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Photocatalytic Degradation of Paraquat Dichloride using TiO_2-Fe Nano Powder under Visible and Sunlight Irradiation

Linda J Kusumawardani*, Yulian Syahputri, Ani Iryani

Departement of Chemistry, Faculty of Mathematics and Natural Science, Universitas Pakuan,
PO BOX 452, Bogor, 16143, Indonesia

**Corresponding author: linda.wardani@unpak.ac.id*

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Abstract

Paraquat dichloride, is an active herbicide with the chemical formula $[(C_6H_7N_2)]Cl_2$, and in the last decade became the most widely used agricultural pesticide in Indonesia. It has important role in oil palm plantations but recently appeared many problems and caused environmental pollution. In this research, photodegradation of paraquat herbicide using TiO_2-Fe nano powder was investigated. The TiO_2-Fe catalyst was prepared by the sol-gel method and characterized using XRD and DRS. The characterization results showed that Fe as a dopant on TiO_2 produced a small crystal size. This condition can increase the performance of photocatalysis from the area of UV to visible light. Degradation of paraquat dichloride is carried out under visible and sunlight irradiation to significantly increase photocatalytic activity. Decreasing of paraquat content was observed for each 15 minutes and measured by spectrophotometer UV-Vis. The addition of 0.5 gram of TiO_2-Fe catalyst to 50 mL of sample solution increased the degradation percent by 98.4% for 75 minutes with a concentration of Fe^{3+} 10% (w/w). These results indicate that the presence of Fe dopants on TiO_2 can increase the photocatalytic activity of nano TiO_2 particles from UV light to visible light.

Keywords: TiO_2-Fe, paraquat dichloride, sol-gel, photocatalytic

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1. INTRODUCTION

Paraquat dichloride is a very toxic herbicide, but is widely used in more than 120 countries in the world, and is used in more than 50 factories. In Indonesia, Paraquat, also known as Gramoxone was distributed by Sygenta Coorporate, but several manufacturers sell under different names. Paraquat dichloride compounds cause severe health problems for humans, such as the causes of Parkinson's disease and kidney dysfunction (Arfi *et al.*, 2018). In addition, the formulation and transportation of this herbicide can cause high risks to the aquatic environment. Paraquat classified as a potential groundwater contaminant by the environmental protection agency (EPA) (Desipio *et al.*, 2018). How it works paraquat dichloride by disrupting the process of photosynthesis through increasing the intensity of light and moisture on the leaf surface. Therefore, the degradation or removal of paraquat dichloride from ground water is a very important problem to be studied. Adsorption using activated carbon and purification by degrading chemical compounds are some of the methods used to reduce the removal of paraquat dichloride (Hamadi *et al.*, 2004). Another method used for the degradation of organic pollutants in water is to use heterogeneous catalysts that have the ability to degrade various organic pollutants by producing hydroxyl radicals which are strong oxidizing agents with high oxidative power (Badli *et al.*, 2017). Titanium dioxide (TiO_2) is an effective catalyst used to degrade toxic organic compounds. TiO_2 nanotubes under UV radiation for wastewater treatment have been the focus of research, several studies conducted with the use of visible light irradiation and doped TiO_2 catalysts (Marien *et al.*, 2016). Because of its ability to oxidize large amounts of harmful organic pollutants into non-toxic products, TiO_2 has been promoted as a potential photocatalyst that can

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be used for the degradation of paraquat dichloride. TiO_2 as a semiconductor compound works at the wavelength of UV radiation to activate photocatalysts. Titanium dioxide (TiO_2) has a relatively moderate to low band gap energy between the valence and conduction bands. (Jlenia *et al.*, 2007) carried out paraquat photodegradation using polycrystalline TiO_2 with 0.4 gram photocatalyst per liter of solution after 3 hours of UV irradiation. Other studies using TiO_2 nanotube catalysts under UV radiation for water purification, then several studies report photodegradation by visible light irradiation using doped TiO_2 (Marien *et al.*, 2016).

