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GRAPHENE- TITANIUM DIOXIDE COMPOSITE: A NOVEL PHOTOCATALYST FOR THE DEGRADATION OF ORGANIC CONTAMINANTS

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Abstract: Laboratory experiments were conducted to investigate the photocatalytic degradation of three organic contaminants using powdered titanium dioxide (TiO₂) and a titanium dioxide graphene (TiO₂-Gr) composite. The TiO₂-Gr composite was synthesized using the hydrothermal method. Its performance was compared to that of TiO₂ powder in degrading sulfolane at 365nm, a wavelength at which TiO₂ shows high absorbance. The two photocatalysts were tested in visible blue light ($\lambda = 460\text{nm}$) for the degradation of sulfolane, phenol and methyl orange to test their response in the visible light spectrum in degrading a range of contaminants. 89% reduction of sulfolane concentration was achieved under 365nm irradiation using powdered TiO₂ and 34% was achieved using TiO₂-Gr. No sulfolane degradation was observed under blue LED light using either of the photocatalysts. Phenol degradation was only observed using TiO₂ under blue LED. TiO₂-Gr showed better performance when compared to TiO₂ in degrading methyl orange. The advantage of using TiO₂-Gr with visible light was only displayed for contaminants with a higher absorption in the visible light spectrum and stronger surface interactions with graphene.

1. INTRODUCTION

Heterogeneous photocatalysis has been widely used for the degradation of organic pollutants from water and air. Photocatalysis is a form of advanced oxidation processes (AOP's) which relies on the generation of strong oxidative species such as hydroxyl radicals to treat organic compounds. It uses light energy and a semiconductor catalyst to generate hydroxyl radicals in the presence of water (Gaya and Abdullah 2008). Titanium dioxide (TiO₂) is a powerful photoactive semiconductor that has been studied extensively due to its many advantages including low cost, nontoxicity, stability and strong oxidizing capability (Kim et al. 2012). However, this semiconductor's narrow light response range and fast recombination of photo-induced electrons/hole pairs restricts its use in visible light applications (Khalid et al. 2013). Many strategies have been used to modify TiO₂ to extend its photoactive range. One approach that has been studied widely is the doping of TiO₂ with graphene nanoparticles.

Graphene has emerged as an attractive material owing to its excellent mechanical, optical and electrical characteristics (Yang et al. 2014). Its high electric mobility promotes electron-hole separation, prolonging recombination and enhanced TiO₂ photoactivity (Haldorai et al. 2014). Composites of TiO₂ and reduced graphene have been studied extensively in literature and have shown better performance when compared to TiO₂ in the photocatalytic degradation of dyes (Khalid et al. 2013; Jiang et al. 2011; J. Li et al. 2013). However, limited work has been done in exploring the potential of this novel photocatalyst in degrading more complex and recalcitrant contaminants such as sulfolane and phenol with the use of visible light.

The objective of this study is to investigate the photocatalytic performance of TiO₂ – graphene composites (TiO₂-Gr) in comparison with TiO₂ in the visible light range for the degradation of some organic

contaminants. Ultraviolet A (UVA) and visible light emitting diodes (LED's) were used for experiments as sources of irradiation. LEDs are a novel and robust light source that offer better energy utilization than conventional mercury lamps (Ghosh, Langford, and Achari 2008). To test the applicability of the TiO₂-graphene composite, various contaminants (sulfolane, phenol and methyl orange) were chosen as target compounds for photocatalytic experiments.

Sulfolane is an organosulfur compound used in many applications such as gas treatment and electronics manufacturing (Canadian Council of Ministers of the Environment 2006). Sulfolane has been reported to contaminate soil and water near gas plants in North America and, as a result, has emerged as a contaminant of concern (Stewart and Minnear 2010). Phenol is a precursor for many chemical products and causes adverse effects to biota when released into aquatic environments (Michałowicz and Duda 2007). Organic dyes, like methyl orange, from printing and textile industries pose a threat to animals and humans due to their carcinogenic properties (D. Li et al. 2014).

2. MATERIALS AND METHODS

2.1 Chemicals

Sulfolane (99% purity), dichloromethane (99%), phenol (99%), powdered methyl orange and HPLC grade acetonitrile were procured from Sigma Aldrich, Canada. Degussa P25 powdered TiO₂ was bought from Degussa, Germany. Graphene oxide suspension in water and ethanol was bought from ACS Material, USA. Milli-Q water was used for all experiments.

