Fabrication of Covalently Linked Ruthenium Complex Onto Carbon Nitride Nanotubes For The Photocatalytic Degradation of Tetracycline Antibiotic

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Research Article

Keywords: Graphitic carbon nitride nanotubes (g-C3N4 NTs), Dichloro(p-cymene)ruthenium(II), Photocatalyst, Tetracycline antibiotics

Posted Date: November 22nd, 2021

DOI: https://doi.org/10.21203/rs.3.rs-1016964/v1

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Abstract

Due to the problem of direct disposal of effluents contains antibiotics to the environment and the emergence of resistant bacterial pathogens, the wastewater treatment of pharmaceutical industry has known as an importance research background. In this study, the refinement and photodegradation ability of one of the most widely used antibiotics, “tetracycline” was investigated by ruthenium complex immobilized on the modified graphitic carbon nitride nanotubes. For this purpose, graphitic carbon nitride nanotubes (g-C$_3$N$_4$ NTs) were successfully synthesized by the hydrothermal method and functionalized with 1,10-Phenantrone-5,6-dione ligand during another step. Then, the functionalized g-C$_3$N$_4$ NTs were reinforced with immobilization of dichloro(p-cymene)ruthenium(II) dimer. The structure and morphology of the prepared photocatalyst was studied by X-ray diffraction (XRD), fourier transform infrared (FT-IR), scanning, and transmission electron microscopy (SEM & TEM) analyses. In the following, the photocatalyst's ability to optically degrade the tetracycline antibiotics was performed in a suspension reactor equipped with a LED lamp (60 W) and effective parameters such as the amount of catalyst, irradiation time, temperature, and pH were optimized. The results showed that the immobilization of Ru complex onto functionalized g-C$_3$N$_4$ NTs improved the photocatalytic activity and increased the degradation efficiencies to amount 43%. Furthermore, COD analysis was used for the determination of the amount of mineralization and results showed that the mineralization of 10 mg/L tetracycline solution of about 90% can be performed using 20 mg of Ru (II) complex/ g-C$_3$N$_4$ NTs at pH=7 after 480 min without any additive oxidant.

1. Introduction

Tetracyclines are known as a group of broad-spectrum antibiotics that have a common basic structure and one of the most widely used these antibiotics is tetracycline. This antibiotic is used to treat humans and stimulate the growth of livestock and birds (Chopra and Roberts, 2001). According to the World Health Organization (WHO), the presence of this substance in nature is dangerous (Conde-Cid et al., 2020). Tetracycline finds its way to surface and groundwater through domestic and hospital effluents so livestock and poultry farms that it enters the human food cycle by drinking water and consuming fruits and vegetables (Fiaz et al., 2021). This antibiotic causes genetic resistance and accumulates in the skeletal tissues of the human body through the formation of a stable complex with calcium (Smith et al., 2015; D’Costa et al., 2011). Tetracycline is not biodegradable and disrupts in the biological treatment units, and also produces more toxic products in many chemical treatment processes such as chlorination and ozonation (Borghi et al., 2014; Park et al., 2007). On the other hand, the use of the surface adsorption technique only transfers tetracycline from one phase to another and does not eliminate its contamination (Homem and Santos, 2011). Therefore, it can be said that the common removal methods of organic contaminations are inefficient and troublesome for this antibiotic (Rodriguez-Narvaez et al., 2017). Instead, the advanced oxidation processes, especially photocatalytic systems, are a good way to remove these compounds and are based on the production of hydroxyl radicals (Hong et al., 2017; Al-Marzouqi et al., 2021; Chang et al., 2015). These radicals are able to oxidize all organic compounds to the stage of
carbon dioxide and water production (Zhang et al., 2018). Most of the photocatalysts presented so far are efficient only in the ultraviolet range (Vasei et al., 2019; Yadav et al., 2018), and since only a small percentage of sunlight is made of ultraviolet light and most of that is visible light, so it needs to design and fabrication of the new generation of active photocatalysts in the visible range. In recent years, a lot of research has been done on semiconductors that have a suitable gap and can be used in the visible range (Zhang et al., 2020; Yu et al., 2020; de-Moraes et al., 2021). Graphite nitride carbon is one of the semiconductors that has a smaller bandgap (∼2.7 eV) than many other common photocatalysts such as titanium oxide and zinc oxide, and as a result, it is more efficient at absorbing sunlight (Dong et al., 2014; Zhang et al., 2021). This substance is non-toxic, cheap and easy to prepare (Cui et al., 2018). However, the most important weakness of g-C₃N₄, which reduces its performance in optical degradation, is the rapid recombination of electron-hole pairs (Shi et al., 2021; Liu et al., 2021). Increasing efficiency in the optical degradation operations depends on the degree of separation of electron-hole pairs. To produce active oxygen species, it is necessary that the electrons and produced holes can react separately with the water or oxygen molecules around them (Chen et al., 2020). There are two major ways to solve this g-C₃N₄ problem and achieve maximum performance; First, changes in the morphology and particle size of the photocatalyst: The particle size of a photocatalyst has a large effect on the energy gap. As the particle size decreases along with increasing the width of the energy gap, and so its oxidation-reduction strength will increase (Singh et al., 2018). Second, the decoration of g-C₃N₄ with other conductive and semiconductor metals; these metals increase the absorption of visible light and the efficiency of the photocatalyst by producing hot electrons and injecting them into the semiconductor (Wang et al., 2017).