Sorolla, *et al* (2012), studied copper (Cu) which is used as a metal dopant to shift photocatalytic activity toward the visible light range. It has been reported that paraquat degradation reached 55% using two (% wt) Cu-TiO_2 / SBA-15 after 4 hours of irradiation, and a 67% reduction in paraquat using five (wt.%) Cu-TiO_2 / SBA-15 (Sorolla *et al.*, 2012). Iron (III) is also a promising transition metal ion to be used as a dopant, because the ionic radius is almost the same as Ti, where the Fe radius is 0.64Å and Ti is 0.745 Å (Sood *et al.*, 2015). Ion Fe can be easily combined with TiO_2 crystal lattice, using the sol-gel method. Kusumawardani and Syahputri (2019), reported that the structural and optical properties of Fe-TiO_2 differ from the addition of 10% Fe^{3+} in the photocatalytic process under visible light. While TiO_2 nanotubes under UV radiation has been a major research focus lately, some work used visible light irradiation and doped TiO_2 catalysts for water purification (Nasralla *et al.*, 2013) .

In this study, the synthesis of TiO_2-Fe nanopowder catalyst was carried out using the sol-gel method. Paraquat degradation was observed by additional 1% (w/v) or 0.5 gram of TiO_2-Fe to 50 mL of sample solution under visible and sunlight. A decrease in paraquat levels was observed every 15 minutes and measured with a UV-Vis spectrophotometer. From previous studies, with the amount of Fe^{3+} dopant by 10% (w/w), reducing the anatase grain size, and increasing the specific surface area of TiO_2 powder (Kusumawardani and Syahputri, 2019).

2. MATERIALS AND METHODS

Materials

Materials which used are Titanium (IV) Isopropoxide (TTIP) 97 %, $FeCl_3$ as iron starter reagent grade purchased from Sigma Aldrich (Hreniak *et al.*, 2015) and Ethanol 96% from Merck, Aquadest, Paraquat dichloride hydrate from Merck, Gramoxone from Syngenta, UV Lamps (Philips, 10 watt) and Halogen Lamps (Philips, 1000 watt) as a visible light source. XRD, DRS used for characterization materials, while UV-Vis spectrophotometer for determining the amount of paraquat dichloride successfully degraded.

Prosedure

The TiO_2-Fe catalyst was prepared by the sol-gel method, as reported by our previous research (Kusumawardani and Syahputri, 2019). Photocatalytic degradation was carried

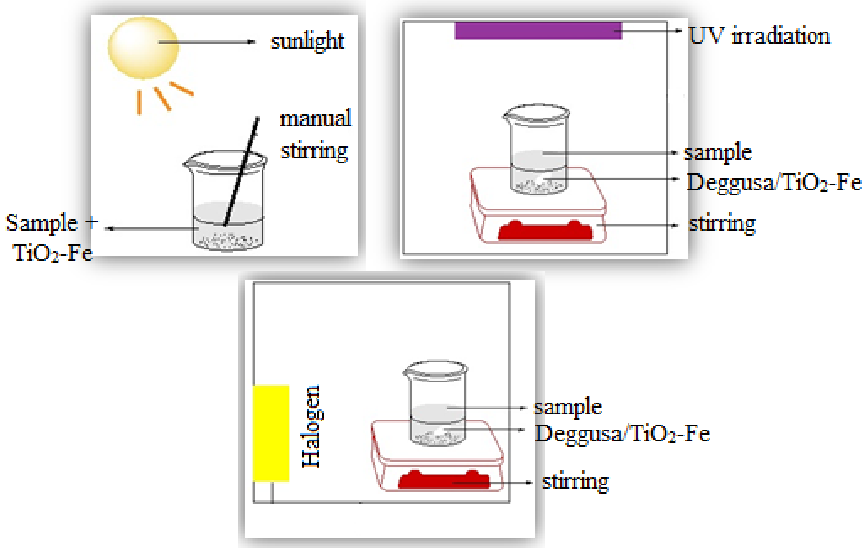


Figure 1. Reactor model for photocatalytic degradation processes, under the sun (A); UV-light (B); halogen light irradiation (C)

