Design a photocatalytic reactor to remove chlorpyrifos from industrial wastewater.

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ABSTRACT

Chlorpyrifos is widely used as insecticide in agricultural crops and it is classified as an emerging contaminant (endocrine disruptor), highly toxic. However, trace quantities are found in water sources, suggesting that chlorpyrifos remains on the ground and reaches the water reservoirs. Currently, heterogeneous photocatalytic oxidation using titanium dioxide as catalyst has been proposed as a promissory technology to remove chlorpyrifos from industrial wastewater. In this work, a continuous photoreactor design was proposed to decrease chlorpyrifos concentration in wastewaters from a chlorpyrifos production factory. To develop the design, kinetic data of photocatalytic chlorpyrifos oxidation were taken from available literature using a first-order equation, calculating a reaction rate constant of 0.005 L/mg h. For an estimated flowrate of 0.4 L/s with an initial concentration of chlorpyrifos of 400 µg/L, the designed photoreactor has a volume of 9,3 m^3, and UV lamps amount of 198 units, obtaining a total power of 1984 kW. The reactor dimensions are 2,2 m x 2,7 m. With the designed reactor, chlorpyrifos removal was calculated in 0,1 ppm in order to comply with Colombian environmental regulations. Total cost of the photo reactor was estimated in $ 80.000 US, which includes costs of manufacturing material, agitation system and flow regulators. The results show that the reactor is capable to oxidize chlorpyrifos at desirable levels. However, its estimated dimensions are still too large and for this reason, additional treatments can be necessary.

KEY WORDS

Chlorpyrifos, photo-reactor, industrial wastewater, endocrine disruptor, heterogeneous photocatalytic oxidation.

INTRODUCTION

Agriculture is considered to be one of the most important sectors for the development and generation of employment in the country, however, this has led to problems of environmental and public health in recent years, due to the high consumption of agrochemicals and the inadequate provision of containers of these substances (FAO, 2014). By the year 2015, a study of the National University of Colombia, revealed that in the last two decades, rose by 360% the use of these compounds, in addition, these substances poisoning ranks second of all emergencies that occur in Colombia (Praguer, 2013).

Agro-industrial level reported waste effluents with high concentrations of toxic substances such as organophosphorous compounds, which includes Chlorpyrifos, (Morales & Rodriguez, 2004), which is not removed in traditional treatment processes, or alternative such as artificial wetlands and (Agudelo, Peñuela, & Jaramillo,) 2010 electro oxidation and therefore fails to meet the requirements of the current regulations.

Chlorpyrifos (C9H11Cl3NO3PS), is considered as a substance capable of altering the central nervous system, causing convulsions, difficulty to speak and move, in addition, in the case of acute poisoning can cause death. To be an emerging contaminant, the conventional technologies used (PTAR) sewage treatment plants are not enough to carry out effective removal, in such a way that it is necessary for the adaptation and implementation of new treatments (Garcés, Mejía, & Santamaría, 2004).

Currently, the photocatalytic processes have become an efficient alternative for cleansing and purification of water, with great acceptance; Since presenting not only efficiency in removal of substances whose degradation is complex, but also their low costs that are comparable to the latest technologies such as reverse osmosis or DAF (dissolved air flotation).

The photocatalytic degradation of these compounds can be through the use of photoreactors, using TiO2 as a catalyst and UV radiation as a source of photons required to promote redox reactions. The effectiveness of this technique lies in the formation of hydroxyl radicals, product of the Government, and the oxidizing effect on polluting compounds to treat. One of the advantages of this treatment is the degrading action in which are generated in the reaction intermediate, forming harmless products that do not represent a danger to the environment or the health of humans (white, both the initial compounds Rodriguez, fire blight, & Cardona, 2007).
Most research on the modeling of photoreactors have approached projections at low level (experimental use), which mainly seek to model already conditions to be real and determine optimal operation conditions or the development of models to analyze the problem of different geometries of reactor irradiation, thus optimizing energy system efficiency. The purpose of this paper is to explore the feasibility and efficiency of removal and removal of chlorpyrifos in aqueous solution by UV process / TiO2-H2O2 in continuous reactors and to develop an equation of the design that scale up to the industrial level the degradative process this type of pollutants in wastewater effluents.

