that the diphenylamine removal increases with the discharge time, and it can be

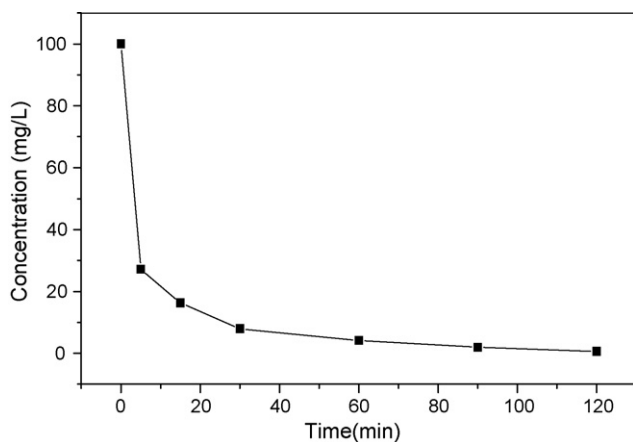


Fig. 3. Time profile of diphenylamine degradation ( $U=600$  V, pH 6.98,  $V=150$  ml,  $c_0=100$  mg/L).

completely removed within 120 min. This indicates that glow discharge electrolysis is a very efficient tool for diphenylamine degradation because generally the pollutant cannot be completely removed in other processes.

### 3.3. The variety of pH in the degradation process

It is reported that there are some carboxylic acids such as formic, oxalic, and malonic acids and so on were formed in the oxidation process [4]. Fig. 4 shows the variety of pH in the degradation process of diphenylamine. Obviously, the pH value decreased evidently with the discharge time, but the pH value increased gradually after 120 min. It can be explained by the fact that there are some carboxylic acids which were generated in the reaction process and were oxidated simultaneously.

### 3.4. Effect of $H_2O_2$

In order to investigate the role of  $H_2O_2$  in removing diphenylamine from the aqueous solution, 2, 4, 6, 8, and 10 g/L  $H_2O_2$  were added into the diphenylamine solution respectively. Fig. 5 shows the concentration of the diphenylamine at reaction time

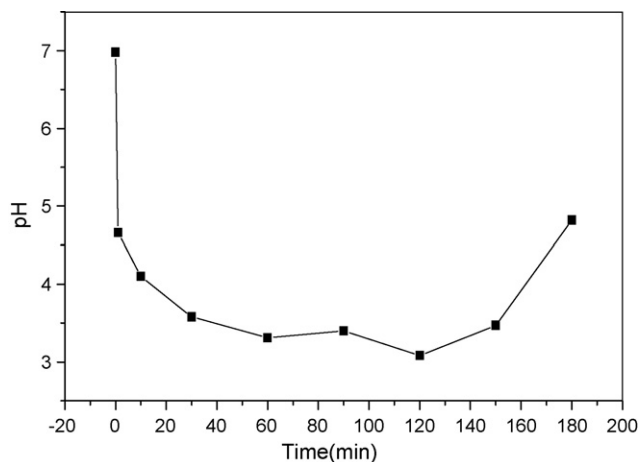


Fig. 4. The variety curve of pH in the degradation process ( $U=600$  V,  $V=150$  ml,  $c_0=100$  mg/L).

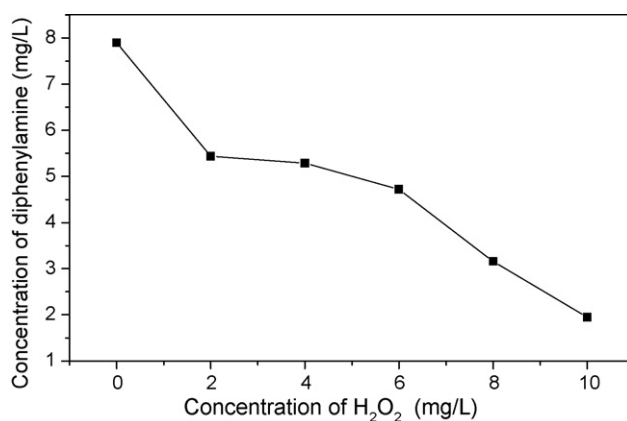


Fig. 5. Effects of  $H_2O_2$  to the degradation ( $U=600$  V, pH 6.98,  $V=150$  ml,  $c_0=100$  mg/L,  $t_m=30$  min).

of 30 min. Obviously, the removal efficiency of diphenylamine with  $H_2O_2$  is higher than without  $H_2O_2$ . It is also observed that higher  $H_2O_2$  concentration is beneficial the removal of organic compounds. It may be explained by the concentration of  $HO^\bullet$  which increased when  $H_2O_2$  was added into the diphenylamine solution.

