

PHOTODEGRADATION SCREENING ON CHLORPYRIFOS AND BENZOIC ACID USING TITANIA-BASED PHOTOCATALYST SUPPORTED ON PULASAN PEEL ACTIVATED CARBON

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Abstract

Chlorpyrifos and benzoic acid are harmful and toxic organic compounds which contribute to the damage of the environment and human health. Therefore, any organic or inorganic pollutants present in water system should be treated in an appropriate way and low-cost before they can be safely disposed to the environment. In this research, TiO₂ modified with PPW activated carbon, TiO₂/AC was synthesized. The pulasan peel was treated with sulphuric acid to obtain activated carbon. Various ratios of TiO₂/AC (90:10, 50:50, 10:90) with various calcination temperatures (500, 600 and 700°C) were prepared by physical mixing. Titania-silver oxide was also prepared with various ratios (90:10, 50:50 and 10:90) and calcined at 500°C and prepared by wet-impregnation method. All the prepared photocatalysts were screened on chlorpyrifos and benzoic acid degradations under UV irradiation ($\lambda=365$ nm), monitored by UV-Vis spectrophotometer. The main absorption measured at wavelength $\lambda_{max}=210$ nm for chlorpyrifos and $\lambda_{max}=227$ nm for benzoic acid were recorded. Among the photocatalysts prepared, the catalyst which gave maximum percent degradation was 5T/3SAC (50:50) compared to single TiO₂ and other modified photocatalysts. The best photocatalyst was assessed on the effect of various catalysts loading (0.1, 0.2 and 0.3 g) on the benzoic acid solution and result shows that as catalyst loading increase, the rate of degradation was also increased. The prepared photocatalysts were characterized by X-ray diffractometer (XRD), Brunauer-Emmett-Teller (BET) and field emission scanning electron microscopy-energy dispersive X-ray (FESEM-EDX). It is proven that (5T/3SAC 50:50) is the most efficient photocatalyst with the presence of anatase phase, and homogenous distributed porous surface with average size (1.48 μ m) and from BET surface area of 4SAC showed highest surface 228.49 m²/g.

Keywords: Pulasan peel waste, activated carbon, photodegradation, chlorpyrifos, benzoic acid

INTRODUCTION

Environmental pollution is a common issue in this century. Most of the pollution present is due to the disposal of organic and inorganic substances into water sources such as rivers. Besides that, aquatic environment, underground water layer, and the surface of the habitat is often contaminated by waste which are mostly disposed by various source such as industrial, agricultural chemicals, agricultural runs off and others.

The types of chemicals that are difficult to degrade naturally by biological method are comes from the group of dyes, aromatic carboxylic acid group, and pesticides. Therefore, the materials are accumulated for a long time and will cause harm to the environment and living things.

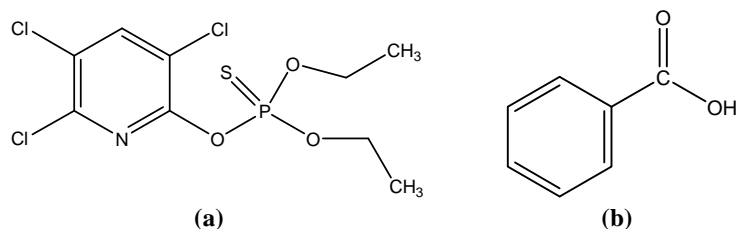
In recent years, photocatalytic degradation has become a promising techniques for wastewater treatment and removal of organic pollutants. Photocatalytic degradation is actually an Advance Oxidation Process (AOP) which can degrades and mineralizes most organic contaminants into carbon dioxide and water without any formation of any stable intermediate species. The process operates by the presence of heterogeneous semiconductor as a catalyst, and also in the presence of source of light such as UV light radiation or high intense of sunlight. The process occurs at ambient temperature and pressure. The most outstanding and stable photocatalyst which shows tremendous activity is titanium dioxide. However, zinc oxide also shows a high efficiency in photocatalysis but it has low stability which makes its aqueous suspensions stable only at basic pH. The efficiency of photocatalysis process depends on several characteristic of semiconductor particles, such as their surface properties, the position of their band gap potentials, mobility and recombination rate of the charge carriers generated by UV-light absorption [1]. However, a few drawbacks were investigated by researchers such as low degradation due to recombining process of positive holes and generated electron. As responds to these problems, support materials with large surface areas were used on TiO₂ such as activated carbon from pulasan peel waste to increase the absorption of substare and metal oxide as co-dopant was also added to retard the recombination process. This development would be great significance to enhance the photodegradation efficiency [2].

