Photocatalytic Degradation of Carbamate from Wastewater

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ABSTRACT

Carbamates group having a very huge family used as insecticides, herbicides and fungicides. Carbamates are commonly used as insecticides similar to organophosphates and contains carbaryl compound which is highly toxic in nature. Exposure of carbamate insecticide can cause a range of health effect like skin irritation, throat irritation, vomiting, neurological problems, potential cancer risk, diarrhea, and abdominal pain. Exposure of carbamate insecticide can cause an environmental effect like toxicity to non-target species, disruption of ecosystem, toxic to aquatic and wildlife, contamination of water and soil. Treatment of insecticidal wastewater using photocatalytic degradation with help of semiconductors like TiO_2 and ZnO in presence of UV or solar light is an environmentally friendly and ecological process. Zinc oxide and Titanium dioxide considered as a catalyst of choice for such surface reactions as it has good chemical stability, low cost, and high UV/solar photoactivity. Photocatalytic degradation of carbamate insecticide by using TiO_2 and ZnO in presence of UV light the parameter that impact on rate of reduction are contact time, concentration of insecticide, pH of solution and mass of catalyst. The maximum reduction of carbamate insecticide using ZnO/UV and TiO_2/UV process up to 92 % and 94 % at contact time 90 min., concentration of solution 10 ppm, mass of catalyst 2 gm/l, and pH 2 resp. As per results % reduction of carbamate insecticide by using both the catalyst and both processes almost same.

Keywords –AOPs, Photo Catalytic Degradation, UV/TiO_2, UV/ZnO, Insecticide, Carbamate.

1. INTRODUCTION

Pesticide is any substance or mixture of substances used to directly control pests or to prevent or reduce the damage they cause. Pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest. Any preparation containing any one or more of such substances is a pesticide. Formulation of pesticide containing active and inert ingredients. First one ingredient is killing the pest, and second ingredients help active ingredients to work more effectively. Synthetic pesticides are insecticides, which are designed to kill insects, and herbicides, which are designed to kill plants [1].

Carbamates group having a very huge family used as insecticides, herbicides and fungicides. Carbamates are commonly used as insecticides similar to organophosphates and contains Carbaryl compound which is highly toxic in nature. Exposure of carbamate insecticide can cause a range of health effect like skin irritation, throat irritation, vomiting, neurological problems, potential cancer risk, diarrhea, and abdominal pain. Exposure of carbamate insecticide can cause an environmental effect like toxicity to non-target species, disruption of ecosystem, toxic to aquatic and wildlife, contamination of water and soil [2,3]. The sources of carbamate are Carbaryl, Aldicarb, Methomyl, Carbofuran

1.1 Methods for Carbamate Removal from wastewater

1.1.1. Adsorption

In this method activated charcoal, metal oxide compound, synthetic zeolites and silica wieldy used adsorbent for removal of insecticide like carbamate.

1.1.2. Biological Treatment

In this method activated sludge treatment used for removal of carbamate insecticide in which mixed microbial culture for treatment.

1.1.3. Chlorination and ozonation

In this method electrophilic attack by hypochlorous acid and electrophilic attack by ozone use for treatment of carbamate.

1.1.4. Membrane Technologies

In this method nanofiltration can be separate and removal of carbamate. UF and RO process can also use for removal of carbamates.

1.1.5. Physical Treatment

In this method filtration is a used to remove the pesticide from water, and the type of membrane depends on the targeted pesticides. Filter containing membranes with an average size between 10-2 and 10-3 µm are ideal for removing bacteria's and organic molecules.

1.1.6. Advanced Oxygen Process

In this photochemical oxidation like UV/TiO_2, UV/ZnO types of processes are used for removal of carbamate from wastewater.

1.2 Limitations of Treatment methods

For adoption process the degradation and stability of most adsorbents are low, for complex wastewater treatments. Another limitation for adoption method is reusability and recovery of adsorbents low. For biological treatment has limitations such as process requires longer time for treatment, and effectiveness of treatment depends on the environmental factors.

Chlorination and ozonation process has most drawback as both the processes can produce harmful disinfection byproducts.

Membrane process for insecticide wastewater treatment has most limitations like membrane fouling, potential toxicity, high capital and operating cost.

