Enhancement of g-C_3N_4 via Acid Treatment for the Degradation of Ciprofloxacin Antibiotic

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Abstract

The viability of graphitic carbon nitride (g-C_3N_4) in photocatalytic discipline has been studied before but its extensive usage has been halted due to large band gap energy. Therefore, this study is to enhance the photodegradation efficiency of g-C_3N_4 by treating them with acid. The precursor of synthesizing the photocatalyst, melamine was treated with several acids to determine which acid treatment would yield the best antibiotic ciprofloxacin removal. The melamine was calcined at 550 °C for two hours to produce g-C_3N_4. The experiment outcome was that g-C_3N_4 treated with sulphuric acid have the highest performance with 71.3% of ciprofloxacin removal after 120 minutes under visible light irradiation. FESEM, BET, FTIR, and XRD analysis were also performed on the as-developed catalyst. As for overall result, it is found that the g-C_3N_4 treated with H_2SO_4 exhibited the best ciprofloxacin removal efficiency in comparison to the pristine g-C_3N_4 and g-C_3N_4 treated with HCl and HNO_3.

Keywords: graphitic carbon nitride, acid treatment, degradation, antibiotics

Article Info

Received 4th November 2019
Accepted 14th February 2020
Published 1st April 2020
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ISSN: 1823-7010, eISSN: 2600-7444

Introduction

Human daily lives highly depended on the continuity supply of clean water. However, the amount of clean and potable water supply has been diminished by human industrial activities when pollutants being discharged into the river or sea. One of the toxic chemicals being discharged is the considerable discharge of antibiotics in the pharmaceutical industry. Among the antibiotics discharged into the water, namely is ciprofloxacin (*1-cyclopropyl-6-fluoro-4-oxo-7-piperazin-1-ylquinoline-3-carboxylic acid*) [1]. These discharge has an adverse effect on human health and ecological balance, by lowering human body's resistance to antibiotics when they unknowingly consumed water that contain antibiotics. This may results lower efficiency of these antibiotics against virus when it is crucially needed [2]. Currently, the main treatment technologies for antibiotic wastewater are biological degradation, physical adsorption and chemical oxidation [3]. However, these methods practiced are not flexible, high operating costs, and low removal efficiency.

Globally, researchers are still exploring the possibility of replacing or improving current wastewater treatments with new technology. One of the technologies is advanced oxidation process, specifically photocatalytic process. Photocatalysis is considered to be safe, non-toxic, flexible, environmentally friendly, and economically viable as the photocatalysts are capable of repeated use without loss of catalytic activity [4]. Photocatalytic process would emphasize on utilizing the band gap between valence band and conduction band. The photocatalysts used, mostly semiconductors would harness light energy whenever irradiated to excites an electron as soon as the photon absorbed is equal or greater than the band gap. The excited electron would form a positive hole in the valence band, h^+ which considered to be strong oxidizing agents [5].

g-C_3N_4 is one of the emerging semiconductors used in photocatalysis process due to its interesting electronic band structure, high physiochemical stability, and can be synthesized conveniently by thermal annealing of nitrogen-rich precursors such as urea, thiourea, melamine and ammonium thiocyanate [6]. However, g-C_3N_4 have dubious properties as a photocatalyst such as high band gap energy and a rapid rate of the recombination of photogenerated electron-hole. These questionable features have lowered its catalytic activity potential and deterred the practical application of pristine g-C_3N_4 from being widely used as compared to other semiconductors. Thus, multiple strategies have been conducted in order to improve the viability of g-C_3N_4 and compensate these individual properties such as adding non-metallic elements by doping the photocatalysts and the development of a heterostructure system [7].

One of the methods is surface modification in which photocatalysts are treated with inorganic acids, such as HCl, HNO_3, H_2SO_4, H_3PO_4 and HF. These acids would improve the active site of the photocatalysts and consequently, more free radicals would be produced [8]. There are also studies reported on the improved photocatalytic performance when g-C_3N_4 is soaked in acids. One reported an improvement of photodegradation activity by treating g-C_3N_4 with HCl and HNO_3 in reducing aqueous Cr(VI) solution under visible light (λ>420 nm) [9]. Another research mentioned that samples synthesized from pre-treated melamine with H_2SO_4 would have the photocatalytic activity in H_2 production two times higher compared to the sample synthesized from the untreated melamine [10].