EXPERIMENTAL

Reagent and materials

Previously synthesized activated carbon from pulasan peel waste was used in this work as adsorbent for titania. The dried pulasan peels were soaked in 20% sulphuric acid solution with 1:4 ratio (pulasan peel (g): v H₂SO₄)

for 24 hours. Then, the acid was poured off and the pulasan peel was dried in the hot air oven at 95°C and left for two days. Next, the sample was washed with hot distilled water and the sodium bicarbonate (1% w/v) was used to remove the acid until the precursor was fully free of acid and dried in hot oven at 95°C. Then, the activated carbon was activated in a muffle furnace with different temperatures which were 300, 400 and 500°C for 2 hours. Coupled of titania-activated carbon was prepared with various ratios and calcination temperatures by physical mixing. TiO₂/AgO was also prepared by wet-impregnation method. Photocatalysts prepared were screened on chlorpyrifos (a) and benzoic acid (b) to get an optimum photocatalytic activity.



Instruments

The evaluation of photocatalysts efficiency on chlorpyrifos and benzoic acid were monitored using UV-Visible spectrophotometer, Shimadzu UV-25000PC model and to obtain information on structural properties and crystalline phase of the prepared photocatalyst, it was analyzed by using Siemens D5000 X-ray diffractometer equipped with Cu-K α ($\lambda = 1.54 \text{ \AA}$, 40 kV, 30 mA) radiation. The morphology of several photocatalysts were examined using FESEM- Zass Supra 35 VP with Gemini Column and to determine surface area of the prepared activated carbon, single point BET was used. The specific surface area was determined by single point BET using nitrogen as the adsorption gas.

Plant Material

Nephelium Mutabile (Pulasan) bought from Tampoi Market and was used to prepare activated carbon.

RESULTS AND DISCUSSION

Characterization

X-ray Diffraction (XRD) Techniques

X-ray diffraction is a technique to identify and determine the crystallinity or phase transformation of powdered compounds. The effect of TiO₂/AC ratios and calcination temperature was studied in this study. The phase and structural of photocatalysts were identified by matching the 2θ with the powder diffraction file (JCDPS) obtained and studied on both anatase and rutile phases of TiO₂ to determine the peak crystallinity from its peak intensity.

Figure 3.1 shows the XRD diffractograms of TiO₂/3SAC with ratio 50:50 calcined at 500°C (a) (5T/3SAC 50:50), while (b) was single TiO₂ calcined at 500°C (T-500) and (c) titania-activated carbon calcined at 700°C (7T/5SAC 10:90) photocatalysts. The result indicates that the synthesized TiO₂/AC consists of pure phase and no other characteristic peak can be found from other phase or impurities. The XRD patterns of single TiO₂ and coupled TiO₂ photocatalysts showed the presence of peaks at 2θ values of 25.6, 37.9, 48.1, 55.2, 62.6, 68.9 and 75.2° corresponding to the anatase phase (JCDPS No. 21-1272). However, peaks at 2θ values of 54.2, 69.0 and 70.2° are characteristic of TiO₂ rutile phase (JCDPS No. 21-1276).

Based on Figure 3.1 5T/3SAC 50:50 (a) and single TiO₂ (b) calcined at 500°C consists of anatase phase with small amount of rutile phase while TiO₂/AC calcined at 700°C (7T/5SAC 10:90) consist of rutile phase with small amount of anatase phase. The phase transformation of TiO₂/AC photocatalyst occurs at the temperature of 500°C where anatase shifts gradually to rutile phase during calcination process [4].

It is apparent that thermal annealing greatly affects the structure and the size of the resulting TiO₂ crystal. The crystal sizes for both anatase and rutile increased with increasing of calcination temperature, indicating aggregation of TiO₂ nanoparticles upon annealing. The fraction of rutile becomes greater with increasing reaction temperature accelerates phase transformation from thermodynamically metastable anatase to most stable and more condense rutile phase [4].

Lastly, a rough baseline was obtained as shown by Figure 3.1 (c) when 90% AC present in the photocatalyst. This result obtained was due to the highly content of amorphous activated carbon in the photocatalyst.