In the present project, the above two techniques were used to fabricate an efficient photocatalyst in the visible range. In this regard, the g-C₃N₄ nanotubes were synthesized instead of g-C₃N₄ bulk and it cause to improve the energy band gap and reduce the recombination rate of the electron-hole pair. In addition, the use of g-C₃N₄ nanotubes increases the surface area and has a positive effect on photocatalyst performance. To implement the second approach and further enhance the photocatalytic properties, the surface of the nanotubes was decorated with a ruthenium complex. The ruthenium complexes have the ability to absorb light in the wavelength range of 400-800 nm and cause the formation and injection of electrons into the photocatalytic system. In the end, the photocatalytic ability of Ru(II)complex/g-C₃N₄ NTs was investigated in the decomposition of tetracycline antibiotic under visible light and the effect of factors such as radiation time, amount of photocatalyst, pH, and temperature on degradation efficiency was investigated. The advantages of this method are maintaining the photocatalyst stability and reusability in the heterogeneous system.

2. Experimental

2.1. Material and methods

Cyanoric cloride (99%), and 1,10-Phenanthroline (99.5%) were purchased from Merck- Millipore chemical Co. and used as received. Melamine (99%), Dichloro(p-cymene)ruthenium(II) dimer (99%), and
Tetracycline (98%) were obtained from Sigma-Aldrich. The prepared Ru(II) complex/g-C₃N₄ NTs was characterized by Fourier transform infrared (FT-IR, Bruker, Germany, RT-DLATGS detector) spectroscopy, scanning electron microscopy (FE-SEM, TESCAN-MIRA3), transmission electron microscope (TEM, EM10c-100 KV) and the concentration of tetracycline solutions have been monitored using Ultraviolet-visible (UV-Vis) spectroscopy was performed in the range of 200–900 nm wavelength on a Cary 50 single detector double beam in time spectrophotometer (Varian, Australia).

2.2. Synthesis of g-C₃N₄ NTs

The preparation of g-C₃N₄ NTs was done in two separately steps. First, white crystals of melamine-cyanuric acid were prepared by a hydrothermal method briefly, 0.5 mmol of melamine and 0.5 mmol of cyanuric chloride were dissolved in 75 mL deionized water and kept stirring for 30 min. The resultant transport solution was transferred to an autoclave flask and maintained at 180°C for 6 h. After this time, the autoclave was cooled until to ambient temperature and the obtained white needle-like crystals were centrifuged and washed several times with deionized water to remove organic impurities and freezer dried for 24 hours.

The second step was the calcination process as follows the melamine-cyanuric chloride crystals were calcined at 450°C for 5 h with a heating rate of 1°C min⁻¹ under nitrogen inert atmosphere.

2.3. Functionalization of g-C₃N₄ NTs with phenantroline-5,6-dione

In order to functionalize graphitic carbon nitride nanotubes, 250 mg of g-C₃N₄ NTs along with 1 mmol of phenantroline-5,6-dione ligand were dispersed in 50 ml of acetonitrile and after equipping the reaction vessel with the condenser it was refluxed for 60 hours at 60 °C. At the end of the reaction time, the functionalized g-C₃N₄ NTs were collected by centrifugation and dried at 50 °C after washing several times with acetonitrile.