2.2 Synthesis of TiO₂-Gr

TiO₂-Gr composites were prepared in the lab using the hydrothermal method. This method involves the reduction of graphene oxide to graphene and the deposition of graphene onto the TiO₂ surface. Following the same approach as used by Yanhui Zhang et al. (2011), 1.6mg of graphene oxide was sonicated along with 1.6g of P25 in a solution of water and ethanol combined in a 2:1 volume ratio. The mixture was then sealed in autoclave for reaction under 120°C for 3 hours. The resulting suspension was then filtered, rinsed and dried to yield the TiO₂-Gr composite photocatalyst powder with 0.1wt% of reduced graphene.

2.3 Photocatalytic Reactions

Batch photocatalytic experiments were conducted in a LED reactor lined with lamps of either 365nm or 460nm. 80mL solutions of sulfolane (50mg/L), phenol (10mg/L) and methyl orange (10mg/L) were prepared in 100mL glass beaker. 2000mg/L of photocatalyst was added to each solution before placing in the reactor. The solution was stirred continuously using a magnetic stirrer throughout the experiment. Samples were collected at predetermined intervals, filtered and stored in the dark before analysis. A 30-minute dark experiment was conducted for each target contaminant and photocatalyst to determine the amount of adsorption, prior to exposing the samples to light.

2.4 Analytical Methods

Sulfolane was extracted using a 1:1 ratio of sulfolane containing sample and dichloromethane (DCM). The samples were shaken in a mechanical shaker for 5 minutes for the sulfolane to partition to the DCM phase. The DCM phase was then extracted and analysed using an Agilent 6890 Gas Chromatograph (GC), equipped with flame ionization detector. Once injected into the GC, chromatographic separation was achieved on a fused silica capillary column (ZB5MSI, Phenomenex). High purity helium, at 250 kPa, was used as the carrier gas. The injection port temperature was kept at 165°C and the injection volume was set to 1.0 μ L. temperature was ramped from 90°C to 175°C at the rate of 10°C/min where it was held for 3 minutes. The FID detector temperature was set to 250°C.

Concentration of phenol in the samples was quantified using Varian Prostar 210 high performance liquid chromatography (HPLC) equipped with UV-visible detector. Sample injection volume was set to 20 μ L and

acetonitrile was used as the eluent. Pinnacle DB C-18 (15 x 4.6mm, 5 μ m) column, supplied by Restek Corporation, USA, was used to achieve chromatographic separation of the phenol sample. The wavelength of the UV-visible detector was set at $\lambda = 280\text{nm}$.

Methyl orange concentration was quantified using the HACH DR/4000 UV– VIS spectrophotometer. The absorbance of each sample was measured at a wavelength of 464nm with a path length of 1cm using a quartz cuvette.