Single Point BET Surface Area

The surface area of activated carbon after calcination at various temperatures (300, 400, 500°C) was determined and was shown in Table 3.1. Activated carbon that was calcined at 400°C (4SAC) has the highest surface area compared to AC that were calcined at 300 and 500°C. BET specific surface area increases with activation temperature (See Table 3.1) with the most significant increase being between 300 and 400°C. When the activation temperature was increased from 400°C to 500°C, the effect of activation temperature on BET specific surface area was dramatically decreased. This can be attributed to high activation temperatures allowing easier removal of organic matter, formation of more micropores, and an increase in specific surface area, but also easier collapsed of micropores, backfilling, and formation of graphite-like carbon structures, thus decreasing the BET specific surface area [5].

Table 3.1: Surface area for prepared activated carbon (activated with sulphuric acid)

Label	Activation Temperature (°C)	Surface Area (m ² /g)
3SAC	300	96.20
4SAC	400	228.49
5SAC	500	41.83

Field Emission Scanning Electron Microscope (FESEM)

In this research, FESEM micrographs (Figure 3.2 -3.4) were used to study the morphology and composition of single TiO₂ which were calcined at various temperatures, 500, 600 and 700°C. Besides that, the coupled photocatalysts morphologies were also studied using this instrument. Figures 3.2 shows the micrographs of single TiO₂ calcined at 500°C, 600 and 700°C with magnification of 5000x respectively. The energy bombardment applied was 10 kV and working distance was 8.5 and 8.6 mm.

From the results shown, the particles size of TiO₂ increase after calcined at 600 and 700 °C. The formation of tetragonal shape was clearly observed at these calcination temperatures due to the rutile phase that started to form at these temperatures. The increase of size was due to the agglomeration process which involves combination of primary particles and secondary particles that occur at high temperature. TiO₂ calcined at 500°C and 600°C were considered as mesopores category due to its mean size was 20.87 nm and 38.22 nm. It was spherical in shape and homogenous. However, TiO₂ calcined at 700°C was in macropores category because its mean size of particle was 128.94 nm. The size of particles was measured using J image software. According to IUPAC recommendation, total porosity usually classified into micropore (< 2 nm) mesopores (2-50 nm) and macropores (> 50 nm).

Figure 3.3 shows the surface micrograph of activated carbon calcined at 300 and 400°C. From Figure 3.2, the morphological structure of 3SAC shows highly defined pores that the surface was rough and dented [6]. There was major development of internal pores that could be seen and the pore size distributions were non-uniform. However, 4SAC morphology shows cleaner and smooth surface. The pore development was larger and it was an external pores [5]. This explained why BET surface area value (see Table 3.1) for 3SAC was lower than 4SAC. The quality of the activated carbon seemed to be deteriorated as the calcination temperature was increased. This might be a result of the collapse of micropores as it was heated at higher temperature [7].

Based on Figure 3.4, the 5T/3SAC (50:50) photocatalyst obviously have larger surface area and pore size (1.48 μm) suitable for the degradation. This type of titania-activated carbon shows the highest percent of degradation due to ability of activated carbon acts as adsorbent to enhance the photocatalytic activity. The calcination temperature of 500°C also plays as important role because calcinations at higher temperature might destroy the pore structures, as well as change the active phase of anatase to more rutile which is inactive.

Photodegradation of Chlorpyrifos Using Single TiO₂ Photocatalyst

Degradation rates for all single TiO₂ that were calcined at various temperatures (500, 600, 700°C) on chlorpyrifos (see Figure 3.5) showed that 500 TiO₂ gave the highest percentage of photodegradation with 71.47

followed by 46.43 and 49.9% for 600 TiO₂ and 700 TiO₂. The best performance of 500 TiO₂ is due to the presence of anatase phase at temperature 500°C which was more stable than the other phase. From the results obtained it was shown that the crystallinity, crystal phase and crystallite size were influenced by varying the calcination temperature. Calcination temperature was important for removing the organic molecules from the final products and completing the crystallization. However, very high calcination temperature will result in aggregation and phase transformation and affect the microstructure as well as the properties of TiO₂. Photocatalytic activity of TiO₂ strongly depends on its crystal structure. Anatase phase TiO₂ crystallite are generally found to be more active than rutile. Therefore, 500 TiO₂ gave the highest percent of degradation on chlorpyrifos.

