

Sunlight mediated enhanced removal of metoprolol using graphitic carbon nitride (g-C₃N₄)

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Abstract. Graphitic carbon nitride (g-C₃N₄) is a photocatalyst that has recently been given a lot of attention due to its effectiveness in wastewater and environmental treatment, solar energy utilization, biomedical applications, etc. In this study, g-C₃N₄ was synthesized and characterized to carry out the degradation of metoprolol tartrate salt (MET), which is classified as an emerging contaminant. MET is one of the most commonly used pharmaceuticals to treat patients with cardiovascular diseases and disorders, a common disease in Malaysia. Recent discoveries of MET in surface waters and drinking water raise awareness and concerns. g-C₃N₄ was synthesized using solid urea by placing it in a muffle furnace of 550°C for 3 hours. The photocatalytic activities of g-C₃N₄ were investigated by photodegradation of MET, g-C₃N₄ of different dosages were added into MET-containing solution, and a dark reaction was carried out for 24 hours for complete adsorption equilibrium. Various physical and chemical analyses were conducted to elucidate the properties of g-C₃N₄, such as FESEM, FTIR and UV-Vis. The absorbance and reflectance graphs of g-C₃N₄ show that there will be higher absorption in the visible light spectra. The results show that the optimum dosage to treat 10 ppm of MET is by using 0.3 g of g-C₃N₄. Under sunlight irradiation of 4 hours, the degradation of MET achieved 54.6% of removal. Hence, it proves that g-C₃N₄ nanosheet can be applied to remove complex pollutants such as MET under sunlight irradiation. This path is an alternative removal method for MET in a sustainable approach.

Introduction

Pharmaceuticals and personal care products (PPCPs) pollutants are a highly recalcitrant aquatic micropollutant that severely harms the water source. Pollutants such as metoprolol, amoxicillin, ciprofloxacin, triclosan, carbamazepine are common PPCPs pollutants that are even detected at the tap water source in Kajang and Putrajaya, Malaysia [1,2]. This is an alarming and needed immediate remediation as such pollutants will pose adverse effects to human growth, allergies, lung diseases, obesity, and other waterborne diseases. Furthermore, PPCPs pollutants can generate various toxic effects on aquatic life. It will retard the reproduction of aquatic diseases. Furthermore, PPCPs pollutants can generate various toxic effects on aquatic life. It will retard the reproduction of aquatic life and increases the rate of malformation and mortality. Critically, most of these pollutants are persistent and pass through conventional biological treatment systems without any significant changes in their chemistry or concentrations. Moreover, the conventional treatment processes for water, such as filtration, coagulation and chlorination usually remove part of the PPCPs. [3] A promising treatment option for eliminating PPCPs completely from water is advanced oxidation technology (AOPs) which can degrade various active PPCPs pollutants in water based on the generation of active radicals.

In AOPs based on solar photocatalysis, a heterogeneous catalyst is employed to activate the generation of reactive oxygen species (ROS) through the free electron mobility mechanism under the presence of sunlight. The intensity of sunlight exceeded the catalyst bandgap energy will then excites the electron from the valence band to the conduction band. It will then generate an electron-hole pair that leads to a series of electrons mobility to the photodegradation of pollutants [4,5]. The movement of these electrons and holes leads to the formation of active radicals. This ROS formation is responsible for breaking the target PPCPs pollutants' and degrading them down into harmless by-products. These radicals' strong oxidation potential can destroy stable bonds and unreactive organic molecules to form organic intermediates, resulting in CO_2 and H_2O [6]. Due to the importance of generating these active radicals, sunlight mediated photocatalysts is important to maximise the absorption of sunlight for the generation of active radicals. Therefore, it can promote the massive generation of ROS and improve photocatalytic degradation efficiency. Moreover, such photocatalysts can enhance the entire solar spectrum's harvesting to promote a sustainable water treatment process.