2.4. Synthesis of Ru (II) complex/ g-C₃N₄ NTs

A 250mL flask was charged with the g-C₃N₄ NTS bearing the phenantroline-5,6-dione ligand (250 mg), [RuCl₂(p-cymene)]₂ (0.2 mmol) and 200 mL anhydrous dichloromethane. The obtained suspension was refluxed for 2 h at 50°C. After that, the resultant product was separated through decanting of the solvent and the nanotubes were washed several times with dried dichloromethane to remove extra values of ruthenium moieties. according to ICP-OES analysis amount of Ru was 10 % in the obtained photocatalyst.

2.5. Study of the photocatalytic activity of Ru (II) complex/ g-C₃N₄ NTs
All photocatalytic reactions were performed in a 50 ml beaker containing 25 ml of tetracycline solution (10 mg/L). During irradiation of visible photons, the sample containing the nanocomposite was stirred by a magnetic stirrer to homogenize the system and prevent photocatalytic precipitation. The 60-watt visible light source was placed directly on top of the beaker at a distance of 15 cm from and at a distance of 15 cm from it, and despite the heat generated by the lamp, no cover was used. At the beginning of the test, from the moment that the samples were immersed in the solution, placed in the dark for 30 minutes to reach the adsorption /desorption equilibrium. The concentration of initial and residual tetracycline in the samples that irradiated by UV-Vis spectrometer at different times were measured after separating of nanocomposite by centrifuge and then the percentage of drug removal was calculated according to Equation 1.

Photocatalytic destruction (%) = \((C_0 - C)/C_0 \times 100\) (1)

In this equation, \(C_0\) is the initial concentration of tetracycline and \(C\) is the concentration of the tetracycline remaining in the solution, after the photodegradation reaction. It should be noted that all experiments were repeated twice and the average value was reported. In addition, the COD of the samples was measured every hour by FAS titration with potassium permanganate (Goh and Lim, 2008).

### 2.6. Adsorption kinetics study

The kinetic of photocatalytic degradation of pesticides in the heterogeneous oxidation systems with visible light follows the Langmuir-Hinslowwood kinetic model (Equation 2) (Wang et al., 2019; He et al., 2019; Wang et al., 2018).

\[
r = \frac{dC}{dt} = \frac{kKc}{1 + KC} \quad (2)
\]

Where \(r\), \(C\), \(t\), \(k\) and \(K\) are the oxidation rate (mg/L min), herbicide concentration (mg/L), irradiation time (min), reaction rate constant (1/min) and reaction adsorption coefficient (L/mg), respectively. At low initial concentrations of herbicides, Equation 2 is changed to the quasi-first-order equation (Equation 3).

\[
\ln \left(\frac{C}{C_0}\right) = kKt = k_{app}t \quad (3)
\]

By plotting \(\ln (C/C_0)\) versus \(t\), the slope of the diagram shows the apparent rate of photocatalytic degradation.