Effect of Calcination Temperature On Activated Carbon Preparation

The results obtained in Figure 3.6 showed that the titania coupled with activated carbon calcined at 300 and 400°C gave the higher activity compared to 500°C. Activated carbon calcined at 300°C gave high porosity which can help an adsorption of benzoic acid on the surface or pores when the active species of •OH radical was available in high concentration that help to degrade the substrate. However, at high calcination temperature the pores might collapse and reduce the adsorption activity.

Photodegradation of Benzoic Acid using Various Ratio of TiO₂/AC Photocatalysts

Among all the photocatalysts with ratio (90:10) and (10:90), TiO₂/4SAC with ratio (90:10) that was calcined at 500°C shows the highest percentage of degradation (46.85%) followed by 500 TiO₂/3SAC that gave percentage degradation of 29.20%. According to the results shown by titania-activated carbon with ratio (10:90), as the calcinations increased, the degradation of benzoic acid was also decreased. This is due to agglomeration of particles that will reduce the surface area. The similar trend observed with ratio (90:10). Ratio (90:10) gave higher degradation due to the high contents of titania can provide higher active site to generate more hydroxyl radicals. However the high contents of activated carbon in the catalysts can increase the adsorption but lack of active site of TiO₂ that make the benzoic acid degradation become less effective. As a photocatalyst, the presence of titania in TiO₂/AC composites will increase the surface area of adsorption and photocatalytic reaction so it can serve as hydroxyl radicals source that significantly increase the benzoic acid degradation [8]. An excessive amount of activated carbon might also blocked the TiO₂ surface.

In addition the result also showed that the degradation 5T/4SAC (90:10) (46.38 %) was higher than 5T/3SAC (90:10) (29.2%). In this case, 4SAC activated carbon which was calcined at 400°C has higher surface area than 3SAC which were 228.49 and 96.2 m²/g respectively. The larger surface area of 4SAC contributed to the higher degradation of 500 TiO₂ rather than 5T/3SAC (90:10). As reported by Patnukao *et. al* [7], the surface area of activated carbon leads to high adsorption of pollutants on the catalyst surface, and therefore it might accelerate the process of decomposition through the transfer of the adsorbed molecules to the surface of the photoactive titania.

Effect of TiO₂/AgO on Photodegradation of Benzoic Acid

In order to improve the photocatalytic activity of benzoic acid, the coupled photocatalysts of titania-silver oxide (AgO) was prepared in different ratios (90:10, 50:50 and 10:90) which were calcined at 500°C. Results showed TiO₂/AgO (90:10) gave 31.40% degradation on benzoic acid but for TiO₂/AgO with ratio 50:50 and 10:90 did not show good degradation activities. The small adsorption band gap energy of 1.02 – 2.07 eV for AgO make the excitation of electrons from valence band to conduction band easier and thus the photocatalyst can achieve a higher photocatalytic activity but the recombination process might also occurs faster [9]. The impregnated photocatalyst can prevent the recombination of electrons with h⁺ holes in valence band by transferring the electrons from the conduction of catalyst to the conduction band of co-catalyst. Therefore, the recombination process is delayed [10]. The coupling of AgO as co-catalyst is expected to give higher result due to the delay of electron hole recombination process but not observed in this research. It might due to the other factors such as the properties of the substrate, pH of the reaction mixture and the co-catalyst chosen is not active.

Effect of Loading 500 Ti/3SAC (50:50) On Benzoic Acid

The amount of photocatalyst can play an important role in influencing the degradation rate. Due to this, the optimum amount of catalyst used to degrade benzoic acid was studied in order to achieve the maximum photocatalytic activity. Figure 3.7 shows effect the of different loading of the best photocatalyst among all the sets of photocatalysts 5T/3SAC with ratio 50:50 was chosen to test its efficiency on benzoic acid when used in

different loading. Range between 0.1 to 0.3 g were used to investigate the effect loading of the catalyst. The photodegradation efficiency increasing with loading was increased from 51.20% to 65.14% . This results can be explained by the fact that, when larger amount of photocatalyst was used in the reaction, the availability of active site on the surface of the catalyst for reaction to occur increased. Thus, the photodegradation rate was higher [11].