3. RESULTS AND DISCUSSION

3.1 Photocatalytic Degradation of Sulfolane with UVA LED Reactor and Graphene TiO₂ Composite

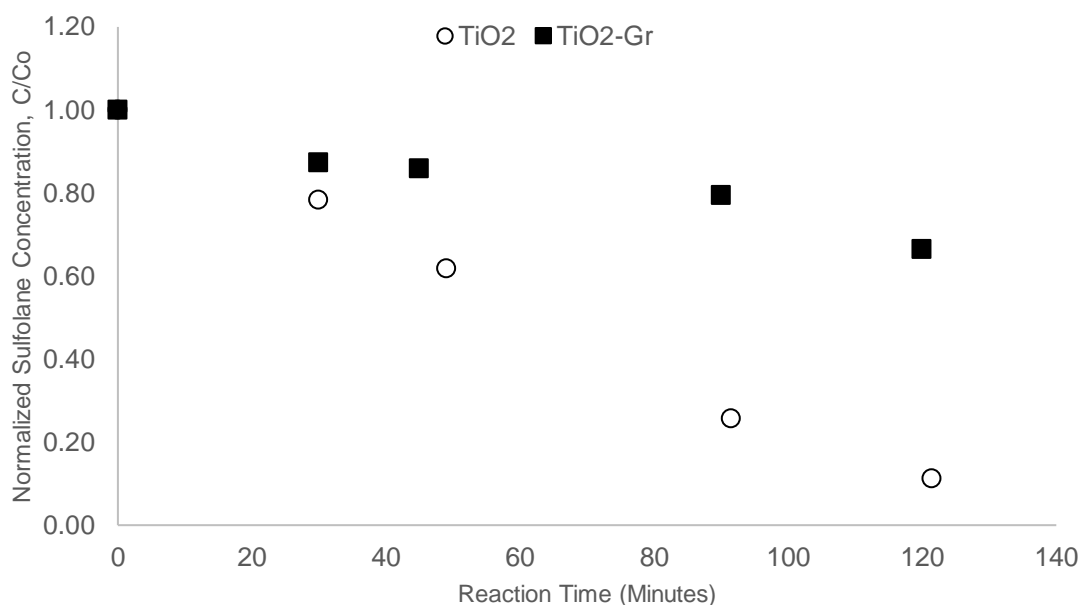


Figure 1. Photocatalytic degradation of 50ppm of sulfolane under 365nm irradiation, using 2000ppm of TiO₂ and 2000ppm of TiO₂-Gr

TiO₂-Gr was used to degrade sulfolane under UVA LED irradiation ($\lambda=365\text{nm}$) to evaluate its effectiveness as a photocatalyst. The results from this experiment are shown in Figure 1. As a comparison, the results from the sulfolane degradation experiment using powdered TiO₂ and UVA irradiation are also reported in Figure 1. Results from the 30-minute adsorption experiments, conducted for each condition, are reported in table 1. Reduction of sulfolane concentration can be observed in the presence of TiO₂ and TiO₂-Gr. The results show that the TiO₂-Gr degraded 34% of the sulfolane contained in the solution within 2 hours of irradiation. The adsorption experiments indicate that sulfolane did not adsorb on the surface of TiO₂-Gr (< 3%). In the experiment where powdered TiO₂ was used, 89% of sulfolane was degraded in 2 hours. This showed a 55% greater reduction in sulfolane concentration when compared to the sample with TiO₂-Gr.

An adsorb and shuttle mechanism has been proposed to explain the advantage of TiO₂ coated with adsorbents. Adsorb and shuttle is an approach that uses a photocatalyst that consists of two phases; the first phase adsorbs the substrate and transfers it via diffusion to the second phase, the photoactivated site (Langford et al. 2014). In the current study, graphene is expected to act as the adsorbent phase which absorbs contaminants and transfers them to photoactive sites on the surface of the TiO₂. However, due to the weak adsorption of sulfolane onto the TiO₂-Gr particles, the adsorb and shuttle phenomenon was not prominent.

Past research has suggested that the reduction of graphene from graphene oxide during the synthesis of TiO₂-Gr leads to agglomeration and loss of the 2-dimensional structure of graphene (Yang et al. 2014). This significantly alters graphene's electrical conductivity, surface area and optical transparency, potentially blocking active sites on the surface of TiO₂. Reducing the surface area of TiO₂ exposed to irradiation and water molecules also reduces electron hole and hydroxyl radical formation, therefore, reducing photocatalytic activity (Yanhui Zhang et al. 2011).

Table 1. Adsorption of different contaminants on the surface of TiO₂ and TiO₂-graphene composites

Type of contaminants	Percent Adsorbed after 30 Minutes	
	TiO ₂	TiO ₂ -Gr
Sulfolane	< 3%	< 3%
Phenol	5%	< 3%
Methyl orange	< 3%	13%