METHODOLOGY

Initially designed reactor (CSTR) continuous flow study, where the total volume of the tank is set and determines the amount of UV-C lamps necessary to activate the titanium dioxide (TiO2) and thus form the oxidizing species (OH-) necessary for the mineralization of the contaminant chlorpyrifos.

Subsequently, the determination of the type of Shaker and characteristics of mixing system chosen for the CSTR reactor, which will be used for the efficient homogenization, which will also prevent the formation of vortices or the existence of volumes was carried out dead. The calculations also includes the determination of hydrodynamic design and weight of load of the system, including accessories and volume of effluent.

For agitation system was convenient to use a Shaker type turbine impeller, which conforms to the specific viscosity range (< 2500 cps) for homogenization of the catalizador-fluido suspension. In addition, managed to establish an optimum range of turmoil between 45 rpm to 70 rpm to maintain the mix conditions specified in the methodology (table 3-4) and ensure that there are no managed affectations to the reaction speed in the development experimental.

Finally, was the cost of the reactor, including the variables of greatest relevance for the operation. For the cost of the agitator is estimated according to the commercial references taking into account the volume of mixture and maximum rpms of operation and for the cost of the lamps was taken under the references of companies according to the available commercial power.

MATERIALS AND METHODS

were adopted an approach of three consecutive levels for the design of the reactor, which includes:

1. Obtaining and setting of experimental data and operating conditions. The experimental data were obtained according to recent scientific publications, about the process of photocatalytic of chlorpyrifos in water, these data are reported by Kumari Dev and John Siby (Singh, Kumari, & Siby, 2017), where with the implementation the image analysis Software XY_data, experimental under these conditions of design data were initial extracted:concentracion of chlorpyrifos, determined by studies carried out in the South East of the Tolima region (CORTOLIMA, 2016) and discharges from companies such as Agroz, where three water sources that are discussed in an important area of agricultural influence, with concentrations of chlorpyrifos of 390.9 µg/L (Morales, Garcia, Quintero, Diaz, & Contreras, 2012).

   - Final concentration or expected, set in accordance with Colombian legislation, which sets the resolution 631 2015, chapter IV, the value of maximum allowable limit in discharges of active ingredients in pesticides of Toxicologic category II as 0.10 mg/L, (Ministry of environment and sustainable development, 2015).
   - Flow of treatment, adopted based on volumetric characteristics of effluents of manufacturing industries of pesticides or toxic chemicals, this is on average of 0.4 l/s (Dow Chemical, 2016) 0.04 l/s (Paipa & Santos, 2014)

Reaction conditions denoting in the Table1.

Table1. Optimum reaction parameters used for the degradation of chlorpyrifos in water

PARAMETER	OPTIMAL VALUE
[TiO2]	100 mg/L
T	20ºC
pH	Acid
Supply O2	H2O2
Time of Treatment	3 h
Power	UV-C/60W

   - The density and viscosity whose values are 1001 Kg/m3 and 0.39 Pa.s respectively, were determined experimentally using the method of the pycnometer and field respectively.

2. Design and scale-up of the Reactor

   The reactor design is based on the physic-chemical characteristics (rheological in bedding and kinetic conditions), geometric configuration and type of reactor for the scalation process, which in this case is selected the CSTR catalytic fluidized bed; the reactor was designed based on the ASME technical standard for both the body and the agitation system, respecting the conditions of kinetic, as well as take into account the UV lamps configuration supported by the design of heat exchangers. Subsequently defined under conditions of operation, the selection of material and power.

3. **Costs and recommendations:**

Once established the design of the reactor, establishing the costs required for their correct implementation underway and functionality, establish recommendations on design criteria that should be considered at the time of its construction, as previous analyses of ground for the design of the structure of support and other attachments necessary to ensure that the conditions previously described are working normally

Results

Speed of reaction and determination of the required conversion.