In this present study performed, three different acids were used to treat g-C_3N_4 which are HCl, HNO_3 and H_2SO_4 to improve the photocatalytic performance of the as-developed photocatalysts. The photocatalytic performance of the acid-treated g-C_3N_4 were evaluated via the removal of ciprofloxacin under visible light irradiation. This would be the first report to study exclusively the effect of various acid treatment in improving the photocatalytic degradation performance of g-C_3N_4 in treating the pharmaceutical wastewater according the author's knowledge.

Materials and Methods

Materials and Characterizations

Melamine, $C_3H_6N_6$ (CAS 108-78-1), sulphuric acid, H_2SO_4 (assay: 98%) and nitric acid, HNO_3 (assay: 65%) were purchased from Merck Sdn Bhd. Hydrochloric acid, HCl (assay: 37%) was purchased from Fischer Scientific Sdn. Bhd. The chemicals used were analytical grade and no purification were required. Deionized water was used for the preparations of the solutions.

The photocatalytic degradation activities of as-prepared acid treated-g-C_3N_4 were evaluated by analyzing the absorbance at the characteristic band of 278 nm which the peak for ciprofloxacin using ultraviolet-visible (UV-Vis) spectrophotometer. In addition, Field Emission Scanning Electron Micrograph (FESEM), Brunauer-Emmett-Teller (BET), Fourier-Transform Infra-Red (FTIR) and X-Ray Diffraction (XRD) analysis were conducted to characterize the photocatalysts.

Acid Treatment of Melamine

In a typical solid-liquid state reaction, three sets of beakers with 5.0 g of melamine was individually dissolved in 10 ml of concentrated acids (HCl, HNO_3 and H_2SO_4) and the mixtures were stirred for one hour. The samples were then filtered and washed using deionized water and ethanol. The samples were left in the oven to be dried overnight at the temperature of 80°C.

Synthesis of g-C_3N_4 by facile template free method

Four separate alumina crucibles, each one of them separately filled with untreated melamine, melamine previously treated with HCl, HNO_3 and H_2SO_4 were placed inside a furnace and heated to the temperature of 550°C for two hours. Once the samples cooled down, the yellow solids were ground separately. The yellow powder obtained was the photocatalyst material, g-C_3N_4.

Photodegradation activity of g-C_3N_4 and performance comparison

For the evaluation of photodegradation activity, 0.1 g of prepared g-C_3N_4 (untreated melamine, acid treated melamine) were added into four separate beakers, each filled with 100 mL of ciprofloxacin solution with the initial concentration, C_o of 10 mg/L. To achieve an adsorprtion/desorption equilibrium, the reaction sample was left for 60 minutes in dark reaction conditions before the light irradiation stage. During the light irradiation stage, the reaction mixture was irradiated under a 500W halogen lamp for 120 minutes. 4 mL of the samples were siphoned out using a plastic syringe fitted with 0.45 µm filter at 15 minutes intervals each and labeled as

mL_t, m-HCl_t, m-HNO_{3t} and m-H_2SO_{4t} accordingly. The collected filter aliquots were then analyzed using UV-Vis spectrophotometer (Model; Shimadzu, UV-1800) to obtain the concentration of ciprofloxacin at every sampling time. For the photodegradation analysis, the selected specific absorption peak of ciprofloxacin was 278 nm.

Photocatalysts Characterization

The surface morphology of each photocatalysts was observed by conducting FESEM analysis on the photcatalysts using Zeiss Sura 55VP instrument with a magnification of 1 – 30 Kx. The samples were coated with gold powder before the analysis to obtain better micrograph resolution.

As for BET analysis, the surface of the catalysts were further analysed using a micromeritic ASAP 200 Nitrogen adsorption apparatus to analyse the specific surface area, pore size and pore volume of each catalyst. Prior to the analysis, the photocatalysts were degassed at 110°C for 3 hours.