### 3.5. pH effects

It is well known that the oxidation processes are very sensitive to the pH of the aqueous solution. Fig. 6 shows the results of a series of experiments at different pH at given reaction time of 30 min. The initial conditions for the model were as follows: diphenylamine concentration ( $c_0$ ) was 100 mg/L and applied voltage was 600 V. The degradation rate increased gradually when the pH rose from 4.0 to 6.0. However, the degradation rate decreased when the pH changed from 6.0 to 9.0.

This maybe presumed that more  $OH^\bullet$  was produced from CGDE than  $H_2O_2$  in a little acid conditions, and the former was more active than  $H_2O_2$  (generally the oxidation rate of hydroxyl radicals was  $10^8$  higher than that of hydrogen peroxide [13]). While in an alkaline solution,  $HO_2^\bullet$  ion would be decomposed by the discharge, which scavenged the hydroxyl radicals. Therefore, 6.0 would be the best pH value for diphenylamine degradation. An innovative finding was achieved; there

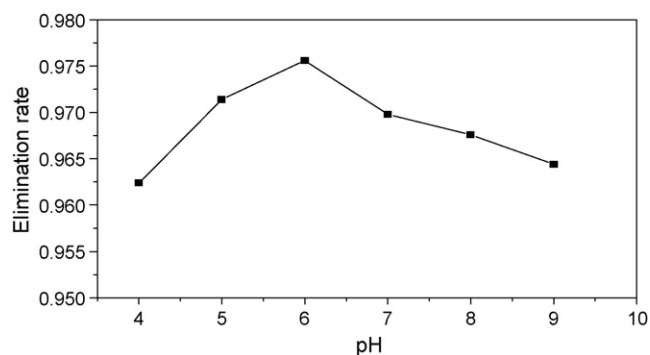


Fig. 6. Effects of pH on diphenylamine removal ( $U=600$  V,  $V=150$  ml,  $c_0=100$  mg/L,  $t_m=30$  min).

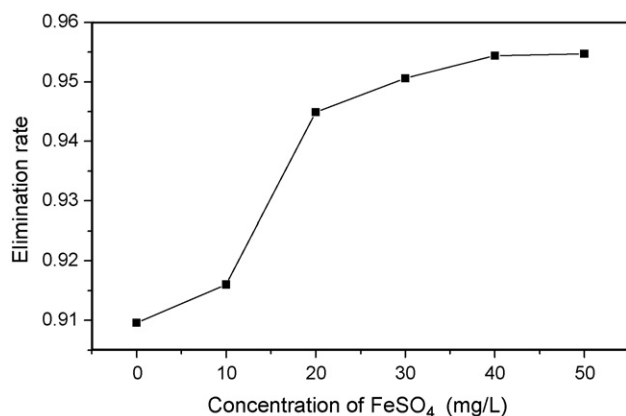


Fig. 7. Accelerated effect of  $\text{Fe}^{2+}$  ( $U=600$  V,  $V=150$  ml,  $c_0=100$  mg/L, pH 6.98,  $t_m=15$  min).

are different optimum pH range for different organic substance [16–20].

### 3.6. Accelerated effect of ferrous ions

The previous studies [9–11] showed that the predominant products were hydrogen and hydrogen peroxide in the gas-phase and the solution respectively, when CGDE was carried out on an aqueous solution without organic substances. Generally, hydrogen peroxide was not able to cause the degradation of pollutants in CGDE. Therefore, the resultant hydroxyl radical from plasma might be responsible for the oxidation of diphenylamine as well as its incompletely degraded products. This can be achieved by Fenton's reaction, therefore, some ferrous sulfate was added into the solution and results were shown in Fig. 7. Here, the initial concentration of diphenylamine was 100 mg/L, pH value was 6.98 and applied voltage was 600 V. It can be seen that  $\text{Fe}^{2+}$  has an evident catalytic effect when its concentration is more than 10 mg/L. Therefore, 10 mg/L is the optimum concentration of the catalyst under experimental conditions.