Due to above limitations of the various methods, we selected the photocatalytic oxidation process for treatment of carbamate from wastewater. This method has lot of advantages over the other methods used for carbamate reduction from wastewater.

1.3 Photocatalytic Degradation

For the treatment of carbamate insecticide wastewater using photocatalytic process the ZnO, TiO_2 act as a catalysts and UV/solar light act as a oxidizing agents. For this process the most parameters that affected are the initial concentration of insecticide, time of contact, mass of catalyst, pH of solution etc. The kinetics of photocatalytic degradation examine using UV spectrophotometric method [2].

Advantages of Photocatalysis [2]

- Cost effective method
- No sludge formation
- No generation any other secondary pollutant.

- Less quantity of catalyst required for the treatment
- Catalyst possess no toxicity to human health.
- Application for complex contaminants
- Low capital investment.
- Ecofriendly and environmentally friendly.
- Energy efficient process UV and solar radiation photocatalysis.

In 2019, Studied by A,Tomasevic et al. [2] photocatalytic degradation of a model compound of the carbamate insecticide carbofuran in water using polychromatic light and ZnO and TiO_2 catalysts. Parameters affected on process such as reaction time and initial carbaryl concentration. Complete removal of 88.4 mg/l of carbofuran occurred within 2 h under optimized conditions. Photocatalytic efficiencies of ZnO and TiO_2 compared under same reaction conditions [2].
Photodegradation degradation proposed as an effective and attractive techniques for degradation of carbamate pesticides methomyl and carbofuran in water. These all processes depend on several main parameters, such as the nature of pesticide, type of light, initial concentration of pesticides, pH of solution, temperature, and presence of an oxidant. Photochemical degradation capable for removal of methomyl and carbofuran is an applicable model for purification of water and wastewater. [4]

Complete degradation of the insecticides achieved under the TiO_2 (s)/H_2O_2/UV system after 320 min of irradiation. Half-life values of the tested insecticides under H_2O_2/TiO_2 (c)/UV 43.86 and 36.28 for dimethoate and methomyl [5].

In 2022, studied by A. El-Dissouky and Mahmoud Samy, photodegradation performance of ZnO and ZnO/Fe using various catalyst doses in a constructed parabolic solar reactor. ZnO catalyst dose and reaction time 1.0 g/L and 135 min. After 135 min of reaction, increasing the ZnO dose from 0.1 to 1 g/L increased removal efficiencies [6].

ZnO/SnO_2 nanocomposite more efficient than the ZnO/MgO nanocomposite for the treatment of pesticide effluent, achieving 98% and 95% of total organic carbon and chemical oxygen demand removals, resp. ZnO/SnO_2 nanocomposite was the more stable and well-organized composite, which could be the preferred treatment of industrial and agricultural wastewater containing organic contaminants [7].

Degradation of chlorpyrifos in terms of reduction in COD calculated. Concentration of the catalyst optimized at 4g/L and pH value at 6, where around 61% degradation of insecticide [8].

The catalyst TiO_2 photocatalyst is more efficient than photolysis process in the degrading of agricultural wastewater with high concentrations of organophosphorus pesticides, with reduced treatment time. Removal efficiency for commercial pesticide around 50% and total mineralization of pesticide achieved at 90 min. Complete degradation product accomplished in the same treatment time. Removal efficiency of methyl parathion 90%, completely mineralized at the end of treatment. [9].

In 2019, studied by Gašić Slavica, Anđelka Tomašević, Dušan Mijin, Aleksandar Marinković, photocatalytic degradation of a model compound of the carbamate insecticide carbofuran in water using polychromatic light and ZnO and TiO_2 catalysts. Complete removal of 88.4 mg/L of carbaryl occurred within 2 h under optimized conditions. Photocatalytic efficiencies of ZnO and TiO_2 compared under the same reaction conditions. Photocatalytic degradation of the carbamate insecticide carbofuran using the ZnO and TiO2 catalysts and polychromatic light. Carbaryl photodegradation affected by initial concentration of carbaryl. [10].

Meta-analysis proved that the photocatalytic processes could remove pesticides with an average acceptable degradation efficiency of 93.36%. Photocatalytic processes for the degradation of insecticides, herbicides and fungicides 93.35%, 90.73 % and 100% respectively [11].

