



Original scientific paper

Decolorization of industrial wastewater using electrochemical peroxidation process

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Abstract

In this study, decolorization of wastewater samples taken from the paper industry is investigated using an electrochemical peroxidation process. The electrochemical peroxidation process is a part of electrochemical advanced oxidation processes, which is based on the Fenton's chemical reaction, provided by the addition of external H₂O₂ into the reaction cell. In this study, iron is used as anode and graphite as cathode placed at the fixed distance of 30 mm in a glass reaction cell. The cell was filled with the solution containing wastewater and sodium chloride as the supporting electrolyte. Factors of the process such as pH, current intensity, hydrogen peroxide concentration, and time of treatment were studied. The results illustrate that all these parameters affect efficiencies of dye removal and chemical oxygen demand (COD) reduction. The maximal removal of wastewater contaminants was achieved under acid (pH 3) condition, with the applied current of 1 A and hydrogen peroxide concentration of 0.033 M. At these conditions, decolorization process efficiency reached 100 and 83 % of COD removal after 40 minutes of wastewater sample treatment. In addition, the electrical energy consumption for wastewater treatment by electrochemical peroxidation was calculated, showing an increase as the current intensity of the treatment process was increased. The obtained results suggest that the electrochemical peroxidation process can remove dye compounds and chemical oxygen demand (COD) from industrial wastewaters with high removal efficiency.

Keywords

Paper industry wastewater; electrochemical peroxidation; Fenton's reaction; decolorization efficiency; chemical oxygen demand

Introduction

Dyes are widely used in various industries such as paper, textile, leather tanning, and printing industries, causing environmental pollution, especially water pollution. Five million quintals of azo dyes are produced each year worldwide, which constitute half of the total dyes produced [1,2].

The paper industry is a type of industry that uses a lot of water and many active ingredients, including dyes [2]. Therefore, besides some active compounds, the wastewater may contain different dyes. Since dye wastewater becomes a problem for the environment, the industry is forced to carry out treatment procedure(s) that can overcome this problem [3–5]. In this context, the removal of active compounds measured as chemical oxygen demand (COD), and decolorization of wastewater, are considered crucial because many dyes and decomposition products are poisonous. Elimination of colours in wastewaters, especially industrial wastewaters, is essential because colour could severely affect the water-living system.

The electro-Fenton's processing is a part of electrochemical advanced oxidation processes (EAOPs) technology. The EAOP process itself pertains to the advanced oxidation processes (AOPs) developed mostly over the last decade by using clean, efficient, and economical processing in removing pollutants in water [6–8]. On the other hand, EAOPs form a group of emerging technologies, where pollutant removal is based on the Fenton's chemical reaction. There are two types of processing, the first one is carried out with the addition of external H_2O_2 , and the second involves internal regeneration of H_2O_2 [3]. The electrochemical peroxidation process is part of the first type, where a sacrificial iron or steel anode is used for electro-generation of Fe^{2+} ions by anodic dissolution. H_2O_2 is externally added to the treated solution to degrade organic pollutants with hydroxyl radicals ($\bullet\text{OH}$) generated by Fenton's reaction [9–11].

The electrochemical peroxidation process has a similar mechanism to electrocoagulation, but better COD removal results were obtained with the addition of H_2O_2 [12–14]. Several studies have reported that COD of coke wastewater can be removed up to 90 % by electrochemical peroxidation, whereas by electrocoagulation, up to 30 % was removed only [13].

During past decades, the electrochemical peroxidation process showed a promising perspective in treating several kinds of dyes that contaminated water, causing pollution. In this experimental study, the application of the electrochemical peroxidation process for the decolorization of paper industrial wastewater was explored. Based on previous studies that showed successful decolorization by the Fenton's oxidative processes, in the present study, the opportunity of decolorization of paper industry wastewater has been investigated using the Fenton's oxidation processing. This study will explore the effects of various operating parameters, including the initial pH of the solution, applied current strength, the dosage of H_2O_2 , and treatment time on decolorization and COD removal. Energy consumption was also studied to determine the most efficient process conditions for paper industry wastewater treatment. Positive results of this research should increase the knowledge of those responsible for wastewater treatment in the paper industry.