The reason is as follows:

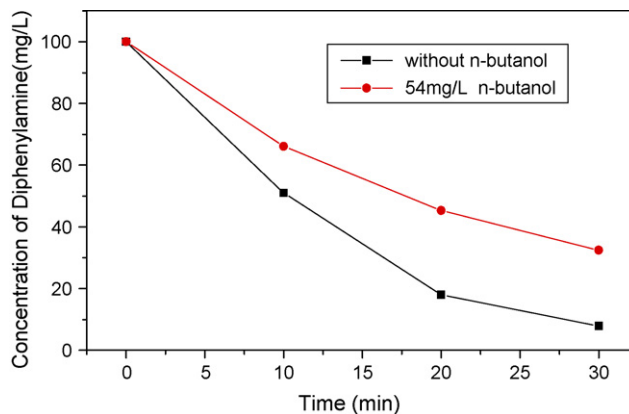
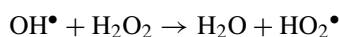
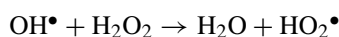
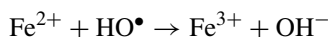
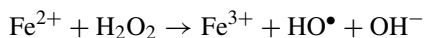
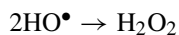
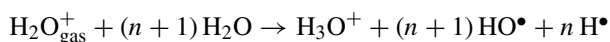
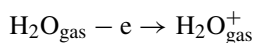


Fig. 8. Scavenging effect of *n*-butanol on diphenylamine degradation ( $U=600$  V,  $V=150$  ml,  $c_0=100$  mg/L, pH 6.98).

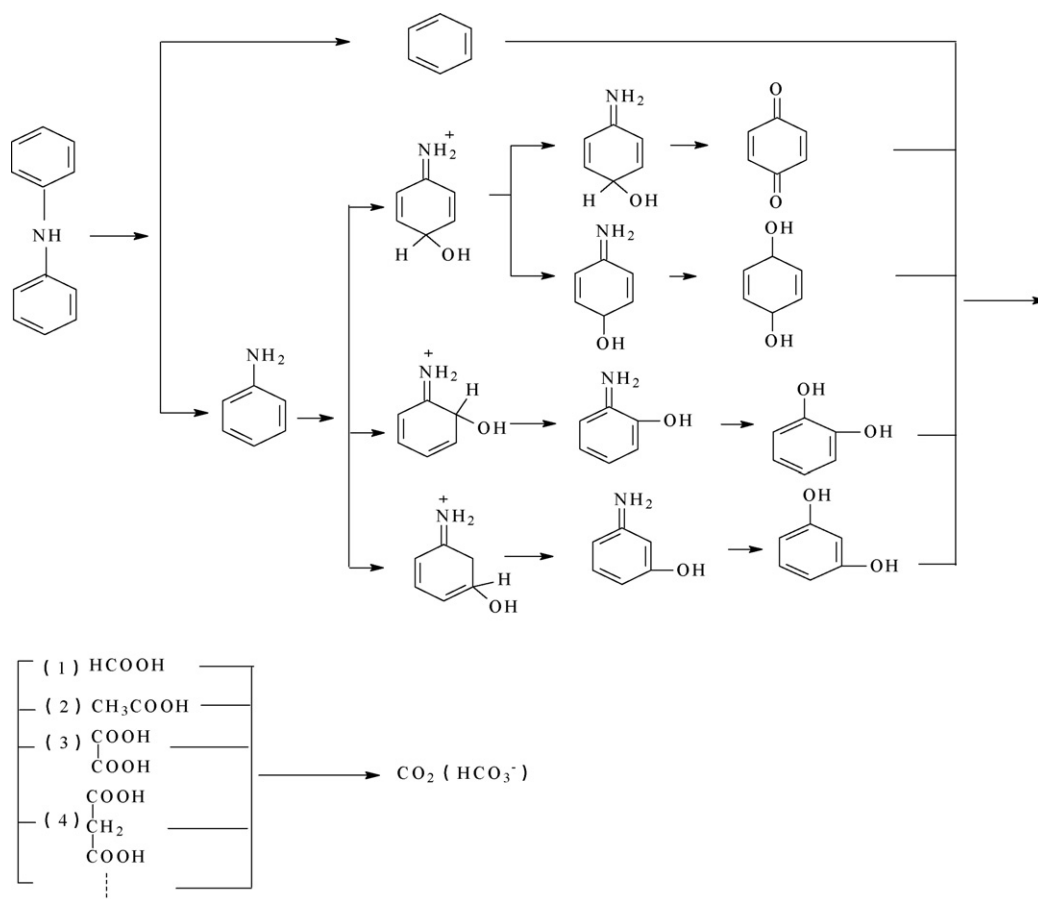
From the above reactions, it can be found that in the presence of  $\text{Fe}^{2+}$ , the  $\text{H}_2\text{O}_2$  produced by the discharge was converted to  $\text{HO}^\bullet$  again, which in turn, accelerates the degradation. In addition, it was found that the most favorable pH is 5.6 in the presence of  $\text{Fe}^{2+}$ , this maybe due to the synergistic effects of the coagulation action of  $\text{Fe}(\text{OH})_3$  produced by the induced reaction.