The FTIR analysis was conducted in the scanning range of 400 - 4000 cm^{-1} using Shimadzu 8400S Spectrometer and for XRD analysis, the crystalline structure of the photocatalysts were examined using X-Ray diffractometer (XRD; Model: X'Pert^3 powder and Empyrean, PANalytical), excited by Cu Kα radiation from 20 to 80° with a step size of 0.017° and exposure time of 51 sec/step.

Results and Discussion

Evaluation of Ciprofloxacin degradation efficiency

The rate of ciprofloxacin removal (degradation efficiency) was calculated and illustrated in Fig. 1. Deducing the results from the bar chart, it was found that H_2SO_4-g-C_3N_4 has the best photocatalytic degradation performance which is 71.3% of total ciprofloxacin removed within 120 minutes under visible light irradiation.

The efficiency of photocatalytic degradation of the catalysts increase in the following order: g-C_3N_4 < HCl-g-C_3N_4 < HNO_3-g-C_3N_4 < H_2SO_4-g-C_3N_4. Untreated g-C_3N_4 demonstrated the lowest photocatalytic degradation performance with only 58.3% of total ciprofloxacin removed after 120 minutes under the irradiation of visible light. The g-C_3N_4 treated with HCl and HNO_3 showed the results of 59.5% and 63.3 % of total ciprofloxacin removed respectively. Consistent with the findings reported in [9,10], that acid treated g-C_3N_4 performed better compared to pristine g-C_3N_4.

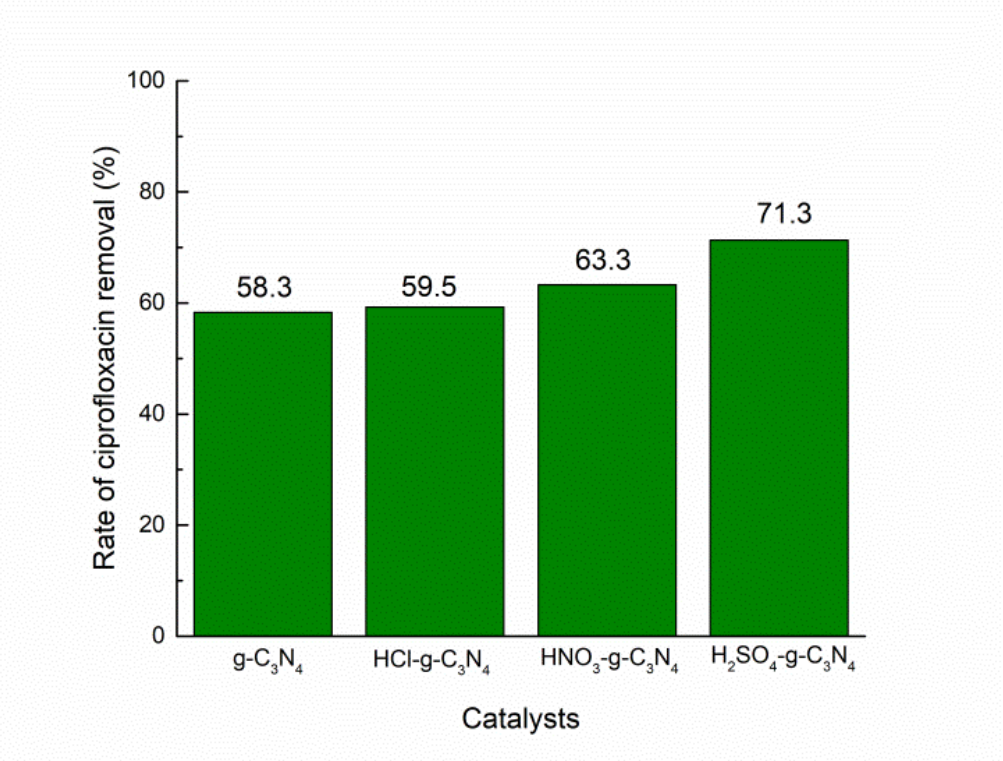

Figure 1: Photocatalytic degradation efficiency of acid treated g-C_3N_4 under light irradiation

FESEM Analysis

The g-C_3N_4 (Fig. 2a) and HCl-g-C_3N_4 (Fig. 2b) samples are composed stacked lamellar sheets with small grains formed on the surface of the HCl-g-C_3N_4, similar to the images reported in other literature [9,11,12]. The HNO_3-g-C_3N_4 (Fig. 2c) also has stacked lamellar textures with small pores formed on the sheets. As for H_2SO_4-g-C_3N_4 (Fig. 2d), the catalyst is seen to be porous compared to the previous three samples.