Experimental

Materials and chemicals

Paper wastewater samples were taken from the equalization tank effluent in the paper mill plant in Kudus, District Central Java Province, Indonesia. The physicochemical characterization of these effluents showed COD of 240 mg/L, pH 6.8 and dark yellow colour. H_2O_2 (30 %, w/w), H_2SO_4 , and

NaCl were obtained from Merck, Germany. All chemicals were of analytical grade and directly used without purification process.

The experiments were performed at room temperature, using the open single-cell glass reactor with dimensions of 12 × 10 × 12 cm (1.4 L) (Figure 1). The reactor is equipped with two vertical plate electrodes, graphite as cathode and iron plate as anode with 376.2 cm² of the total surface area (10×9×0.3 cm). Two electrodes were put at a distance of 3 cm and connected to a DC power supply (MDS PS-305DM). A magnetic stirrer was used to homogenize the electrolyte solution. Distilled water was used throughout this experiment.

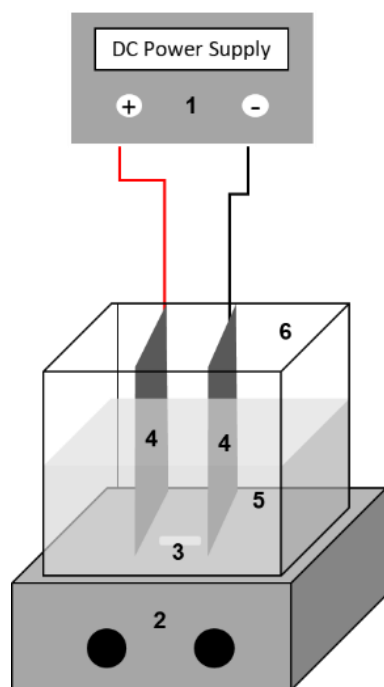


Figure 1. Glass reactor setup: DC power supply (1); magnetic stirrer (2); magnetic bar-stirrer (3); electrodes (4); solution (5)

Experimental procedures

The electrodes were cleaned before the experiment by soaking in 0.5 M H₂SO₄ solution for 15 minutes. One litre of wastewater solution was put into the reactor, together with 0.585 g of NaCl (0.01 M) as the electrolytic support, and H₂O₂ was added externally. The batch experiments were carried out in a homogeneous solution. To decrease the pH value, 0.5 M H₂SO₄ was added stepwise to reach the desired pH value. 15 ml of the treated solution were taken at regular intervals and filtered before further analysis.

A water quality meter (Trans Instruments HP9000) was used to test solution pH values. COD samples were tested using a closed reflux titrimetric method based on SNI-06-6989.2-2009 and colour tested using SNI 6989.80:2011. A double-beam UV-vis spectrophotometer (Shimadzu UV-1700, Japan) equipped with a 10 mm quartz cell was used to measure colour and COD concentration by determining absorbance at $\lambda = 450\text{--}465$ nm for colour and 600 nm for COD.

The removal efficiency was determined by the following equation:

$$Ef = \frac{C_o - C_s}{C_o} 100 \quad (1)$$

where C_o and C_s refer to initial dye concentration and dye concentration at time t , respectively. The electrical energy consumption for a liter of the solution was calculated by:

$$E = Vit \quad (2)$$

Here E is the energy consumption in J, V is the cell voltage in V, I is the current in A, and t is the reaction time in s [15].

Results and discussion

The electrochemical peroxidation is one kind of electro-Fenton's process, where the anode is used for electro-generation of Fe^{2+} ions according to:



H_2O_2 is added from outside to degrade organic pollutants with hydroxyl radicals ($\bullet\text{OH}$) created from the Fenton's reaction:



Fe^{3+} ions formed by Fenton's reaction (4) are continuously reduced at the cathode according to:



In this process, a part of Fe^{3+} ions formed by the Fenton's reaction (4) precipitates as $\text{Fe}(\text{OH})_3$ by the reaction, which depends on pH and the applied current value. These deposits can catalytically decompose H_2O_2 to O_2 but also be an alternative for the removal of organic pollutants by coagulation [9].