### 3. Results And Discussion

#### 3.1. Investigation of Synthesis of Ru (II) complex/ \(g-C_3N_4\) NTs
So far, various methods have been introduced for the synthesis of g-C\textsubscript{3}N\textsubscript{4}, all of which use nitrogen-rich precursors including cyanamide, dicyandiamide, melamine, urea, thiourea, triazine derivatives, and heptazine (Thomas et al., 2008; Alwin et al., 2020). One of the simplest and most common methods for synthesizing this substance is the condensation method (Zhao et al., 2005; Jin et al., 2015; Hu et al., 2017; Chen et al., 2020). In this method, the mentioned precursors are converted to g-C\textsubscript{3}N\textsubscript{4} at 550 °C. But the main challenge of this method is the variable condensation efficiency, which leads to the production of a product with a small surface area and, of course, limits its application to photocatalytic processes (Ismael and Wu, 2019). However, the surface area of g-C\textsubscript{3}N\textsubscript{4} depends on the type of precursor and synthesis conditions, and by changing the above factors, a high surface area can be achieved. Typically, the use of melamine precursors results in the production of g-C\textsubscript{3}N\textsubscript{4} with a high N/C ratio (Yan et al., 2009). The higher the N/C ratio, the lower the energy bandgap and the higher the photocatalytic property. If melamine is used in combination with an oxygen-containing precursor to making g-C\textsubscript{3}N\textsubscript{4}, the product has more porosity and a higher surface area (Zhao et al., 2019). The use of chlorine-containing precursors has a similar effect, increasing the porosity and surface area, possibly due to the evaporation of chlorine ions in the form of HCl (Goglio et al., 2008). The second approach to achieve a high surface area is to change the synthesis conditions to create nanostructures. Most reports on nanostructures derived from graphite carbon-nitride are about nanoporous and nanoplate (Gan et al., 2018; Bai et al., 2013). In addition to these two structures, nanotubes have recently been introduced as a new morphology of g-C\textsubscript{3}N\textsubscript{4}, which, due to their high specific surface area, regular crystalline walls available for mass transfer, have desirable semi-conductivity properties (Yin et al., 2017). There are two general methods for synthesizing g-C\textsubscript{3}N\textsubscript{4} NTs: First method, hard templating method (Marcos-Hernández and Villagrán, 2019), which is done by polymerizing the precursors in the created space of the template (such as silica) and then removing the template by reagents that dissolve the silica. Although the g-C\textsubscript{3}N\textsubscript{4} NTs obtained from this method has a high surface area, its crystallinity has decreased. Crystallinity is an effective parameter against the separation of excited charges in the photocatalytic process (Wanget al., 2014). The second method is the soft templating (Chen et al., 2021), which its general mechanism is based on the polymerization of nitrogen-rich precursors in the space that has been created by soft template such as trithion X10, P12, and F124 (Rastogiet al., 2008). The disadvantage of this method is the high polymerization temperature, which leads to the loss of the template before the complete formation of the nanotube. In the present project, g-C\textsubscript{3}N\textsubscript{4} NTs were synthesized by the joint polymerization of nitrogenous (melamine) and chlorinated (cyanuric chloride) precursors through the hydrothermal process without the use of any template. The cyanuric chloride is unstable under aqueous conditions therefore; it was converted to cyanuric acid as an oxygenated precursor created melamine-cyanurate crystals through a series of hydrogen bonds with melamine. Finally, the growth of these crystals within 6 hours and calcination at 450°C, it cause to produce g-C\textsubscript{3}N\textsubscript{4} NTs. Because of incomplete polymerization of melamine, there are free amine groups at the outer edges of the prepared g-C\textsubscript{3}N\textsubscript{4} NTs and these defects in the structure cause to balance in the energy bandgap and also it facilitates the functionalization of the surface. So here, the functionalization was done in the through formation imine band between carbonyls of phenantroline-5,6-dione ligand and free amines of g-C\textsubscript{3}N\textsubscript{4} NTs. In the end, the coordination of
immobilized bidentate ligands with dichloro(p-cymene)ruthenium(II) led to the stabilization of the relevant complex on the outer edges of g-C$_3$N$_4$ NTs. Scheme1 depicted the steps of the synthesis of the photocatalyst.

3.2. Catalyst characterization

3.2.1. Fourier transform-infrared spectroscopy (FT-IR)

The functional groups of melamine-cyanuric acid, g-C$_3$N$_4$ NTs, Ru(II) complex/g-C$_3$N$_4$ NTs samples were confirmed by FTIR spectroscopy. The melamine-cyanuric acid spectrum (Fig. 1a) is extremely crowded, which can be attributed to the formation of a complicated network of hydrogen bonds. The appeared peaks at 3088, 3230, and 3391 cm$^{-1}$ are due to the symmetric stretching vibrations of the amine groups of melamine cations that have shifted to shorter wavelengths (blue shift) than pure melamine (Sangeetha et al., 2013; Luo et al., 2019). The asymmetric stretching vibrations of the amine groups attributed to bored peaks around 2500-2700 cm$^{-1}$. In additional, the intense peak at 1731 cm$^{-1}$ is assigned to carbonyl stretching vibrations of cyanurate anions which produced from hydrolysis of cyanuric chloride. The strong peaks in region 1400-1700 cm$^{-1}$ corresponded to bending vibrations of N-H and stretching vibrations of C-N and C=N. These peaks in the assembly indicate the successful synthesis of melamine-cyanuric acid crystals. After pyrolysis treatment, the arrangement of the absorption bands was changed (Fig. 1b). For example, the intensity of absorption bands attributed to N-H groups dropped sharply in region >3000 cm$^{-1}$, and also the assigned peak of carbonyl at 1731 cm$^{-1}$ disappeared which confirmed the release of NH$_2$ and H$_2$O during pyrolysis treatment to the formation of g-C$_3$N$_4$. Figure 1c again shows the decreasing of the vibrations of the amino groups, which, together with the new appeared band at 1650 cm$^{-1}$, proves the chemical modification of the nanotubes through the formation of the imine band with phenantroline-5,6-dione ligand.