2. MATERIALS AND METHODS

2.1 Chemicals

ZnO and TiO_2 use as catalyst photocatalytic degradation process. Both are the strong oxidant and its application in the treatment of various inorganic and organic pollutants. H_2SO_4 acid or NaOH alkali to be used for Ph maintain of waste water. pH is a one of the important parameters that impact on reduction of pollutants from wastewater. UV light used as an oxidizing agent for catalyst photocatalytic degradation process which oxidize the reaction for degradation of organic matter presents in the wastewater. Carbaryl insecticide from carbamate group that has use for treatment of various insects. This is use for preparation of synthetic wastewater of various concentrations. [12,13]

Chemical Specification:
Carbaryl – ($C_{12}H_{11}NO_2$) Chem. Name–1-napthyl Methylcarbamate. Molecular Wt. 201.22 gm/mol. Solubility in water 0.7 gm/l. CAS No. 63-25-2. Colorless crystalline solid, M. P. – 142 ^{O}C, density – 1.2 gm/cc, Wavelength in water solution – 540-590 nm.
TiO_2 - Molecular Wt. 78.86. Insoluble in water, organic solvent. CAS No. 13463-67-7, extra pure 99%. Lobogens India, Rahon road, Ludhiana.
ZnO - Molecular Wt. 81.38. Insoluble in water, organic solvent. CAS No. 1314-13-2, extra pure 99%. Lobogens India, Rahon road, Ludhiana.

2.2 Synthetic wastewater of solution

Carbaryl insecticide from carbamate group use for preparation of synthetic wastewater. Take 0.5 or 1 L of distilled water. Take 25 mg of carbaryl and add 1liter distilled water. The concentration of 25 mg/l synthetic wastewater is 25 ppm. Mixed by proper agitation. Follow same procedure to make various concentrations solution [14].

2.3 Experimental Setup

Figure.1. Photochemical Reactor

The photochemical reactor which is manufactured by Trident Labortek, Mumbai, India as shown in Fig. 1. Photochemical reactor unit is 500ml capacity consisting of 500ml Borosilicate rector with 5 nozzles, central double "GE" Quartz UV jacket. 450 Watts MPMVL UV Lamp and 240 W UV Lamp. Digital UV lamp controller panel with volt meter, and eye protection safety. The UV lamp controller box consisting of 230V Main power cord, it provides power to complete unit from 15 amps power source located on your wall. UV

Power box cord port provides power from UV box to safety cabinet 230 V indicated by a RED Marker strip. UV 450 Watts Port provides power from 450 Watts UV Lamp Present inside the safety cabinet indicated by a RED Marker strip. UV 250 Watts Port provides power from 250 Watts UV lamp Present inside the safety cabinet indicated by a blue marker strip. Temperature portprovides a yellow cable with 2 pin sensors which displays product temperature when the reaction has started. The display has been provided on the extreme right side of the UV controller unit.

2.4 Analysis

Analysis carried out using colorimeter. With the help of colrimeter we measure the absorbance of solution. % reduction of pollutant calcultaed using intial and final absorbance of solution. Anlysis carried out at various contatct time, concentration, pH and mass of catalyst [15,16]. The pecentage reduction of pollution is calculate as:

% Reduction of Pollutant = [(Initial absorbance – Final Absorbance)/ Initial Absorbance] x 100

Figure. 2. Colorimeter

Figure. 2. Shows the EQ-650A is a microcontroller-based digital colorimeter designed for precise and efficient colorimetric analyses. It features disc-mounted filters and is suitable for various laboratory applications. The features are as follows: Measurement Modes: % Transmittance (%T) and Optical Density (OD); Wavelength Filters: 8 disc-mounted German glass filters at 400, 420, 470, 500, 530, 620, 660, and 700 nm; Display: 3-digit LED display; Accuracy: ±1% in %T; ±0.01 in OD; Cuvette: 10 mm path length square cuvette with optical glass window; Light Source: LED with infinite life; Detector: Photocell; Power Supply: 230 V AC ±10%, 50 Hz; Warm-up Time: Approximately 5 minutes; Dimensions: 90 mm (H) x 225 mm (W) x 220 mm; Weight: Approximately 1 kg; Body Material: ABS plastic; Sample Volume: 1 mL; Accessories: Includes matched square cuvettes and a dust proof cover