Effect of initial solution pH

As pointed out in previous studies, the pH of the solution is one of the significant factors affecting the electrochemical work process [16–18]. pH value determines the speciation of iron in solution, and pH 3 was found as the optimum value for dye degradation by electro-Fenton's process. In acidic conditions, iron anode dissolves as Fe^{2+} ions in water according to reaction (3), which will be the catalyst to produce $\bullet\text{OH}$ radicals with the added H_2O_2 according to reaction (4). At pH 3, iron ions (Fe^{2+}) and hydrogen peroxide will remain stable. Therefore, the Fenton's reaction can occur perfectly under this condition [20,21].

As presented in Figure 2, 100 % decolorization in acidic conditions (pH 3) was obtained after 60 min of treatment at 0.5 A, when the blue colour changed into clear watercolor. On the other hand, when pH was 6.8 (normal pH), 99 % decolorization was obtained only at the maximum electrolysis time of 120 min.

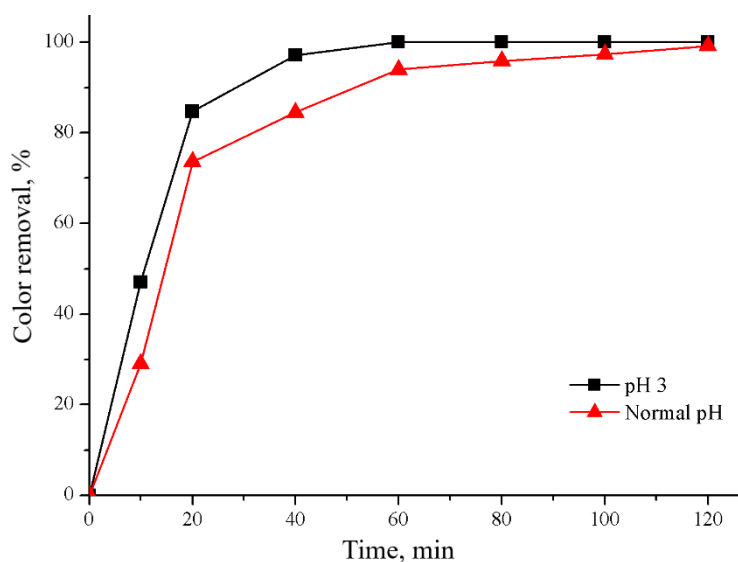


Figure 2. Decolorization efficiency vs. treatment time at 0.5 A of wastewater samples containing 0.033 M H_2O_2 and 0.01 M NaCl, at pH 3 and 6.8

COD levels were also tested at two pH values, and Figure 3 presents the results of these experiments. By acidifying the solution, COD was removed up to ~65 % in 120 min. COD removal started immediately with a decrease in COD value, reaching 100 mg/L after 20 min of treating (140 mg/L removed). After 20 min, COD removal did not increase significantly, which can be due to the pH increase of the solution to 5. Previous research on optimal electrochemical peroxidation processes in acidic conditions showed that increased solution pH significantly inhibited COD removal [18,20]. The electrochemical peroxidation process removal decreases rapidly at higher pH values, especially at pH higher than 5 [19]. An increase of pH during the electrochemical peroxidation process leads to the domination of the electrocoagulation process due to the conversion of Fe^{2+} and Fe^{3+} to $\text{Fe}(\text{OH})_n$ [21].

In acidic solutions, pH increased significantly during COD removal. As seen in Figure 3, COD removal slowed down after 20 min (pH 4.3 and removal efficiency 59 %). After 120 min, however, pH 9.21 and 62 % removal efficiency were reached. This reinforces the common statement of previous researchers that the best removal in the electrochemical peroxidation process is carried out in acidic conditions [21–23].