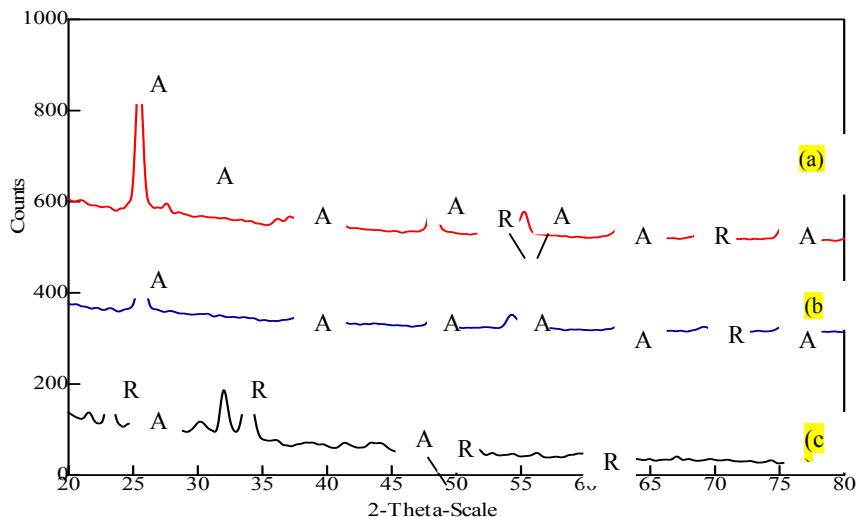


Figure 3.1: XRD patterns of (a) 5T/3SAC (50:50) (b) sol gel TiO₂ (T-500) and (c) 7T/5SAC (10:90)

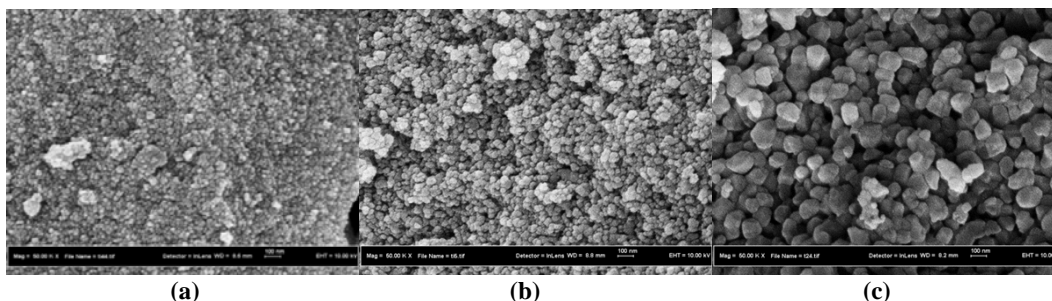


Figure 3.2: FESEM micrograph single TiO₂ calcined at 500°C (a), 600°C (b) and (c) 700°C with 5000x magnification.

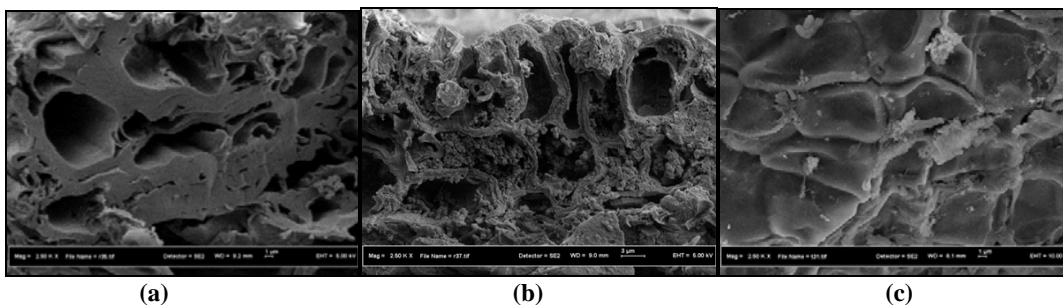


Figure 3.3: FESEM micrographs of activated carbon (a) and (b) calcined at 300°C (3SAC) while (c) was 4SAC with the magnification 2500x.