3.2.2. Ultraviolet and visible absorption spectroscopy (UV-Vis)

To get the UV-Vis absorption spectrum of g-C$_3$N$_4$ Nts, this material was dispersed in ethanol by ultrasonic bath for 20 minutes and then its adsorption was measured. As shown in Figure 2, g-C$_3$N$_4$ NTs have maximum adsorption at 368 nm, which has a blue shift (the transition to a higher energy level or shorter wavelength) relative to the bulk sample (Xin and Meng, 2013). In nanomaterials, the distance between the electron-hole is controlled by the particle size, so that as the particle size shrinks to the nanometer scale, the movement of excitons are limited and a transition in the optical spectrum is observed (Ren et al., 2016). In general, the transfer of optical spectrum to higher energies due to the decreasing of particle size means an increase in the forbidden band energy. The energy difference (in units of electron volts) between the highest valence band and the lowest conduction band is called the energy bandgap (Kumar et al., 2016). To calculate the bandgap energy of a material, the absorption coefficient parameter of the material must first be obtained. The absorber coefficient is an important parameter in optical applications and is calculated for a transparent thin film from the following relation:
\[ \alpha = \frac{1}{d} \ln \frac{1}{T} \]  

Here, \( d \) is the thickness of the thin film in nanometers and \( T \) is the percentage of light transmission. Since \( \text{g-C}_3\text{N}_4 \) has a direct energy gap, so by direct electron transfer between the capacitance band and the conduction band, the band gap energy \( (E_g) \) is obtained from the Tuac equation (5).

\[ (ah\nu)^{(1/n)} = A(h\nu - E_g) \]  

Here, \( A \) is constant, \( \alpha \) is the absorption coefficient, \( E_g \) is the width of the energy gap, and \( h\nu \) is the energy of the emitting photon with respect to the absorption spectrum of the synthesized \( \text{g-C}_3\text{N}_4 \) NTs. Also, \( n \) for \( \text{g-C}_3\text{N}_4 \) NTs with a straight and permissible bandgap is equal to 1/2. According to Figure 2, the energy gap of \( \text{g-C}_3\text{N}_4 \) NTs can be calculated by drawing \((ah\nu)^2(\text{eV.cm}^{-1})^2\) in versus of \( h\nu \) (eV) and extrapolation its linear part. This energy gap was obtained 2.96 eV.

### 3.2.3. X-ray diffraction (XRD)

The prepared melamine-cyanuric acid sample and its Ru(II)complex/\( \text{g-C}_3\text{N}_4 \) NTs have been characterized by X-ray powder diffraction technique (figure 3). The presence of sharp diffraction peaks in the XRD of the synthesized melamine-cyanuric acid sample during the hydrothermal process confirms that the obtained product is highly crystalline (Liu et al., 2017). The X-ray diffraction pattern changed completely after the pyrolysis process and the formation of \( \text{g-C}_3\text{N}_4 \) NTs nanotubes, followed by chemical modification.

New peaks have appeared around \( 2\theta = 13.1 \) and 27.2 and confirm the formation of graphite nitride carbon phases in the sample (Pattnaik et al., 2019). An important point that can be seen in this image is the decrease in the intensity of the peaks after heat treatment, which indicates the percentage of crystallinity of the sample is reduced, or in other words, the long-range order of the structure is reduced.

During the heat treatment, the carbon nitride surfaces appear to be oxidized and the layers separated. Also, due to the oxidation process, the structure is defective and its effects in reducing the peak intensity of this material have appeared. Another reason for the low intensity of peaks is the modification process when an element enters the structure of the compound through chemical bonding, causing the corresponding peaks to flatten or shift and due to the stabilization conditions of the complex, there is no possibility of ruthenium phases in the final structure.

### 3.2.4. Scanning Electron Microscopy (SEM)

Scanning electron microscopy provides useful information from topography and morphology of the prepared photocatalyst. Scanning electron microscope images of the sample are shown in Figure 5. These images were taken with different magnifications to determine the overall morphology of the sample and how the nanotubes are arranged. As you can see, the study sample contains clusters of orderly nanotubes and the amount of unwanted particles in that is very low.
To determine the composition of the elements in the prepared photocatalyst, the distribution of active sites, and to determine whether the ruthenium complex is embedded in the surface of the nanotube matrix or in the inner part of the matrix, two complementary analyzes of energy-dispersive X-ray pattern and element distribution map (EDS & Map) were used. The EDS spectrum confirmed the presence of the elements carbon, nitrogen, ruthenium, and chlorine with the appearance of the corresponding peaks and the mapping analysis of polymer shows uniform distribution and non-accumulation of elements that enhance the properties of the photocatalyst.