BET Analysis

Generally, the surface area of the pristine g-C_3N_4 derived from melamine is 8.526 m^2/g [9]. Interestingly, it was found that H_2SO_4-g-C_3N_4 have the highest surface area and pore volume compared to the other photocatalysts. The degradation efficiency can be associated with higher availability of photocatalytic sites with larger surface area as they possessed better adsorption and photocatalytic ability [10–12]. The data is presented in Table 1.

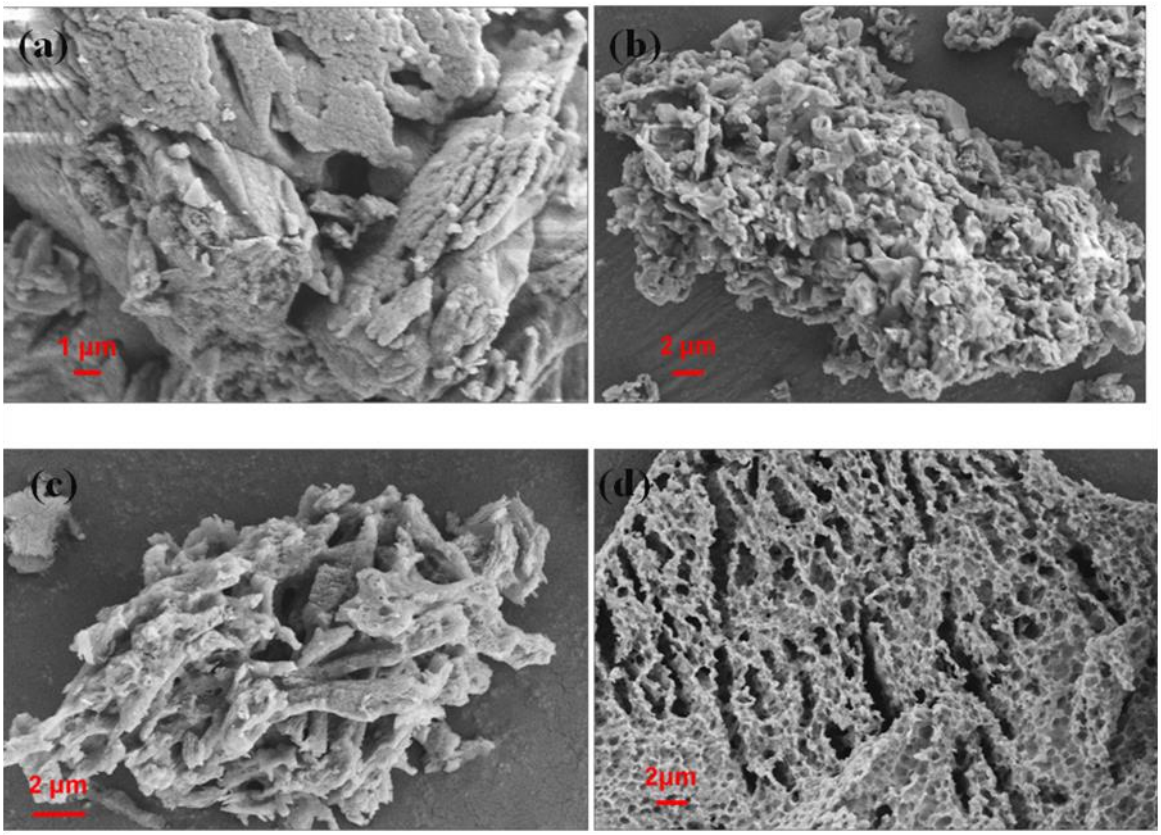

Figure 2: SEM images of (a) g-C_3N_4, (b) HCl-g-C_3N_4, (c) HNO_3-g-C_3N_4 and (d) H_2SO_4-g-C_3N_4