out by adding 0.5 gram of TiO_2-Fe nano powder to 50 mL of the sample solution with a concentration of 30 ppm paraquat dichloride. The light sources used are UV lamps, halogen lamps and sunlight. The reaction vessel is equipped with magnetic stirring. A decrease in the amount of paraquat was observed at 15; 30; 45; 60 and 75 minutes. Figure 1. shows a photocatalytic degradation reactor model. The absorbance of each solution was measured with a UV-Vis spectrophotometer at λ_{max} 290 nm. Preparation of a standard solution of paraquat dichloride was carried out at a concentration of 0 mg/L; 5 mg/L; 10 mg/L; 15 mg/ L; 20 mg/L; 25 mg/L and 30 mg/L as much as 100 mL. The percentage of photocatalytic activity was calculated using Eq. (1), where % D is the percentage of degradation, Co is the initial concentration of the sample before the UV irradiation, visible light or sunlight, and Ct is the final concentration after UV irradiation, visible light or sunlight (t-minutes).

$$\%D = \frac{Co - C_t}{C_o} x\, 100 \qquad (1)$$

3. RESULTS AND DISCUSSION

Material Characteristic

First, reconfirming the character of TiO_2-Fe(III) powder, by measuring bandgap energy and spectrum from FTIR analysis. Analysis of band gap energy with UV-Vis diffuse reflectance spectra (DRS) is shown in Figure 5. Absorption of TiO_2 that is not doped in visible light is not significant, while TiO_2 which has been doped Fe shows increased adsorption. F (R) is the Kubelka-Munk function, R is the ratio of radiation intensity reflected diffusely from known samples and samples, K is the radiation absorption coefficient and S is the DRS scattering factor which shows that Fe doping in TiO_2 has a band gap energy decreasing from 3.2 to 2.3 eV. This value indicates the midgap level in the band gap originating from the 3d electron from Fe^{3+}. The absorption wavelength value shifts from the UV range to the visible light range as a result of Fe doping which indicates the possibility of sunlight activity. These results are in accordance with the references (Sun *et al.*, 2009).

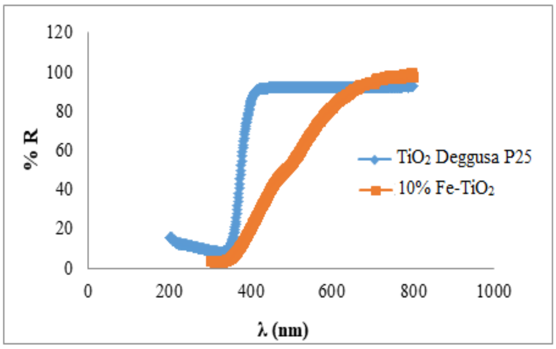


Figure 2. Diffuse reflectance spectra of TiO_2 Degussa P25 and TiO_2-Fe.