3.2.5. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) images showed that the structure of g-C$_3$N$_4$ is in the form of hollow curved tubes with an outer diameter of less than 10 nm and a length of several hundred nanometers (Figure 5). It appears that after chemical functionalization of nanotubes and loading of ruthenium (II) complex, failure has occurred in areas where defects such as pentagons and heptagons. In addition, the modification process has resulted further distance between the nanotubes, which has a constructive effect on increasing the surface area of the photocatalyst. The Ru(II) complex/g-C$_3$N$_4$ NTs show accumulations in some areas, which possibly due to the agglomeration of graphitic nanotubes. This re-stacking of graphitic nanotubes is dependent on strong van der Waals forces and π-π interactions of sp$^2$ structures and hydrogen bonding.

3.3. Investigation of effective factors in optical degradation of tetracycline

3.3.1. Influence of amount of photocatalyst

As shown in Figure 6, the degradation efficiency of tetracycline increased with increasing photocatalyst concentration to 30 mg, after which the degradation efficiency remained almost constant. This can be attributed to the fact that when all the antibiotic molecules landed on the nanotubes, the excess amount of photocatalyst due to the lack of antibiotic molecules had no effect on the percentage of degradation and even slightly reduced the reaction rate. The decreasing in reaction rate at a dose of 40 mg was caused by two main factors. First; g-C$_3$N$_4$ nanotubes tend to agglomeration due to their nanometric size and high surface energy, and when the concentration of these nanotubes exceeds a certain limit, the activated nanotubes will be deactivated by contact with the base catalyst, and to follow it, the catalytic efficiency decreases. Second, with the increasing amount of photocatalyst, the turbidity increased and the light scattering occurs due to the collision of optical rays with the catalyst particles scattered in the solution and a number of light photons lose their energy and thus the efficiency of photocatalytic processes decreases.

3.3.2. Influence of irradiation time
To investigate the effect of irradiation time on degradation efficiency, a certain concentration of tetracycline was exposed to an optimized amount of photocatalyst (30 mg) and a frequency of 60 watts at different times. The results are shown in Figure 7. As you can see, the percentage of antibiotic degradation increased with increasing reaction time, so that in 90 minutes, more than 99% of the tetracycline molecule was broken down into smaller components. This step was followed by monitoring the UV spectrum. But the degradation of the small organic components until producing carbon dioxide and water takes longer so that after 6 hours, 30% of the smaller molecules are still present in the solution. Chemical Oxygen Demand (COD) technique was used to determine the concentration of organic components in the second step. In this method, the sample is strongly refluxed by acidic solutions and a certain amount of potassium dichromate ($K_2Cr_2O_7$). After digestion of the sample to determine COD, the residual and unoxidized amount of potassium dichromate is titrated with ammonium sulfate to determine the amount of potassium dichromate consumed and the oxidized material is calculated in the oxygen equations.

### 3.3.3. Influence of temperature

The influence of temperature on tetracycline degradation was shown in figure 8. Changes in process velocities in the range of 0 to 75 °C indicate that degradation rate is directly related to reaction temperature (figure 8). In fact, the reaction temperature, on the one hand, contributes to the production of dissolved $O_2$ and the degradation of $H_2O_2$, which ultimately leads to the production of active hydroxyl radicals, and on the other hand, it provides the activation energy for the reaction. Based on this, it can be said that the catalytic process is exothermic and by drawing $\ln k$ (rate constant) versus the inverse of the temperature (kelvin) and in accordance with Arrhenius equation (Jensen, 1985) (Eq. 6), the activation energy of the reaction was obtained from the slope of the straight line. The value of the slope is equal to $-E_a/R$ where $R$ is a constant equal to 8.314 J/mol K. (Fig. 9).

$$\ln k = \ln A - \frac{E_a}{RT}$$ (6)

The activation energy ($E_a$) of tetracycline degradation is estimated to be 0.94 kJ/mol.

### 3.3.4. Influence of pH

In optical degradation processes, pH can affect the desired decomposition rate of the contaminant. Previous studies have shown that pH plays an important role in the breakdown and elimination of antibiotics. As shown in Figure 5, there is a significant difference between the percentage of tetracycline degradation at different pHs and the rate of decomposition at alkaline pH is significantly higher and optimized at pH=9. The pH variable affects the adsorption and dissociation capacity of the target compounds, the electric charge distribution on the surface of the catalysts, and the oxidation potential of the conduction band.