Table 1: Surface area and pore volume of g-C_3N_4, HCl-g-C_3N_4, HNO_3-g-C_3N_4 and H_2SO_4-g-C_3N_4

Photocatalyst	Surface Area (m^2/g)	Pore Volume (m^3/g)
HCl-g-C_3N_4	11.00	0.0578
HNO_3-g-C_3N_4	19.31	0.1252
H_2SO_4-g-C_3N_4	28.87	0.1820

FTIR Analysis

All of the as-developed photocatalyst shows a similar pattern of the FTIR spectra, as depicted in Fig 3. The peak at 806 cm^{-1} can be assigned to the s-triazine ring modes and the 888 cm^{-1} peak attributed to the deformation mode of cross-linked heptazine. Both bands at 1236 and 1317 cm^{-1} are assigned to the vibration modes of secondary bridging N atoms and primary amine groups. As for the 1407 cm^{-1} peak, it is related to the C-N stretching vibration of tertiary bridging N atoms in the centre of heptazine ring and the band at 1639 cm^{-1} is assigned to the C=N vibration mode. Generally, the peaks between 3000 to 3500 cm^{-1} contributed by uncondensed amine groups [11–14]. All four catalysts showed similar FTIR spectra, and this may be due to the introduction of the acid treatment would only caused structural changes to occur mostly on the catalyst surface layer [9,15].

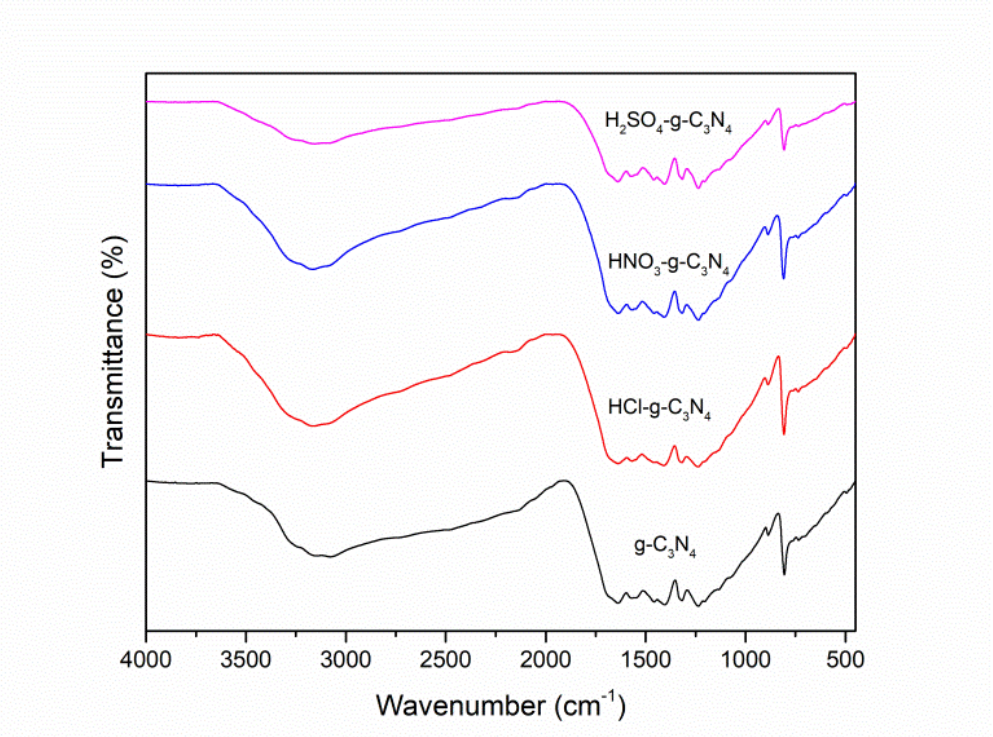

Figure 3: FTIR Spectra of g-C_3N_4, HCl-g-C_3N_4, HNO_3-g-C_3N_4 and H_2SO_4-g-C_3N_4

XRD Analysis

The XRD patterns for each catalyst are illustrated in Fig. 4. The samples displayed two consistent peaks, similarly reported in other literatures [9,11,14,16] with both located $2\theta \approx 13.4°$ and 27.6°. The peak at 13.4° is attributed to the in-plane structural packing motif of tri-s-triazine units. As for the peak at 27.6°, the peak corresponds to the interplanar stacking of the conjugated aromatic systems.