3.2 Application of the TiO₂-Gr composite with Blue LED to Treat Organic Contaminants

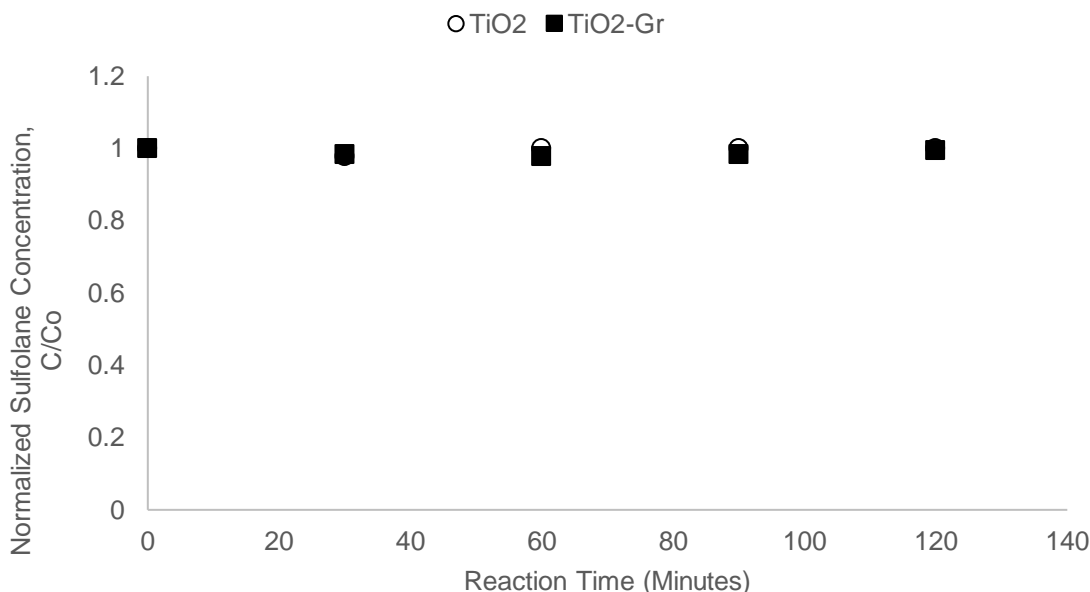


Figure 2. Photocatalytic degradation of 10ppm of sulfolane under 460nm irradiation, using 2000ppm of TiO₂ and 2000ppm of TiO₂-Gr

To study the performance of the photocatalysts in visible light, sulfolane, phenol and methyl orange degradation experiment were conducted in the presence of visible light with a wavelength of 460nm (blue light). The normalized concentration of sulfolane, phenol and methyl orange over 2 hours of reaction time are shown in figures 2, 3 and 4, respectively.

The results depicted in figure 2 show that neither TiO₂ nor TiO₂-Gr were able to degrade sulfolane under blue light conditions. Because of its relatively high band gap (~3eV), TiO₂ can only utilize wavelengths of light less than 385nm to produce hydroxyl radicals (Kim et al. 2012; Chen et al. 2002). The blue LED light used in these experiments displays its maximum emission at 460nm. The results from the current study showed that the emission spectrum used could not sufficiently excite TiO₂. Studies that use graphene as a means of extending the band gap of TiO₂ have shown that TiO₂-graphene composites can utilize longer wavelengths of light (Yupeng Zhang and Pan 2011; Posa, Annavaram, and Somala 2016). These studies

claim that the addition of graphene leads to better charge separation, slower recombination and more efficient production of radical species on the surface of TiO₂. However, this was not observed in the degradation of sulfolane, in the current study. In addition to the inefficient photon utilization by photocatalysts, the weak adsorption of sulfolane onto the surface of both catalysts also inhibits the degradation of this target compound.