The well-known TiO_2 semiconductor is effectively removing different organic pollutants due to its unique properties. The successful application of this catalyst in organic pollutants removal had led to the other environmental application such as PPCPs. However, despite its advantages, it possesses a major drawback of limiting its absorption ability only under the UV light region due to the wide bandgap energy of 3.2 eV. This will retard the ability of TiO_2 to fully utilise the sunlight energy to generate active radicals to promote sustainable photocatalysts. Therefore, enhancing its photosensitivity to utilise the entire solar spectrum from UV is important. Therefore, g- C_3N_4 could be the best alternative to overcome the drawbacks of TiO_2 . This is due to the unique properties of g- C_3N_4 of having strong ability in harvesting the visible light. It will promote the maximise utilisation of solar spectrum to generate active radicals. Hence, this study will focus on the simple synthesis of g- C_3N_4 in removing MET under sunlight irradiation.

Material and Methods

Material

Synthesis of g- C_3N_4

Decomposition of g- C_3N_4 using thermal approach was done by using the precursor of urea. 73g of urea was dried in an oven at a temperature of 80°C for 24h. The dried sample was then placed in a crucible before transferring to a muffle furnace. The temperature is set to 550°C and heated for 3h. Then it formed a yellowish product of g- C_3N_4 . To remove any impurities in the product, nitric

acid and ultrapure water were used to wash the product. It then repeated the washing three times. Finally, the sample was dried in an oven at 80°C overnight [7].

Characterisation

The morphology structure of g-C₃N₄ was analysed using the Field emission scanning electron microscope, (FESEM) Jeol JSM 7601. The presence of the functional elements of g-C₃N₄ was analysed using the Fourier transform infrared (FTIR) spectrum between 400 to 4000 cm⁻¹ using Perkin Elmer Spectrum 400 Spectrophotometer. The optical absorbance ability was examined by using UV-Vis diffuse reflectance spectra, (UV-DRS) with white standard reference (BaSO₄).

Photodegradation of MET

The sustainable g-C₃N₄ photocatalytic activity was evaluated using the removal of metoprolol (MET) under sunlight irradiation. First, 0.3 g and 0.5 g of the prepared photocatalysts (g-C₃N₄) were added to the beakers that contained 10 ppm of MET. Next, the dark reaction was carried out for 24h to achieve an adsorption and desorption equilibrium. Then, it was followed by 24h of dark reaction before it underwent sustainable photocatalysis of MET using sunlight as the light source over 4h. Finally, the beakers were relocated to a location fully exposed to sunlight, as shown in Fig. 1. Samples were collected every 15 minutes intervals. Before conducting High-Performance Liquid Chromatography (HPLC) analysis, the samples will be centrifuged and filtered using a syringe filter. The solvent was filtered using a nylon membrane filter of 0.45µm porosity before conducting the HPLC analysis.