Since the isoelectric point of $g$-$C_3N_4$ based materials is around pH=9 [Zhu et al., 2015] and the tetracycline antibiotic acidic, the effect of pH on the photocatalytic process can be justified by the
presence of electrostatic forces between the surface of g-C$_3$N$_4$ NTs and tetracycline. Thus, at pHs > 9, the g-C$_3$N$_4$ NTs surface has a negative charge and the tetracycline molecules also have a negative charge, therefore, the force between them is repulsive and they don't have any reluctant to react and this cause to decrease resulting in the yield of photodegradation decreased at the pH=11. At pHs < 9, the g-C$_3$N$_4$ NTs surface has a positive charge and the tetracycline molecules also have a positive charge due to protonation. Therefore, the electrostatic force between the photocatalyst and the tetracycline is the repulsive force, which leads to a decrease in degradation efficiency. Although, the highest percentage of pesticide degradation was obtained at an alkaline pH but, due to the economic aspect and ease of operation treatment at the neutral pH, investigation of other parameters in photocatalytic degradation of the mentioned pesticides was performed at pH = 7.

### 3.3.5. Investigation of synergistic effect

In order to study the synergistic effect, tetracycline degradation reaction in the presence of g-C$_3$N$_4$ NTs and Ru(II) complex/g-C$_3$N$_4$ NTs was investigated separately and the results are reported in Table 1. According to the results, g-C$_3$N$_4$ nanotubes alone are able to destroy 62% of tetracycline in 90 minutes. After loading the ruthenium complex, the degradation percentage was higher than 99% for the same period. It seems combining two photon-active substances; g-C$_3$N$_4$ NTs and Ru(II) complex has been able to optimize the prepared photocatalyst bandgap. Therefore, the synergistic effect of Ru(II) complex and g-C$_3$N$_4$ NTs enhances the photocatalytic properties.

| Entry | Photocatalyst components       | Tetracycline Degradation (%) | k (1/min) |
|-------|--------------------------------|-----------------------------|-----------|
| 1     | g-C$_3$N$_4$ NTs               | 62                          | 0.0109    |
| 2     | Ru (II) complex/g-C$_3$N$_4$ NTs| 99                          | 0.0417    |

Reaction condition: tetracycline concentration: 10 mg/L; photocatalyst dosage: 30 mg; irradiation time: 90 min; light intensity: 60 Watt; temperature: 25°C; pH:7

### 4. Conclusions

In this study, Ru (II) complex/g-C$_3$N$_4$ nanocatalyst was synthesized and its photocatalytic properties for the degradation of tetracycline antibiotic was investigated. The synthesized photocatalyst were evaluated by various methods such as Infrared spectroscopy, X-ray diffraction, scanning and transmission electron microscopy, and visible ultraviolet spectroscopy. The results showed the successful synthesis of graphite nitride carbon nanotubes reinforced with ruthenium (II) complex. In general, one of the most important properties of a photocatalyst or a catalyst is its specific surface area. Therefore, the synthesis of g-C$_3$N$_4$ in
the form of nanotubes had a significant performance in photocatalytic properties. In addition to increasing the specific surface area, the accessibility surface for light also increases automatically. Finally, since the bulk graphite carbon nitride alone is a suitable option for photocatalytic degradation of pollutants, the use of improved its, which has a higher specific surface area and better activity, is not far-fetched.

Declarations

Acknowledgments Thanks are due to the Iranian Nanotechnology Initiative and the research council of Shahid Bahonar university of Kerman and chemical engineering department for supporting of this work.

Authors’ contributions This collaboration work was carried out among all the authors. Mohaddeseh Shahabi Nejad designed outlines and wrote the draft of the manuscript. Zahra Vakily prepared the laboratory data of the manuscript. Ali Mostafavi wrote some part of the manuscript. Hassan Sheibani reviewed the manuscript. Mohaddeseh Shahabi Nejad proposed original idea and reviewed the scientific contents of the manuscript. All authors read and approved the final submitted version of the manuscript.

Declarations ethics approval Not applicable.

Consent to participate We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

Consent for publication The authors agree to publish this article in the Environmental science and pollution research.

Competing interests The authors declare no competing interests.

Availability of data and materials Not applicable.