2.5 Reaction Mechanism

This process includes ZnO or TiO_2 injection and mixing followed by a reactor that is equipped with UV light. During this process, ultraviolet radiation is used to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical.
The reactions describing UV/ ZnO process are presented below [17]:

The mechanism of photocatalytic TiO_2 as follows:

$TiO_2/ZnO + h\nu \rightarrow e- + h^+$

$h^+ + H_2O \rightarrow H+ + OH\bullet$

$h^+ + OH^- \rightarrow OH^\bullet$

$e^- + O_2 \rightarrow O_2^-$

$2e^- + O_2 + 2H^+ \rightarrow H_2O_2$

$e^- + H_2O_2 \rightarrow OH\bullet + OH^-$

$\bullet OH + O_2 +$ Organic $\rightarrow CO_2 + H_2O$ + other degradation product

2.6 Experimental Method

2.6.1 Procedure for various Contact Time

Take known ppm insecticidal wastewater solution and measure absorbance using colorimeter. Put the solution photo chemical reactor and add 1-2 gm/ L of ZnO/TiO_2 catalyst in beaker and start UV light. Stirred the solution for 10 min. For various time of interval 30, 60, 90, 120 and 150-min withdrawal of sample. Check absorbance unit for each sample with help of colorimeter. Calculate % reduction of various for insecticides by comparing initial and final absorbance unit taken using colorimeter. Calculate the % reduction for the insecticide.

2.6.2 Procedure for various Concentrations

Take known ppm insecticidal wastewater solution and measure absorbance using colorimeter. Put the solution photo chemical reactor and add 1-2 gm/ L of ZnO/TiO_2 catalyst in beaker and start UV light.
Withdraw sample after 90-120 min of contact time.
Check absorbance unit for each sample with help of colorimeter. Calculate % reduction of various for insecticides by comparing initial and final absorbance unit taken using colorimeter. Calculate the % reduction for the insecticide. Repeat the procedure for various concentrations.

2.6.3 Procedure for various pH

Take known ppm insecticidal wastewater solution and measure absorbance using colorimeter. Put the solution photo chemical reactor and add 1-2 gm/ L of ZnO/TiO_2 catalyst in beaker and start UV light.
Withdraw sample after 90-120 min of contact time. Check absorbance unit for each sample with help of colorimeter. Calculate % reduction of various for insecticides by comparing initial and final absorbance unit taken using colorimeter. Calculate the % reduction for the insecticide. Repeat the procedure for various pH of solutions.

3. RESULTS AND DISCUSSIONS

3.1 Effect of Contact Time

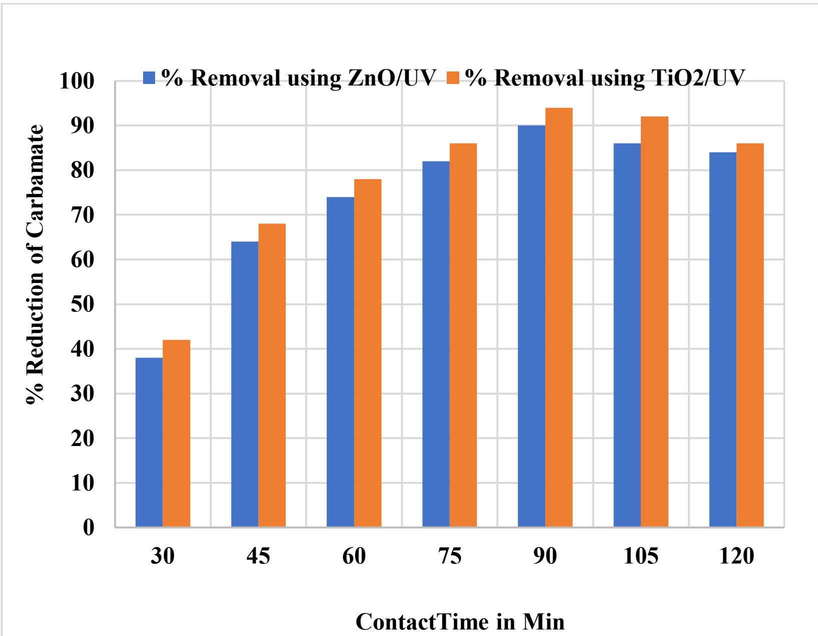

Figure. 3. Effect of Contact Time on Carbamate Reduction Using ZnO/UV and TiO_2/UV