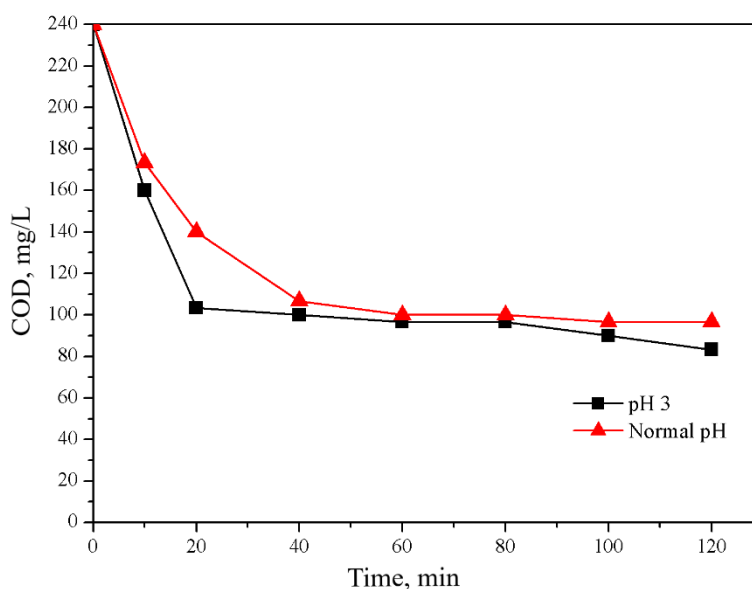


Figure 3 COD concentration vs. treatment time at 0.5 A of wastewater samples containing 0.033 M H_2O_2 and 0.01 M NaCl, at different pH

Effect of H_2O_2

As the main source of hydroxyl radicals, the initial concentration of H_2O_2 plays an important role in the electrochemical peroxidation process of oxidizing the pollutants. It has already been found that the removal efficiency increases with the increasing concentration of H_2O_2 in the solution [13,22,24–26]. As presented in Figure 4, increasing the initial concentration of H_2O_2 in wastewater solution containing 0.585 g NaCl, pH 3, improves colour removal. In the absence of H_2O_2 , where only the electrocoagulation process is operative, the rate of colour removal after 10 min was 19 %, while after the addition of 0.0165 M H_2O_2 , colour removal after 10 min increased to even 30 %. This is due to the presence of more $\text{OH}\cdot$ provided by Fenton's reaction (4) in the reactor, which oxidized more organic compounds. The further increase of H_2O_2 concentration to 0.033 M and 0.0495 M improved decolorization after 10 min to 43% and 79%, respectively. Note that for the highest concentration of 0.0495 M H_2O_2 , full depolarization is

reached within 20 min. This refinement is related to the generation of more hydroxyl radical species in the presence of increasing amounts of hydrogen peroxide [27].

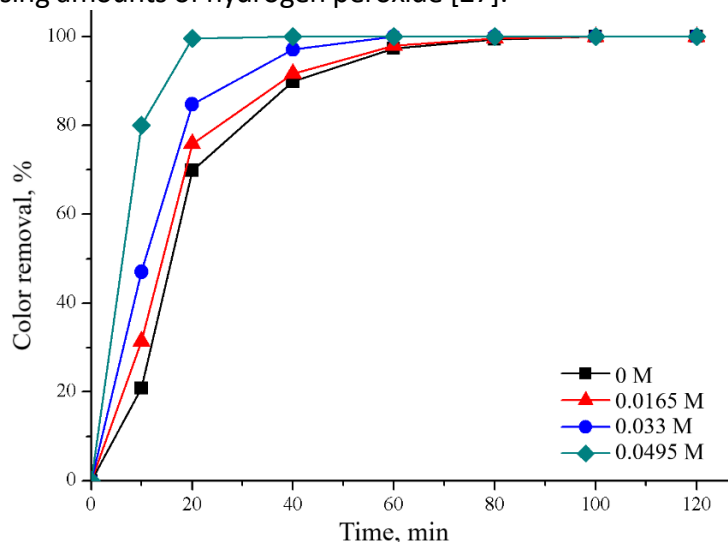


Figure 4. Decolorization efficiency vs. treatment time at 0.5 A of wastewater samples containing 0.01 M NaCl, pH=3 and different concentrations of H₂O₂

The effect of H₂O₂ concentration on COD removal was evaluated at the constant current of 0.5 A and started with the solution of pH 3. The results are presented in Figure 5, where it is seen that in the absence of H₂O₂, the rate of COD removal is 13 % since only electrocoagulation is effective in this case. It has already been revealed by previous researchers that the electrocoagulation process has not a significant effect on COD removal [28]. The mechanism of COD removal in the electrocoagulation process is going exclusively through the adsorption process by Fe(OH)₃. At H₂O₂ concentration of 0.0165 M, however, COD was reduced by 30 % in 20 min, and this is due to hydroxyl radicals produced in the electro peroxidation process caused by added H₂O₂ [9,29–31]. Figure 5 indicates that increased concentration of H₂O₂ improves COD removal since efficiencies after 20 and 120 min were increased from 29.2 to 63.9 % for 0.0165 M H₂O₂, 33.3 to 65.3 % for 0.033 M and 40.2 to 69.4 % 0.0495 M H₂O₂.