### 3.7. Scavenging effect of n-butanol

Generally, it is impossible that there is only one pollutant in the wastewater. Therefore, it is necessary to study the effects of other compounds existing in the aqueous diphenylamine solution. Here, *n*-butanol was chosen as a model radical scavenger to study the diphenylamine degradation behavior since it reacts with hydroxyl radical with a high rate constant ( $10^8$  L/mol/s). Fig. 8 evidently indicates that *n*-butanol has a strong inhibition of diphenylamine degradation, and this suggested that hydroxyl radical is the most responsible oxidants in degradation of diphenylamine [2,3].

### 3.8. Reaction path

In order to obtain the reaction path, a series of experiments were carried to determine the intermediates by HPLC under normal conditions, that is, without any other substance added. By the detailed analysis of the intermediate products and kinetic consideration, it was proposed that the reaction of diphenylamine with the hydroxyl radical might lead to the formation of benzene and aniline as the primary products. As the electrolysis went on, three isomeric aminophenols and hydroxylation of benzene ring were produced, and then some carboxylic acids such as formic, oxalic and malonic acids and so on were formed. The final products were inorganic carbon and inorganic nitrogen, which might exist as bicarbonate, carbon dioxide or nitrates. These results were in agreement with that of references [3–4,10,17–20]. The variation of intermediate products suggests that the degradation of diphenylamine proceeded as described below (Scheme 1).



Scheme 1. Reaction path for CGDE of diphenylamine.

#### 4. Conclusion

From the above experiments, the following conclusions can be drawn:

- (i) Diphenylamine can be exhaustively degraded by glow discharge electrolysis under water. The final products were inorganic carbon and inorganic nitrogen, which might exist as bicarbonate, carbon dioxide or nitrates.
- (ii) Initially the pH value of solution abruptly fell as the reaction processed, then increased gradually after 120 min.
- (iii) The presence of H<sub>2</sub>O<sub>2</sub> benefited the degradation in some degree.
- (iv) The optimum pH value was 6.0 for diphenylamine degradation. A innovative finding was achieved that there are different optimum pH range for different organic substance.
- (v) The degradation can be greatly accelerated in the presence of Fe<sup>2+</sup>. The optimum concentration of Fe<sup>2+</sup> is 10 mg/L.
- (vi) The degradation can be inhibited in the presence of *n*-butanol, showing that the hydroxyl radicals are the most responsible oxidants in glow discharge electrolysis under water.
- (vii) Glow discharge electrolysis was an efficient tool for diphenylamine degradation, and further study is under way.

Among these conclusions, (ii), (iii) and (iv) are main innovative findings in this experiment.

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