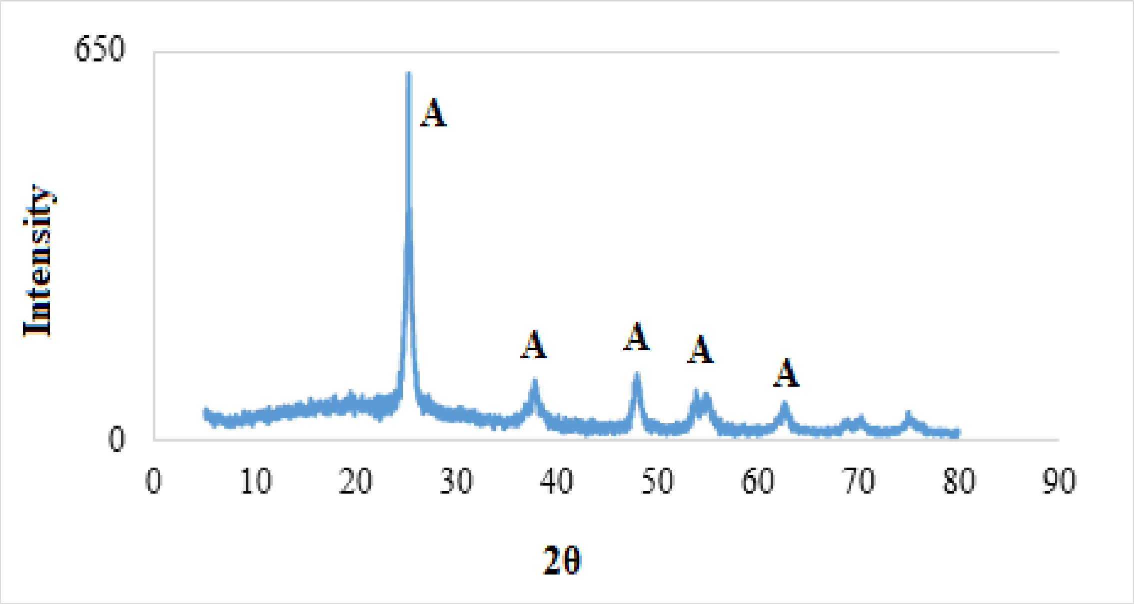


Figure 3. XRD Patterns of TiO_2-Fe Nanoparticle

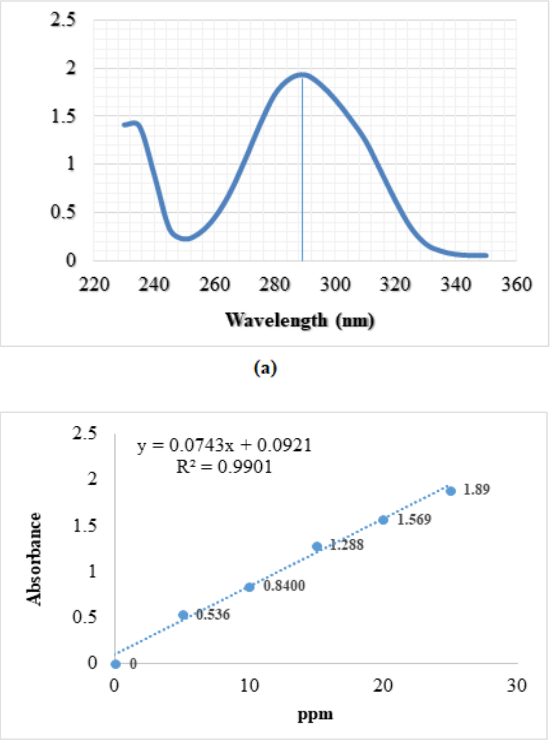
The XRD pattern of the TiO_2-Fe samples is shown in Fig. 3. XRD spectra of the catalysts only show the characteristic peaks of TiO_2 in anatase (2θ = 25º), representing the (101) crystal plane without any characteristic peaks of Fe_2O_3. In addition, the Bragg diffraction peaks were observed at 38.0, 48.1, 54.0, 55.1, 62.1, 68.8, 70.2 and 75.1° corresponding to (004), (200), (105),(211), (204), (116), (220) and (215) crystal planes of anatase according to reference (Koliyat *et al.*, 2013). It explains the anatase phase is stable at smaller grain sizes. The crystal size of catalyst TiO_2-Fe is 68 nm calculated by Scherer's formula.

Photodegradation of Paraquat Dichloride

Before starting the photocatalytic degradation process, the wavelength and absorbance of the paraquat dichloride material are measured to find the maximum wavelength. This method is carried out using a 30 ppm paraquat dichloride solution measured by a UV-Vis spectrophotometer with scanning from 230 nm to 350 nm, and the results can be seen from Fig.4a. Wavelength 290 nm is the highest peak absorption compared to other wavelengths, so the maximum wavelength for paraquat dichloride lies at 290 nm. The determination of the maximum wavelength is used to measure the sample after the photodegradation process.

The standard curve made by measuring the series of standard solutions of paraquat dichloride with a concentration of 0 ppm, 5 ppm, 10 ppm, 15 ppm, 20 ppm, and 25 ppm. The calibration curve of paraquat in Fig.4b showed the regression 0.9901 with the equation of $y = 0.0743x + 0.0921$. This equation was used to determine concentration of paraquat dichloride after t-minutes.

The result of the study shows that there was significant effect of sunlight irradiation time with photodegradation of paraquat. The longer exposure time will degrade more paraquat compounds. Figure 5 shows the percent degradation of paraquat dichloride increased in 15 minutes to 45 minutes. At 45- and 60-minute times, paraquat level tend to stable because of saturation of bound electrons (e^-) and holes (h^+) produced at each degradation time. Stirring can also be influential because by mixing TiO_2-Fe particles will be spread more evenly on the entire surface of the solution so that the interaction between the surface charge of TiO_2-Fe with paraquat dichloride is very perfect, and in a shorter time a higher percentage of degradation can be obtained.