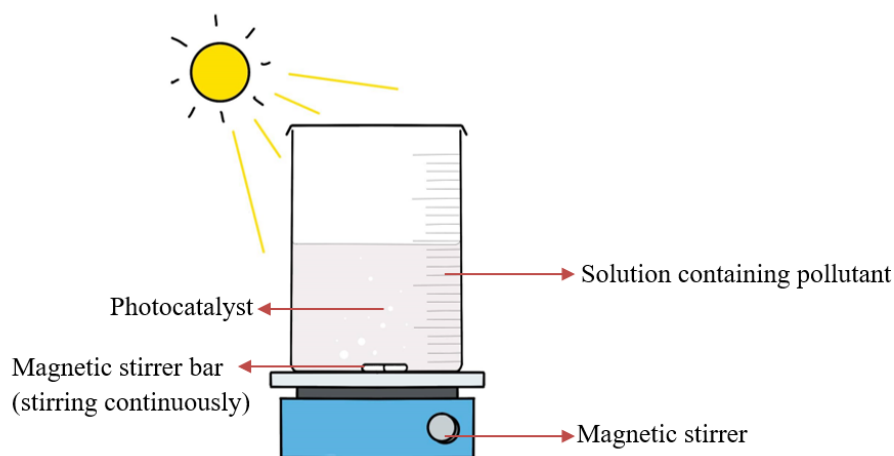


Figure 1: Photocatalysis analysis setup up

Results and Discussion

FESEM analysis is performed to study the microstructure and morphology of the as-synthesized g-C₃N₄, as shown in Fig. 2. It showed that pure g-C₃N₄ photocatalysts displayed fibre-like nanosheets. With the increased magnification, it observed that the nanostructures of g-C₃N₄ are uneven surfaces. In addition, the surfaces are rough and porous. Other researchers also observed similar structure nature and proved the successful synthesis of g-C₃N₄ [8].

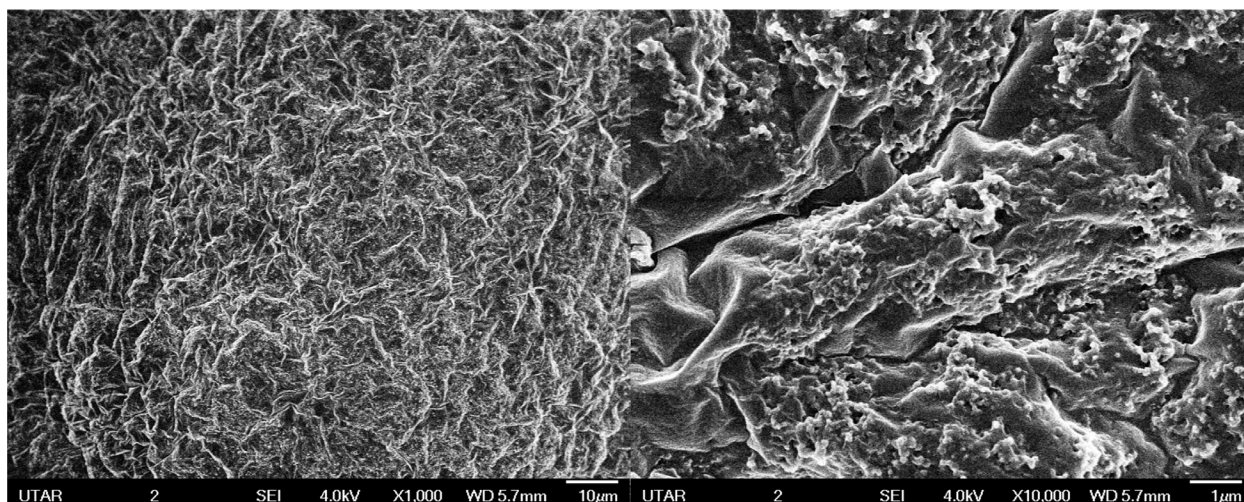


Figure 2: FESEM images of g-C₃N₄

The functional groups of g-C₃N₄ were analysed by FTIR analysis, as shown in Fig. 3. It can be seen that the band was detected at 3413 to 3234 cm⁻¹, which was caused by the stretching vibration of N-H bonds and surface adsorbed molecules. Apart from that, a few peaks from 1200 to 1700 cm⁻¹ were observed, indicating the CN heterocycles stretching modes. In addition, 810 cm⁻¹ peak is caused by the tri-s-triazine units breathing mode, while the consecutive peak of 822 cm⁻¹ is caused by the N-H bonds deformation mode [9]. This observation confirmed the presence of successful synthesis of g-C₃N₄.