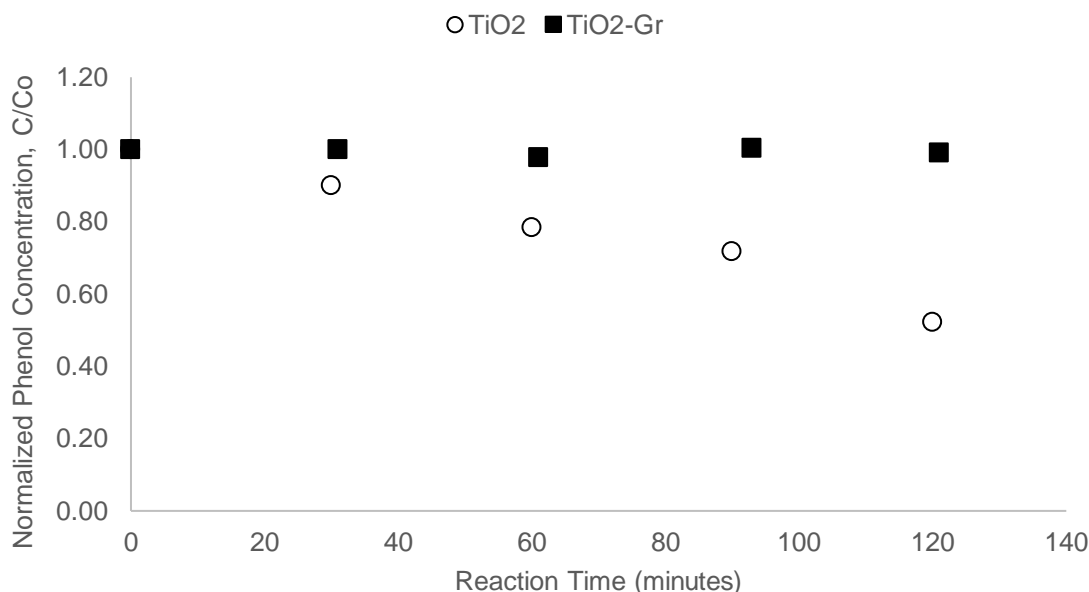


Figure 3. Photocatalytic degradation of 10ppm of phenol under 460nm irradiation, using 2000ppm of TiO₂ and 2000ppm of TiO₂-Gr

Photocatalytic degradation of phenol and methyl orange using TiO₂ and TiO₂-Gr in the presence of blue led light are shown in Figure 3 and Figure 4. 48% of phenol was degraded by TiO₂ in 2 hours while no significant degradation was seen in the sample with TiO₂-Gr. A key observation is that, while 48% of phenol degradation was achieved by TiO₂ in blue LED light, less than 2% of sulfolane was degraded using the same photocatalyst and irradiation conditions. This is because the overall degradation of a contaminant during photocatalysis is governed by a series of intermediate steps including adsorption onto the catalyst surface as well as oxidation by radical species (Istaván, László, and Dombi 1999). The Langmuir Hinshelwood model is commonly used to describe the kinetics of heterogeneous catalytic processes and can be formulated as

$$[1] \frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r K C_0}$$

where, r_0 and k_r are the initial reaction rate and the limiting rate constant at the specific experimental conditions, K and C_0 are the equilibrium adsorption constant and initial concentration of the substrate. This model shows that increases in the equilibrium constant of adsorption (K) leads to increases in the rate of reaction (r_0) (Kumar, Porkodi, and Rocha 2008). In comparison to sulfolane, phenol exhibited a higher amount of adsorption on the surface of TiO₂ during the adsorption experiment (5%). As a result, the lower final concentration of phenol achieved during the experiment using TiO₂ can be attributed to a higher degree of adsorption onto the TiO₂ particles.

Similar to sulfolane, phenol was not effectively degraded by TiO₂-Gr under blue light. Less than 3% of the initial concentration of phenol was adsorbed by the TiO₂-Gr at the end of the adsorption experiment, as shown in table 1, indicating that the addition of graphene into TiO₂ decreases its capacity to adsorb phenol.

The results from the methyl orange degradation experiments are shown in Figure 4. There was a 25% reduction in methyl orange concentration in the sample with TiO₂-Gr and 15% was degraded from the sample with TiO₂. The results from the 30-minute dark time experiment showed a 13% reduction in methyl orange concentration in the presence of TiO₂-Gr, whereas, less than 3% reduction was achieved in the sample with TiO₂. Many studies have used dyes, such as methyl orange, to test the photocatalytic performance of TiO₂-Gr and demonstrated its enhanced photocatalytic performance in comparison to TiO₂ (Khalid et al. 2013; Jiang et al. 2011; J. Li et al. 2013). The composite's improved performance was attributed to strong adsorption resulting from the π - π conjugation between dyes and the aromatic component of graphene (Pan et al. 2012). The electronic properties of graphene are also said to enhance photoactivity of the composite by suppressing recombination of electron-hole pairs. TiO₂-Gr was only seen to improve degradation of methyl orange and did not exhibit any improvement in reduction of sulfolane or phenol concentration in the current study.