The basic information that allows to design a photocatalytic reactor is an analytical expression of the specific reaction rate. With tight experimental data was adopted the model Langmuir-Hinshelwood which leads to a [1] first-order kinetics to medium and low concentration with an additional effect since it incorporates the concentration of catalyst and assumed contribution of oxygen constant at controlled pH.

$$\frac{Vcat}{Wcat}\frac{dCa}{dt} = \frac{k[Ca]}{1+kK[Ca]} = k[Ca] \qquad \textbf{[1]}$$

Design of the reactor

Reactor was designed based on the design of CSTR catalytic reactors [2-3], equation for an inflow of 1.95 mmol/h and capacity of the system of 9.3 m3, considering that to stir the mixture level is increased due to , catalyst, to the form a catalytic bed is must ensure that does not spill out and be complete homogenization. Figure 1 shows schematically the geometric dimension of the photocatalytic reactor which is dimensioned in 2.2 m by 2.7 m, with volumetric capacity of 13.2 m3. The reactor was designed to ensure a 74% conversion, complying with the normative limit Colombian.

$$W = \frac{Fao*(X)}{-ra'} \qquad \textbf{[2]}$$

$$V' = \frac{W}{Ccat} \qquad \textbf{[3]}$$

Irradiation

Suitable irradiation and chemical conversion are the main variables that make the catalyst to improve the performance of the process. The distribution of light does not depend on the degree of reaction, but direct against the catalyst implications, since its proper distribution and intensity regulates homogeneous activation of it, managing to affect the rate of reaction. The number of lamps required scaling, is determined based on the experimental development (Singh, Kumari, & Siby, 2017), which establishes a requirement of 198 lamps with a power of 10kW each one.[4]

$$P' = \frac{V\prime x60}{2.0x10^{-4}x1.0x10^{4}} \qquad \textbf{[4]}$$

Sizing of the Reactor

The sizing of the reactor was conducted based on the standards ASME (American Society of Mechanical Engineers), UG-26 sections 32 UG, establish the calculation of operating conditions such as pressure and temperature design, volume of operation and formation of the body of the reactor (body diameters and heads) (see table 2). Design pressure and temperature are taken in extreme scenarios by which ensures the design to keep their working conditions in wide ranges which is designed. He is set according to the properties of the bedding, the type of material of the system, which under the UG-4-15, according to the conditions of low corrosion and pressure below 20 bar 304 stainless steel is the most suitable for the design.

Table 2. Sizing and structural design of Reactor of complete mixing (CSTR) for the degradation of chlorpyrifos in water

TYPE OF MATERIAL (UG-4-15) **Stainless Steel 304**			
Symbol	***diameter***	***Value***	***Units***
V_{TQ}	Tank volume	9.6	(m^3)
D_{INT-TQ}	Internal diameter of the tank	2.76	m
H_{CIL}	Tank height	1.6	m
P_{DESIGN}	Pressure of Design	2.14	bar
T_{DESIGN}	Desing temperature	40	°C
t_{cab}	Thickness of Compresses	3	mm
D_{extcab}	External diameter of Compress	2775	mm
t_c	Thickness of the Cylinder	3	mm
D_{extc}	External diameter of the cylinder	2800	mm
TH	Height of the compress	0.546≈0.55	m
$H_{TQTOTAL}$	Total height of the tank	2.15	m

Design of agitation system selects a type stirrer turbine, because it is suitable for a regime of mixing of fluids with a viscosity less than 2500 cps, so allow a good homogenization of fluid (Verdugo, 2013) configuration dimensional reactor was developed based on the methodology proposed by McCabe and Kern (McCabe, 2007); the first for the calculation of geometric and spatial relations of the reactor as shown in figure 2 and table 3, the Kern methodology is used to give geometrical distribution of design and the proper configuration of the UV lamps. The arrangement of pipes or structural provision presenting greater efficiency in the process of heat transfer is the square system shown in Figure 2.1 and 2.2, supported by a plate in stainless steel whose size is 2.76. x 0. 2m, where the spacing between lamp is 1.25 (pitch) times the diameter of the Plate.