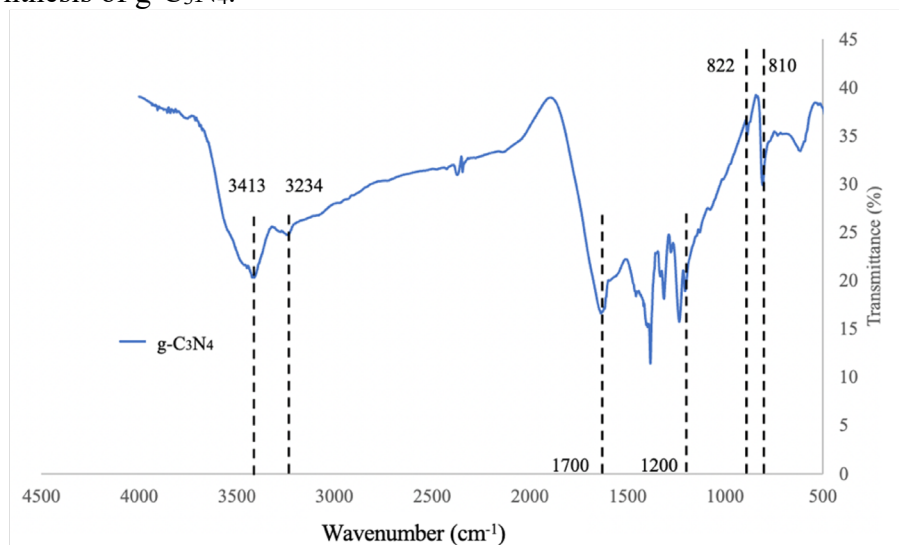


Figure 3: FTIR spectra of g-C₃N₄

The UV-DRS analysis was used to measure the absorption and reflection of g-C₃N₄. As observed in Fig. 4, the g-C₃N₄ photocatalyst possesses a very strong absorbance in UV and visible light regions. This strongly indicates the huge potential of g-C₃N₄ in absorbing the entire solar spectrum to generate active radicals. Due to the strong light g-C₃N₄ harvesting ability, it is the most promising photocatalyst compared to conventional TiO₂ and ZnO, which are limited to UV light absorbance. The harvesting of the entire solar spectrum promotes the excessive electrons and holes generation, which are responsible for the active radical's generation. The formation of these active radicals then be responsible for the removal of MET under sunlight irradiation.

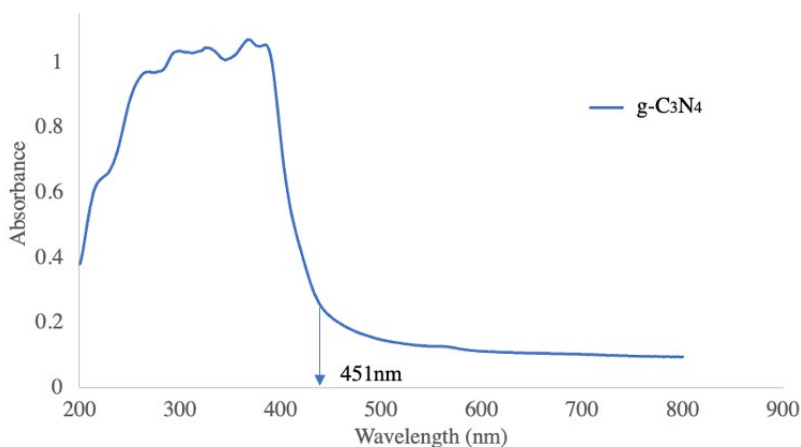


Figure 4: UV-Vis spectra of g-C₃N₄

The MET removal efficiency is shown in Fig. 5. It is observed that there is no degradation of MET during the 24h dark reaction. Thus, it can conclude that MET is not favourable to self-degradation without the presence of any catalyst. In addition, there is no significant removal of MET in the absence of a light source. This is mainly due to the non-photosensitizing properties of MET. Hence, MET degradation solely depends on the photocatalytic degradation of g-C₃N₄ and the light source. However, in Fig. 5, the blank graph increased to around 1.3. This might be due to the clinging of materials in the column contamination, causing some of the graphs to be not symmetrical due to minor errors. Upon the sunlight illumination, MET photodegradation took place rapidly and found that 0.3 g and 0.5 g of g-C₃N₄ resulted in the removal efficiency of 54.6% and 51.6%, respectively. Therefore, it can conclude that 0.3 g is the optimum catalyst dosage for MET removal under sunlight irradiation.