Figure. 3. Shows the effect of contact time on % reduction of carbamate using TiO_2/UV and ZnO/UV processes are shown in figure. Figure shows the % reduction of carbamate using both processes at various intervals of time. As the time increase the rate of reduction also increase. The maximum reduction at 90-105 min for both the processes. Each process shows the % reduction up to 94% for 90 min reaction time. Rate of reduction for both the processes are approximately same so we can choose any of them.

3.2 Effect of Concentration

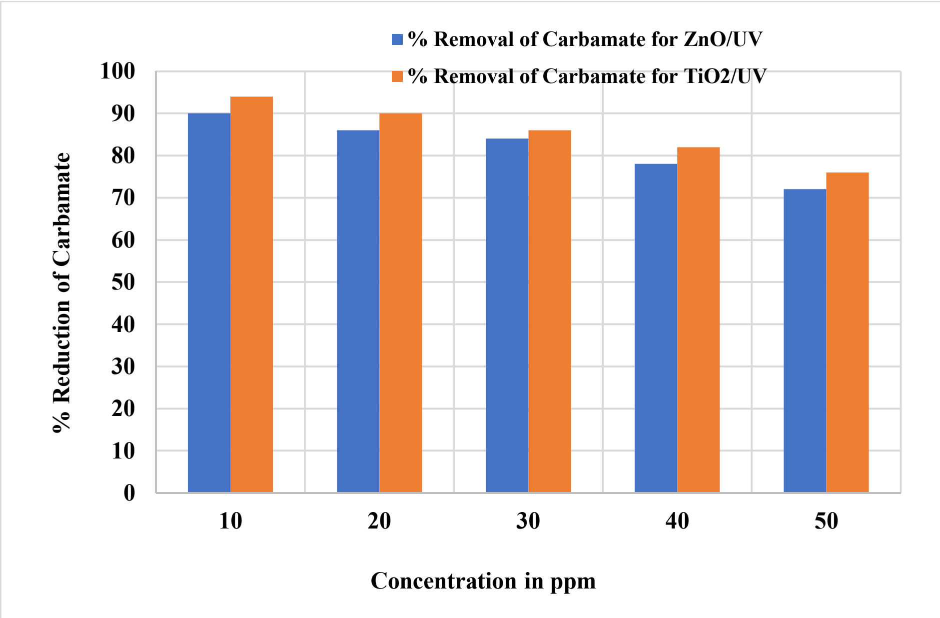

Figure.4. Effect of Concentration

Figure. 4. Shows the effect of concentration on % reduction of carbamate using TiO_2/UV and ZnO/UV processes are shown in figure. Figure shows the % reduction of carbamate using both processes at various intervals of time. As the concentration of pollutant increase the rate of reduction also decrease. Each process shows the % reduction up to 94% for 10ppm concentration solution.