Table 3 . Dimensional relations of the reactor to a given volume

Symbol	*Topic*	*Value*	*Units*
Dt	Total diameter of the tank	2.76	m
Da	Diameter of the agitator	0.92	m
E	Height bases head - Agitator	0.92	m
J	Broad baffles	0.23	m
w	Width of blade	0.18	m
L	Length of arms of agitation	0.23	m

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The agitator design is based on the available diameter under the geometric configuration of the reactor and the intensity of agitation, which is a function of the density and viscosity of the fluid. Initially the cash flow calculation, should be performed using the equation [5] and the number of revolutions per minute of the agitator, which shall be determined by the equation [6-7], and will include average speed (Vb) required for reactions of homogenized, it's 0.11-0.15 m/s.

$$Qe = A * Vb \quad [5]$$

$$N = \frac{Qe}{D_a^3 * N_Q} \quad [6]$$

$$N_Q = \frac{Da}{Dt} \quad [7]$$

Subsequently the power required is 5.88 kW, value obtained by applying equation [8], which related the impeller power defined in turbulent flow Reynolds number or critic, which integrates a power (Np) factor and the characteristics of the agitator selected. (Treybal, 1995). Other design criteria are presented in table 4.

$$Po = \rho * N^3 * Dt^5 * Np \quad [8]$$

For the process are determined the possible ranges that can be immersed in the process (table 4), evaluating the performance of the agitation under the relationship between the power of the agitator and volume of mixture [9] which is 1.2, proving that the design is correct. Start of the process of mixing (table 5) ranges, running between 0.02 and 0.5 kW/m3 and later takes the calculated power to ensure a regime of stable mix your graphics present in figure 4.

$$SpecificPower = \frac{Po}{Vrxn} \quad [9]$$

Figure 3 sets the mentioned agitator design

Table 4. Hydrodynamic design

Np	Power Number	4	ADI
Pw	Mixture Regime	0.7	ADI

Re	Reynolds Number	6148	ADI
N	RPMs Number	2.79	s-1

Table 5. Regime and mixing power applications

Agitation	Applications	Specific Power, kW/m^3
Low	Mixture	0.04-0.10
	Homogenous Reactions	0.01-0.03
Medium	Homogenization	0.03-1.0
	Mixture liquid-liquid	1.0-1.5

Costs and Recommendations

In terms of the costs of the design, settled net values required for both the construction (the reactor body, agitation, UV system system) and the operation of the photocatalytic system (pumping systems, support and dosing tanks of) catalytic, systems control solution) which reported that the cost of steel material and UV lamps have between 80 to 93% of the total reactor (see Figure 5), which has an estimated cost of 80.000 USD, however the value of each team changes according with technical specifications, equipment requirements and offices, so there may be variation in the price over time or by change in the design.
Finally, the general design of the photocatalysis process is established in figure 6, which establishes a general view of the disposition and requirements of the system.

CONCLUSION

It is recommended that in case you want to execute the construction of the proposed reactor, variables such as pressure, temperature and topographic conditions of the area where it is developed will be analyzed, since within the study these factors were estimated under ideal conditions.

The project uses a reference concentration of effluents contaminated with low chlorpyrifos, which is why a cost-benefit study is suggested by implementing adsorption towers to concentrate the pollutant, establishing whether there is a possible cost reduction of the reactor design.

It should be taken into account that the concentration of titanium dioxide (TiO2) used in the design is subject to the experimental development of the referenced study, which may vary depending on the operating conditions required, which suggests a new kinetic study real condition.

ABBREVIATION TOPICS

ABBREVIATION	
$\frac{Vcat}{Wcat}$	Catalyst concentration^{-1}(l/mg)
$\frac{dCa}{dt}$	Variation of contaminant concentration with respect to time (mmol/l-h)
K	Constant Equilibrium of the Reaction
k	Reaction Rate Constant
W	Weight of Catalyst required in the Reactor (kg)
Fao	Mass flow rate of entry of the contaminant (mmol/h)
-ra'	Speed of reaction
X	Pollutant conversion(%)
V'	Volume of Reaction (m^3)
P'	Luminic intensity required in scalation