On the other hand, the research found that increasing the photocatalyst dosage did not drastically increase the photodegradation of MET. This is mainly contributed to the optimization of g-C₃N₄ in generating electrons and holes. Furthermore, the electron and hole pairs will recombine and form heat. This retarded the generation of active radicals.

The enhancement of MET removal by g-C₃N₄ is mainly contributed by the strong UV and visible light absorbance that led to the formation of electron and hole pairs. Once the g-C₃N₄ is illuminated with sunlight, it forms the electrons and holes at the valance and conduction band. The free electrons and holes will undergo a redox reaction to form active radicals such as hydroxyl and super anion radicals. These two active radicals will then attack the pollutant and break its component to form H₂O and CO₂. Therefore, the role of photocatalysts such as g-C₃N₄ will provide practical solutions to tackle the complex nature of the pollutants.

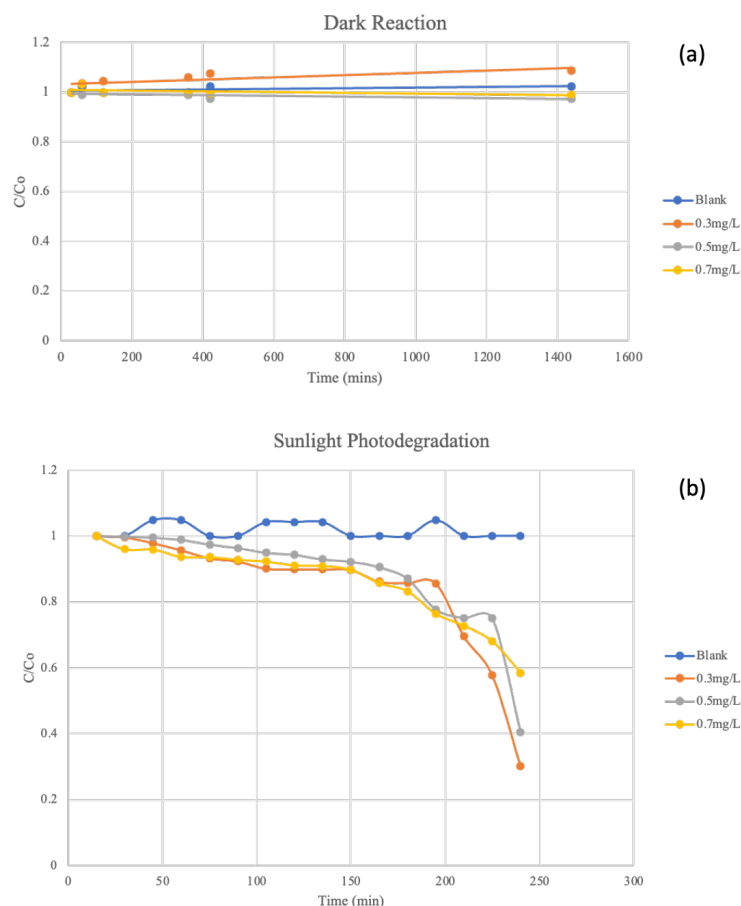


Figure 5: (a) dark reaction and (b) sunlight irradiation for removal of MET

Conclusion

In summary, the usage of $g-C_3N_4$ proves its ability to remove MET under sunlight irradiation effectively. The study of different dosages of photocatalyst showed that 0.3g is an optimum catalyst dosage for maximum removal of MET within 4h of sunlight irradiation. This research strongly indicates that MET will not undergo self-degradation, and the $g-C_3N_4$ catalyst must assist it. This is mainly due to the non-photosensitizing effect of MET. The superior $g-C_3N_4$ properties contribute to this research's positive achievement, that they can absorb UV and visible light due to the low band gap energy. This leads to the massive generation of electron and hole pairs. With the free electrons and holes, it then triggered the active radical's production that are responsible for degrading MET. Hence, this study proves the ability of $g-C_3N_4$ to degrade MET under sunlight irradiation effectively. This positive outcome will surely path a new direction in the field of photocatalysts in removing complex pollutants and promote sustainable remediation.

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