(a)

(b)

Figure 4. Paraquat absorption spectrum (a), calibration curve of paraquat standard (b).

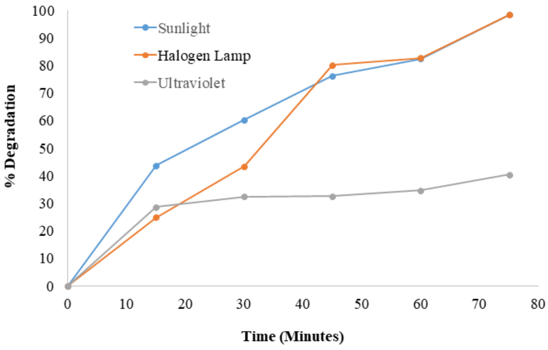


Figure 5. The effect of time toward paraquat dichloride percentage degradation

Figure 5 shows that degradation product with visible and sunlight irradiation for 75 minutes has been degraded by 98.4% from 30 ppm to 0.470 – 0.483 ppm, while uv light only 40.4% from 30 ppm to 17.9 ppm. This is proved that the presence of Fe dopant in TiO_2 can increase photocatalytic activity at visible light. Thus, the photon energy generates stronger oxidizing agent, •OH radical, which will assist in paraquat compounds degradation. A simple scheme is reported in Figure 6 to represent the complete mineralization of paraquat dichloride (Jlenia *et al.,* 2007).

This result shows paraquat degradation using sunlight irradiation is lower than halogen. During the photodegradation process, sunlight intensity gives a different paraquat reduction level due to the amount of •OH radical. The amount of sunlight received play a major role in photodegradation process. It will be attributed by the season, geographical location, and the presence of clouds. In addition, this study was conducted in Bogor, Indonesia on February to March. Bogor's wet season falls between November to March, when rainfall occurs at afternoon or in the early morning. The study was conducted at late morning 10.30 to 11.45 am. However, in some unsuitable climate cases, an acceptable photocatalytic activity could be achieved. This study also investigated triplicate experiments for the sample under sunlight exposure. It is obvious that in clear sky through high intensity sunlight irradiation, photocatalytic degradation of paraquat dichloride was increased. The photocatalytic degradation could be observed also in cloudy sky. Table 1 shows the optimum percentage of paraquat degradation (%D) at (98.85 ± 0.36) %. The results show that 0.5 gram of TiO_2-Fe is sufficient to degrade 50 mL of paraquat dichloride under sunlight. The results also show that the duration of irradiation can increase the usefulness of the degrading waste, the longer the irradiation time, the more the composition of the degraded paraquat. During the irradiation time, the adsorption and desorption process will run continuously until it reaches the optimal condition where the adsorption and desorption occur equilibrium so that degradation increases by almost 100%. This result shows the acceptable formula of TiO_2-Fe Solution and this utilized photo reactor.

The proposed photocatalytic mechanism can be illustrated as in Figure 7. When light on the TiO_2 surface is doped with Fe^{3+} ions, photogeneration of ions (e^-) and holes (h^+) is generated. The Fe^{3+} ions present in TiO_2 can act as electron and hole traps resulting in the formation of Fe^{2+} and Fe^{4+} ions, which are less stable compared to Fe^{3+} ions (because the d5 configuration is half filled with a stable configuration). Therefore, trapped charges can be easily released again to form stable Fe^{3+} ions. This results in the generation of OH radicals and O_2 anions. However, if the Fe concentration is high, it can act as a recombination center for charge carriers thereby reducing photocatalytic activity. Through a series of redox reactions, a number of charged and radical species with high redox potential are produced. These highly oxidizing species subsequently oxidize organic molecules (P) and cause the formation of intermediates (S) and finally complete mineralization occurs. The maximum degradation of paraquat level is 94% in 75 minutes by adding TiO_2-Fe nano powder 1% (w/v) without addition of any oxidizing agents. This work is a promising and easy work in environmental water treatment from toxic molecule such as paraquat dichloride.