FIGURE

Figure 1. Reactor Design

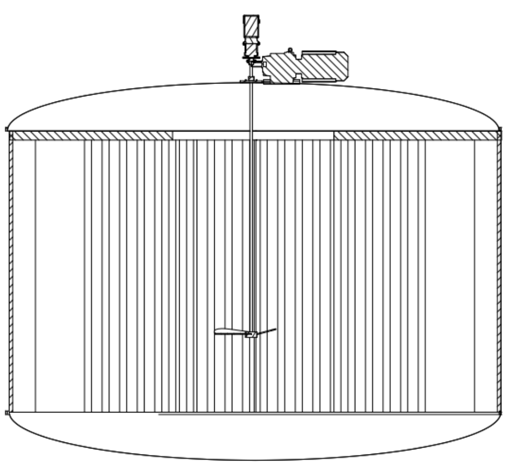

Figure 2. Dimensional Relations of Design

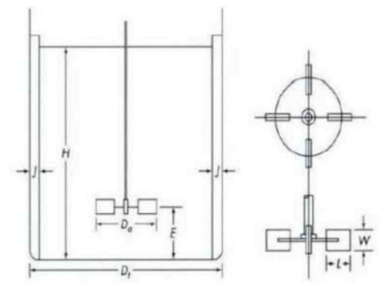

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Figure 2. Lamps Distribution.