3.3 Effect of mass/amount of catalyst

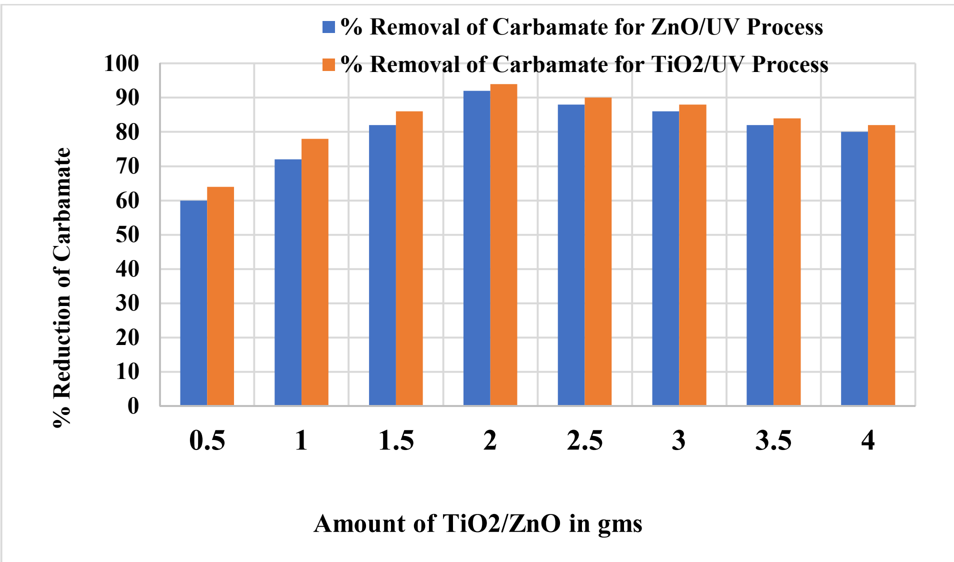

Figure.5. Effect of mass/amount of catalyst

Figure. 5. Shows the effect of amount of catalyst TiO_2 and ZnO on % reduction of carbamate for TiO_2/UV and ZnO/UV processes are shown in figure. Figure shows the % reduction of carbamate using for each process at different amount of catalyst. As the amount of catalyst increase the rate of reduction rate also increase. Each process shows the % reduction up to 94% for 2 gm/L of catalyst utilization. After this amount there with reduction in rate of degradation of pollutants.

3.4 Effect of pH of solution

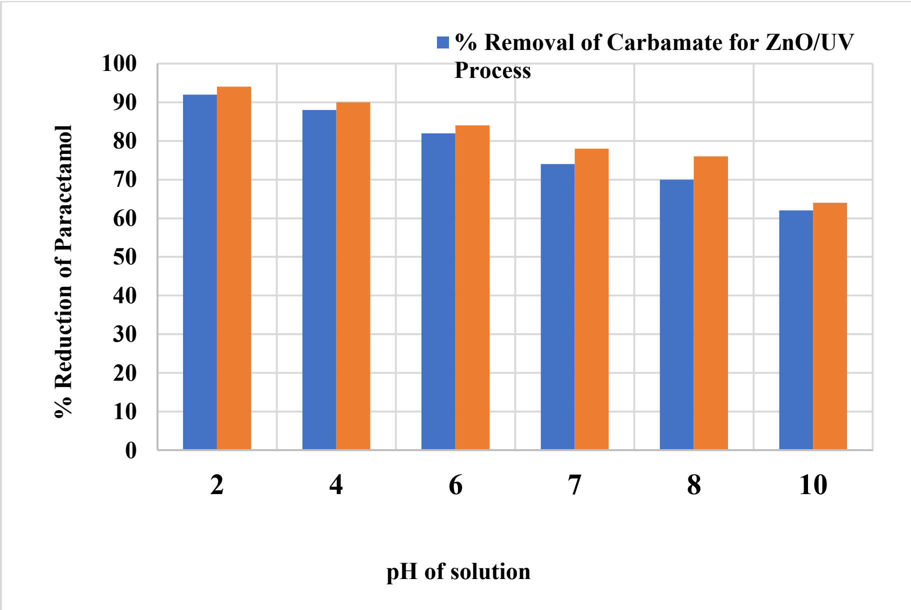

Figure. 6. Effect of pH of solution

Figure. 6. Shows the effect pH of solution on % reduction of carbamate using TiO_2/UV and ZnO/UV processes are shown in figure. Figure shows the % reduction of carbamate for each process at different pH of solution. As the pH of solution increase the rate of reduction rate decrease. Each process shows the % reduction up to 94% for pH value 2. After increase the value of pH the rate of reduction goes on decrease. From the analysis its clear that in acidic pH reduction of pollutant is more.

4. CONCLUSION

Pesticide pollution emerges as the serious environmental concern. Removal of pesticide contaminants has become the key concern of scientific community. Degradation of carbamate using TiO_2 and ZnO nanoparticles is considered as potential and effective technology for the mineralization of pesticide into environmentally friendly compounds. Each process shows the % reduction up to 94% for 90 min reaction time, 2 gm/L of catalyst utilization, for pH solution 2 and for concentration of 10 ppm. Rate of reduction for both the processes are approximately same so we can choose any of them. From the analysis it's clear that in acidic pH reduction of pollutant is more. From the results it's clear that as the concentration of pollutant increase the rate of reduction also decrease.

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