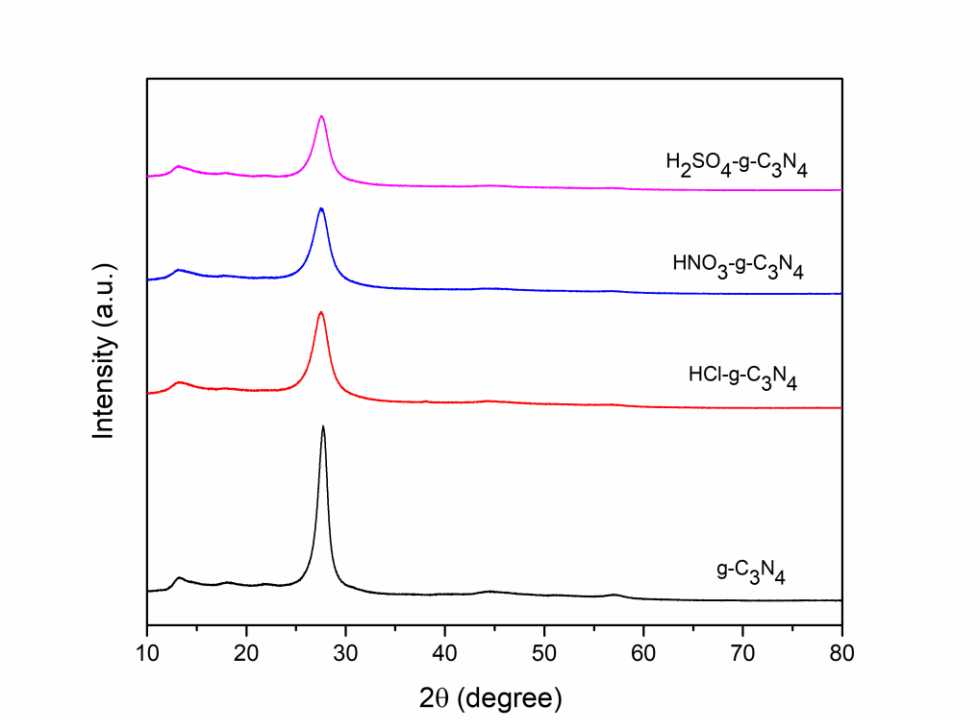

Figure 5: XRD pattern of g-C_3N_4, HCl-g-C_3N_4, HNO_3-g-C_3N_4 and H_2SO_4-g-C_3N_4.

Conclusions

In summary, the removal of ciprofloxacin antibiotics was successfully enhanced via acid treated-g-C_3N_4. The g-C_3N_4 treated with H_2SO_4 exhibited the best ciprofloxacin removal efficiency (71.3% removal) compared to the pristine g-C_3N_4 and g-C_3N_4 treated with HCl and HNO_3. The remarkable photocatalytic activity of this sample was attributed to the high surface area and large pore volume evidently from BET and FESEM analysis, respectively.

Acknowledgements

The authors gratefully acknowledge the financial support from Department of Chemical Engineering, Universiti Teknologi PETRONAS, Malaysia.

Author Contributions

Muhamad Kamarul Ariffin was involved in the experiments and paper write-up. Mohamad Fakhrul Ridhwan Samsudin, Francois Maeght, Coralie Goepp assisted in the experiments and data collection, while Suriati Sufian was supervising the whole research efforts.

Disclosure of Conflict of Interest

The authors declared there were no conflict of interest.

Compliance with Ethical Standards

Any work done during/for the research did not breach any ethical standards.

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