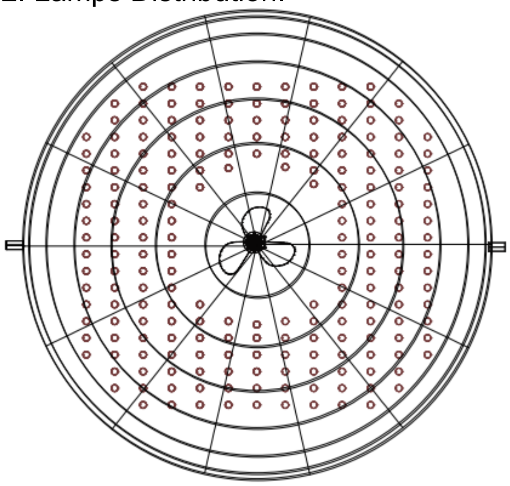


Figure 2.2 Lamps Support

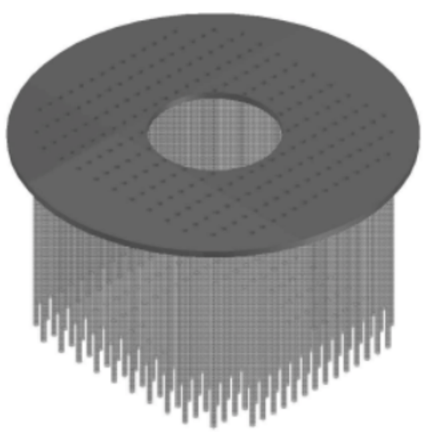


Figure 3 3D CSTR-Design

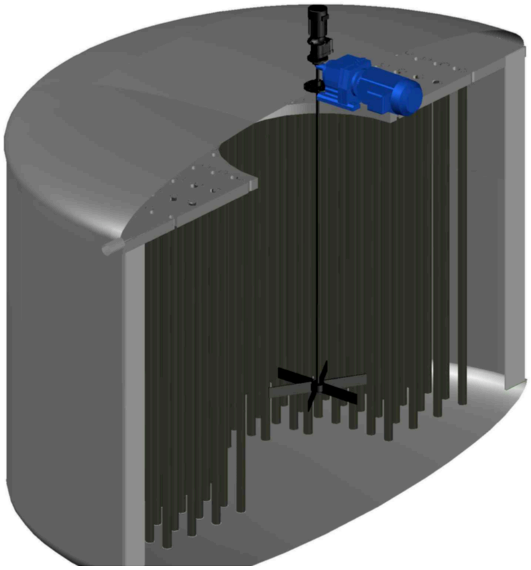


Figure 4.3D View Mixer System

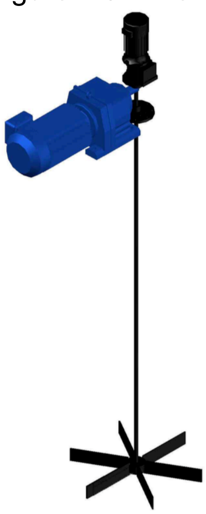


Figure 5. Costs Design Wastewater System

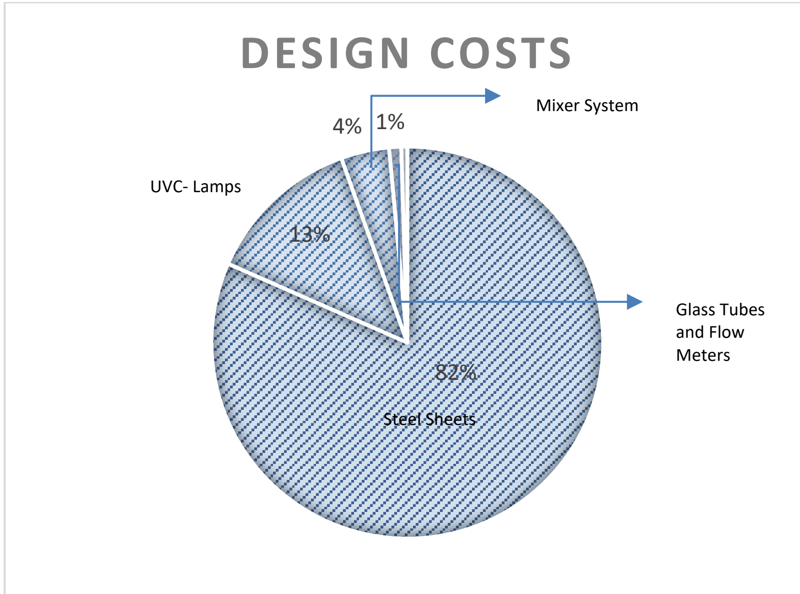
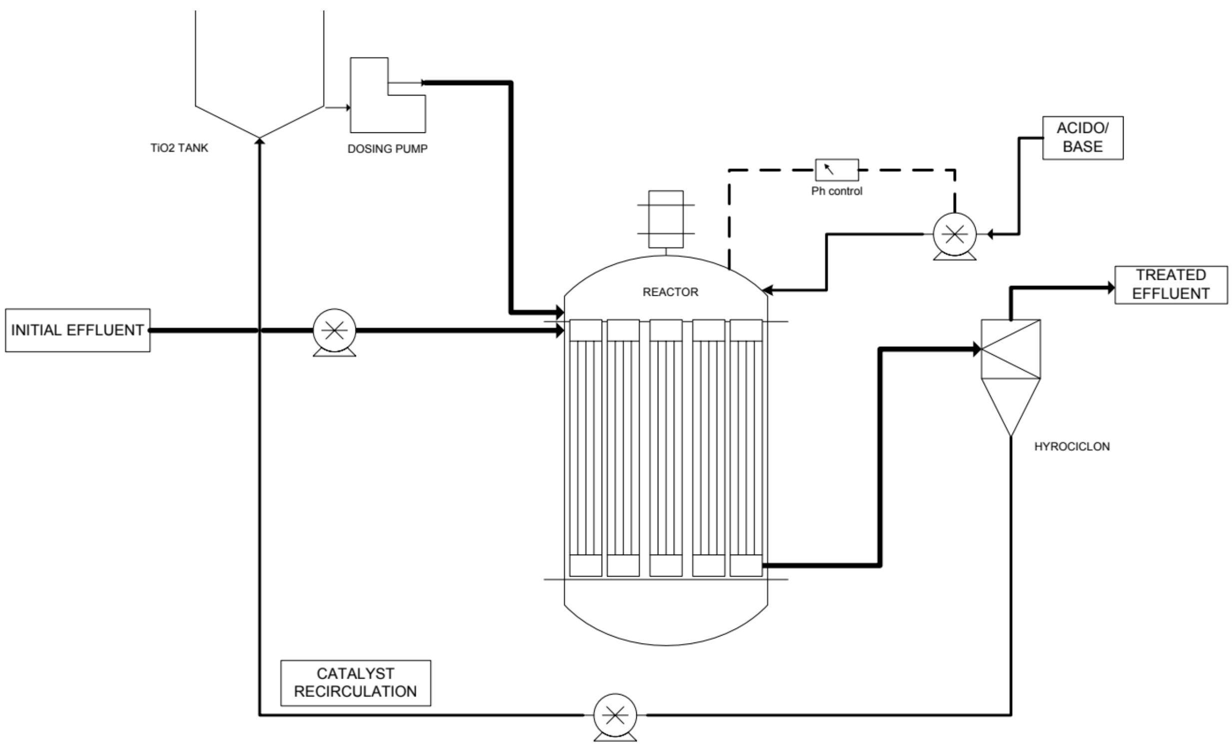


Figure 6. Wastewater Treatment System



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