It is also seen in Figure 5 that after 20 min, COD removal increased only slightly for all samples, which is due to the increasing pH value to 5 in 20 min, and 11.2 in 120 min.

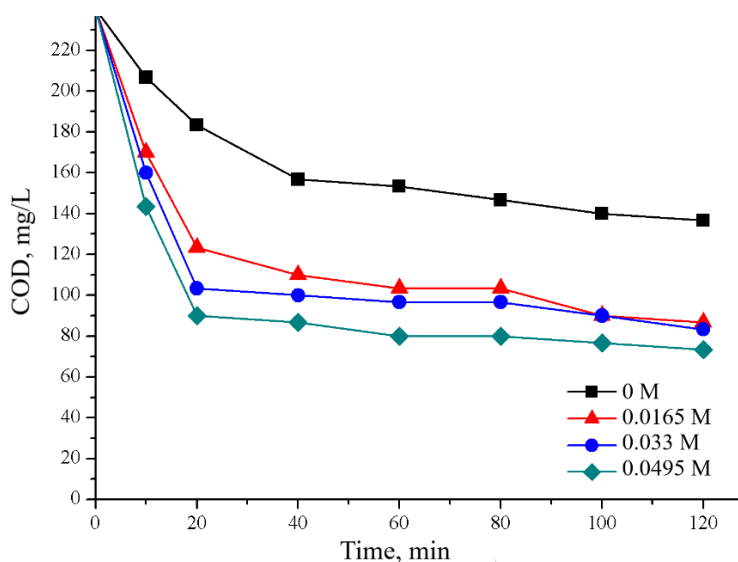


Figure 5. COD removal vs. treatment time at 0.5 A of wastewater samples containing 0.01M NaCl, pH 3, and different concentrations of H₂O₂

This suggests that uncontrolled pH conditions affect the process significantly. The performance of the electrochemical peroxidation process is optimal in acidic solutions, where generation of iron ions would occur and react by the classic Fenton's reaction, developing $\text{OH}\cdot$ as efficient oxidizers of organic compounds [9].

Effect of applied current

The effect of applied current intensity on the electrochemical peroxidation process was also tested. The influence of different applied current intensities on colour and COD degradations was evaluated in 1 L of wastewater solution with 0.05 M NaCl, pH 3 and 0.033 M H_2O_2 . The obtained results are shown in Figures 6 and 7.

Figure 6 shows that different processing results are obtained at different applied current intensities. Generally, colour removal increased with increasing current strength. At 0.3 A, the results showed 10 % decolorization after 10 minutes, while 99 % degradation was observed after 120 minutes. At higher currents of 0.75 and 1 A, respectively, the colour removals reached 79 and 90 % after 10 minutes and 100 % after 120 minutes of treatment. Better colour degradations observed at higher currents may be due to the fact that an increased amount of oxidized iron is generated from the anode at higher currents [32]. On the other side, the high current density is a trigger factor for the oxygen reduction process, which serves to regenerate hydrogen peroxide at the cathode [29,33–35]. The high currents cause an increase in the amount of $\text{OH}\cdot$ so that the degradation process is more reactive and responsive [25]. In addition to the increasing amount of $\text{OH}\cdot$ in solution, the use of high currents also causes the regeneration of iron ions, and the Fenton process's efficiency also increases [36].