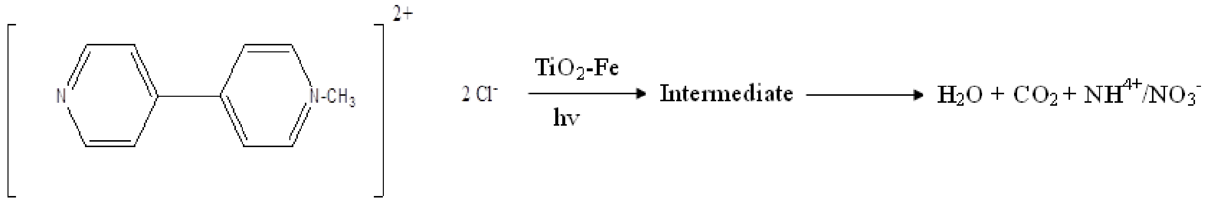


Figure 6. Mineralization of paraquat dichloride (Jlenia et al., 2007)

Table 1. Standard deviation of triplicate sample under sunlight (amount of TiO_2-Fe: 0.5 g; sample volume: 50 ml)

Replicate Experiments	Co (ppm)	t (minutes)	Ct (ppm)	% D
1	30	75	0.279	99.07
2	30	75	0.469	98.43
3	30	75	0.283	99.05
Average				98.85
Standard Deviation (SD)				0.36

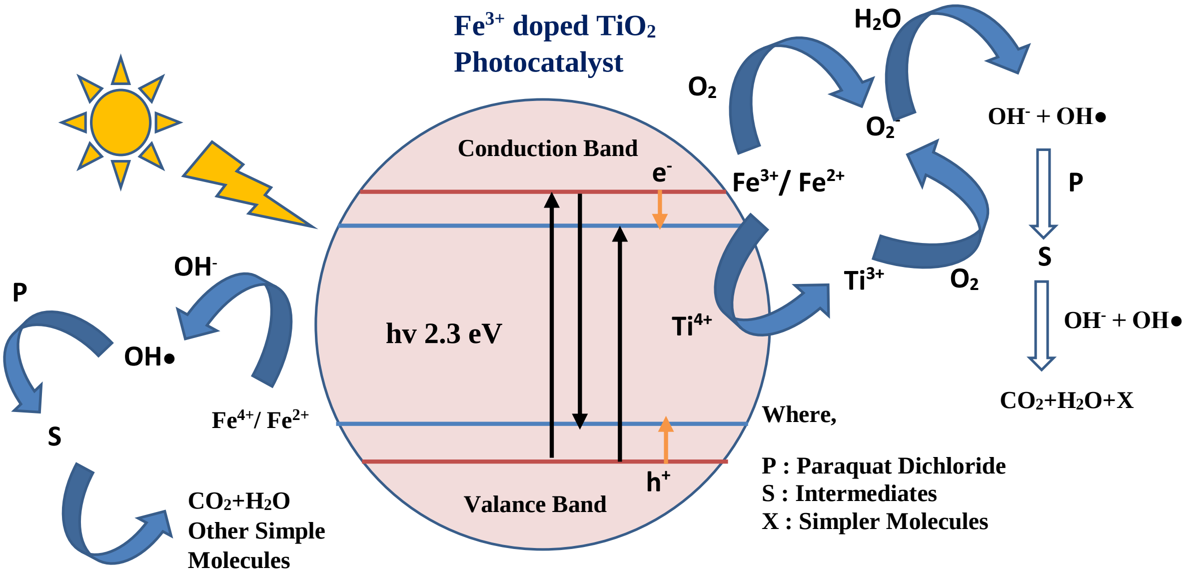


Figure 7. Schematic illustration of the energy diagram for a Fe-TiO_2 system

4. CONCLUSION

The summary of the results of the paraquat dichloride photodegradation test under visible and sunlight irradiation reached 98.4% for 75 minutes by additional 1% (w/v) TiO_2-Fe Solution. Paraquat level significantly decrease from 30 to 0.470-0.483 ppm, while UV light only 40.4% from 30 ppm to 17.9 ppm. Even this study was conducted in wet season, the photocatalytic activity could be achieved. This result shows the acceptable utilized photo reactor and formula of TiO_2-Fe solution. Also a promising and easy work in environmental water treatment from toxic molecule such as paraquat dichloride.

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