The contaminants investigated in this study each display a varied response to different light conditions in addition to a unique interaction with the surface of the photocatalysts. For example, methyl orange displays strong absorption in the 460-470nm range (Gomez et al. 2014). Since 460nm LED lights were used as the source of irradiation in methyl orange degradation, photosensitization of methyl orange may facilitate in the degradation of this contaminant in addition to photocatalytic degradation. Phenol and sulfolane were not expected to display any photosensitization since both chemicals lack absorption bands beyond $\lambda = 300\text{nm}$ (Yu et al. 2016).

Based on this study, we hypothesize that contaminants with higher absorbance in the visible range and better adsorption onto graphene are more susceptible to enhanced degradation in the presence of TiO₂-Gr and visible irradiation. The degradation of these contaminants may be due to adsorption onto the TiO₂-Gr surface, attack by radical species as well as photosensitization.

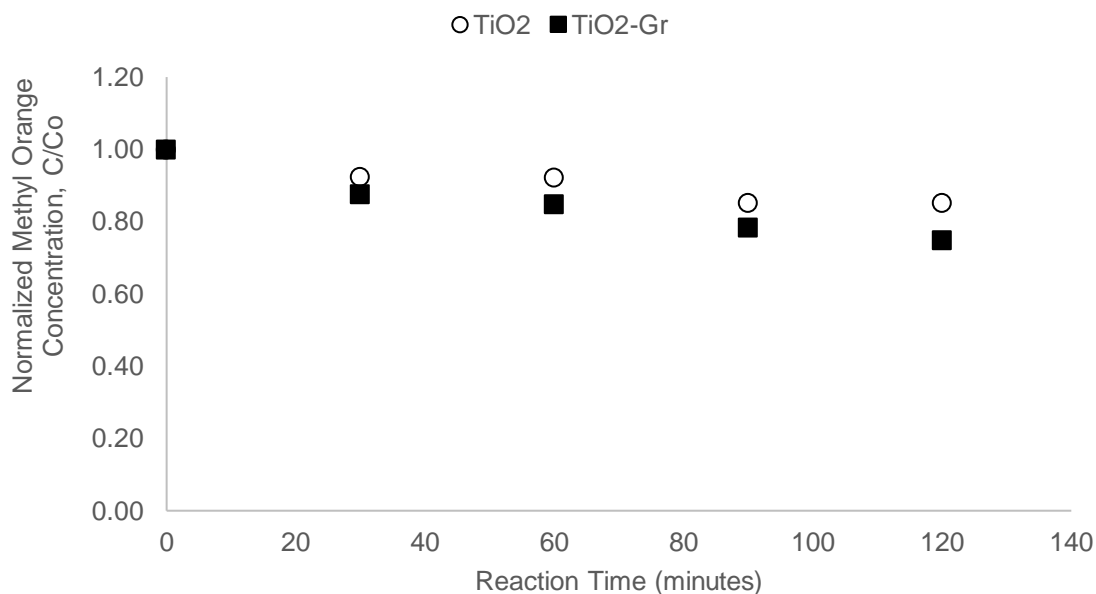


Figure 4. Photocatalytic degradation of 10ppm of methyl orange under 460nm irradiation, using 2000ppm of TiO₂ and 2000ppm of TiO₂-Gr

4. CONCLUSION

TiO₂-Gr composite was synthesized using the hydrothermal method and used to show photocatalytic activity to degrade sulfolane, phenol and methyl orange. The major findings of this study are summarized below:

- Both TiO₂ and TiO₂-Gr were able to degrade sulfolane when irradiated with 365 nm light. 89% removal of sulfolane was achieved with TiO₂ powder, whereas only 34% was degraded by TiO₂-Gr.
- No significant degradation of sulfolane was detected by either photocatalysts when placed in 460 nm irradiation
- TiO₂ was able to degrade 48% of phenol under 460nm irradiation. However, the concentration of phenol stayed constant in the sample with TiO₂-Gr, indicating negligible degradation.
- For the degradation of methyl orange under 460nm, TiO₂-Gr performed better than TiO₂ degrading 25% of methyl orange whereas only 15% was degraded by TiO₂
- The addition of graphene to TiO₂ improved methyl orange adsorption, decreased phenol adsorption and had no significant impact on sulfolane adsorption when compared with the powdered TiO₂ photocatalyst

Based on these results, the performance of TiO₂-Gr as a photocatalyst was shown to be dependent on the contaminant's optical properties and its ability to adsorb onto the surface of graphene.

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