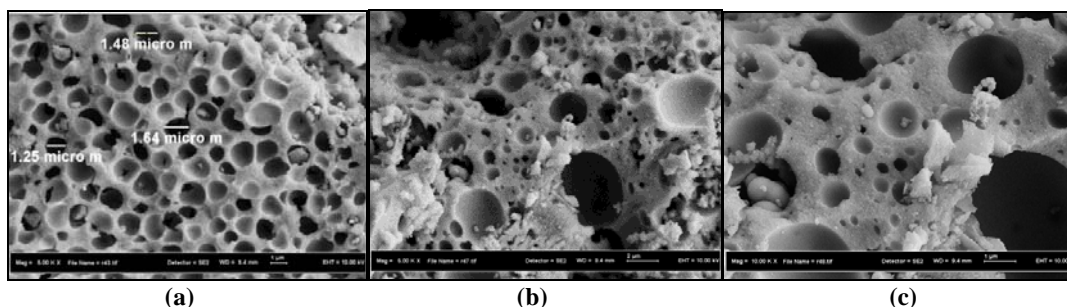


Figure 3.4 : FESEM micrographs of 500 TiO₂/3SAC (50:50) (a) with magnification 5000x while (b) and (c) 10000x magnification

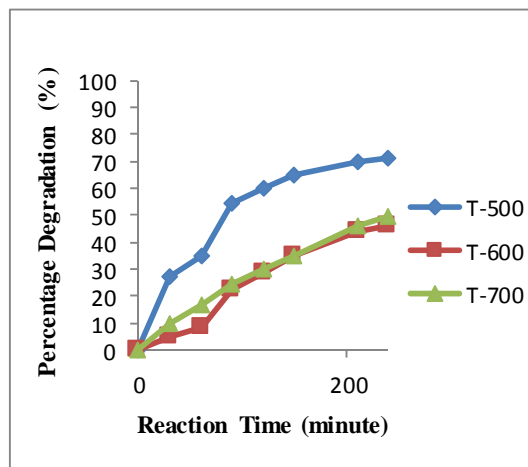


Figure 3.5: Percentage of degradation for chlorpyrifos using sol gel TiO₂ photocatalysts calcined at 500°C, 600°C and 700°C.

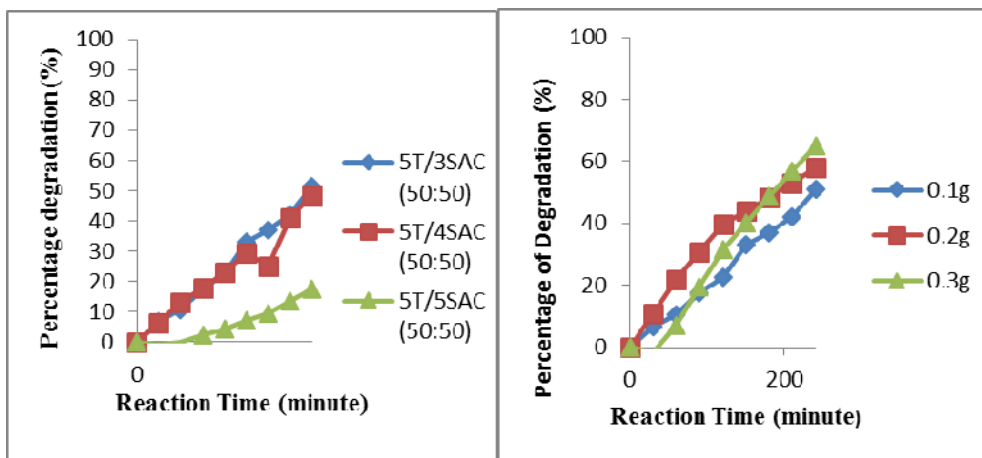


Figure 3.6: Effect of calcination temperature of activated carbon in TiO₂/AC photocatalysts calcined at 500°C towards degradation of benzoic acid.

Figure 3.7: Percentage degradation of benzoic acid using various amount loading of catalysts.

CONCLUSION

Various photocatalysts supported on rambutan peel activated carbon were successfully synthesized. The best photocatalyst that can be applied to degrade benzoic acid was TiO₂/3SAC (50:50) calcined at 500°C which

gave 51.20% degradation compared to single TiO₂ and photolysis which degrade only 37.92 and 9.93% respectively. The addition of activated as an adsorbent increase the photoactivity of TiO₂ catalyst. However, for chlorpyrifos, the highest percentage of degradation was using single TiO₂ photocatalyst calcined at 500. The addition of AgO as co-catalyst slightly decreased the activity.

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