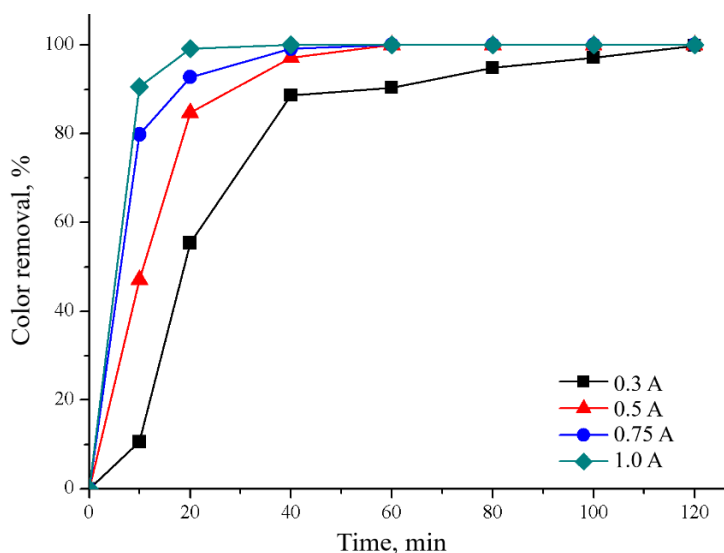


Figure 6. Decolorization efficiency vs. treatment time of wastewater samples containing 0.033 M H_2O_2 and 0.05M NaCl, pH 3 at different current intensities

Figure 7 shows that a decrease in COD concentration with treatment time was observed at all current intensities. For the highest current of 1.0 A, there is a significant reduction of COD in 40 min, leaving the lowest COD concentration of 40 mg/L with a removal ratio of 83 %. At 0.3 A, the lowest removal efficiency was obtained, where the removal ratio reached only 54 and 61% in 120 min, with the remaining COD content 110 mg/L in 40 min. When applying the current intensity of 1 A, there is a decrease in the COD removal efficiency in the treatment period of 60 to 120 min. This is probably due to the increase in the amount of Fe^{2+} ions released at the anode through the electrolysis time,

thereby reducing the efficiency electro-Fenton's process [18]. This study has similarities with previous studies [38–40], which showed that an excessive current or voltage would cause a decrease in COD removal.

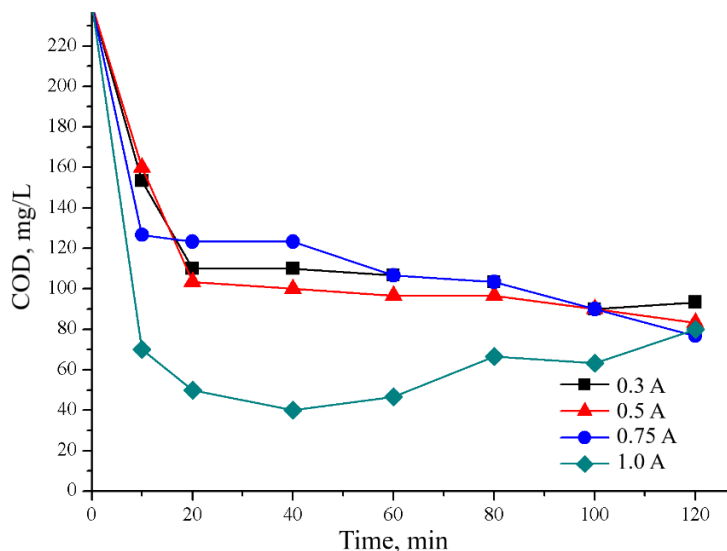


Figure 7 COD concentration vs. treatment time of wastewater samples containing 0.033 M H_2O_2 , 0.05M NaCl, pH 3 at different current intensities

On the other hand, high currents will increase energy consumption in the electrochemical process [37]. The energy consumption in the process was calculated by eq. (2), where electric voltages recorded after 120 min for current values between 0.3 and 1.0 A (Figure 7), were 7.2, 10.5, 14 and 15 V, respectively. It is obvious from these values that rising currents caused rising voltage. According to eq. (2), energy consumption was calculated to be 15.6, 37.8, 75.6 and 108 kJ. The linear correlation between current, voltage, and energy consumption has already been investigated, giving similar results [15].

Conclusions

In this study, a detailed exploration of the electrochemical peroxidation treatment of paper industrial wastewater is described. It was found that process factors such as pH, applied current, and concentration of added H_2O_2 significantly affect decolorization efficiency and COD removal from the paper wastewater solution. The following conclusions can be derived from the present study:

- The electrochemical peroxidation process is facilitated in an acid condition.
- Colour and COD removal continuously increased as H_2O_2 was added to the process up to the concentration of 0.0495 M.
- The current intensity influences colour and COD degradation in the electrochemical peroxidation process, where clear water was obtained for the current of 1 A in 20 min of treatment.
- The electrochemical peroxidation process can be used as an efficient operational process to remove colour and COD from paper industrial wastewater.

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