Funding This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors

References

1. Al-Marzouqi F, Al-Balushi NA, Kuvarega AT, Karthikeyan S, Selvaraj R (2021 Feb) Thermal and hydrothermal synthesis of WO3 nanostructure and its optical and photocatalytic properties for the degradation of Cephalexin and Nizatidine in aqueous solution. Materials Science and Engineering: B 1:264:114991

2. Alwin E, Kočí K, Wojcieszak R, Zieliński M, Edelmannová M, Pietrowski M (2020 Jan) Influence of high temperature synthesis on the structure of graphitic carbon nitride and its hydrogen generation ability. Materials 13(12):2756
3. Bai X, Wang L, Zong R, Zhu Y (2013 May) Photocatalytic activity enhanced via g-C3N4 nanoplates to nanorods. J Phys Chem C 16(19):9952–9961

4. Borghi AA, Palma MS (2014 Mar) Tetracycline: production, waste treatment and environmental impact assessment. Brazilian Journal of Pharmaceutical Sciences 50(1):25–40

5. Chang CT, Wang JJ, Ouyang T, Zhang Q, Jing YH (2015 Jun) Photocatalytic degradation of acetaminophen in aqueous solutions by TiO2/ZSM-5 zeolite with low energy irradiation. Materials science and engineering: B 1:196:53–60

6. Chen Y, Yang B, Xie W, Zhao X, Wang Z, Su X, Yang C (2021 Jul) Combined soft templating with thermal exfoliation toward synthesis of porous g-C3N4 nanosheets for improved photocatalytic hydrogen evolution. Journal of materials research and technology 13(1):301–310

7. Chen Z, Zhang S, Liu Y, Alharbi NS, Rabah SO, Wang S, Wang X (2020 May) Synthesis and fabrication of g-C3N4-based materials and their application in elimination of pollutants. Sci Total Environ 5:139054

8. Chopra I, Roberts M Tetracycline antibiotics: mode of action, applications, molecular biology, and epidemiology of bacterial resistance. Microbiology and molecular biology reviews. 2001 Jun 1;65(2):232-60

9. Conde-Cid M, Núñez-Delgado A, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E, Fernández-Calviño D (2020 Nov) Arias-Estévez M. Tetracycline and Sulfonamide Antibiotics in Soils: Presence, Fate and Environmental Risks. Processes 8(11):1479

10. Cui Z, Yang H, Zhao X (2018 Mar) Enhanced photocatalytic performance of g-C3N4/Bi4Ti3O12 heterojunction nanocomposites. Materials Science and Engineering: B 1:229:160–172

11. D’Costa VM, King CE, Kalan L, Morar M, Sung WW, Schwarz C, Froese D, Zazula G, Calmels F, Debruyne R, Golding GB (2011 Sep) Antibiotic resistance is ancient. Nature 477(7365):457–461

12. de Moraes NP, Goes CM, Sperandio DC, da Silva Rocha R, Landers R, Paramasivam T, Rodrigues LA (2021 Jul) Development of a new zinc oxide/tin oxide/carbon xerogel photocatalyst for visible light photodegradation of 4-chlorophenol. Materials Science and Engineering: B 1:269:115183

13. Fiaz A, Zhu D, Sun J (2021 Dec) Environmental fate of tetracycline antibiotics: degradation pathway mechanisms, challenges, and perspectives. Environmental Sciences Europe 33(1):1–7

14. Gan Q, Shi W, Xing Y, Hou Y A polyoxoniobate/g-C3N4 nanoporous material with high adsorption capacity of methylene blue from aqueous solution. Frontiers in chemistry. 2018 Jan31;6:7

15. Goglio G, Foy D, Demazeau G State of Art and recent trends in bulk carbon nitrides synthesis. Materials Science and Engineering: R: Reports. 2008 Jan7;58(6):195–227

16. Goh CP, Lim PE (2008) Potassium permanganate as oxidant in the COD test for saline water samples. ASEAN Journal on Science and Technology for Development 25(2):383–393

17. He J, Zhang Y, Guo Y, Rhodes G, Yeom J, Li H, Zhang W (2019) Photocatalytic degradation of cephalixin by ZnO nanowires under simulated sunlight: Kinetics, influencing factors, and mechanisms. Environment international. Nov 1;132:105105
18. Homem V, Santos L (2011) Degradation and removal methods of antibiotics from aqueous matrices—a review. Journal of environmental management. Oct 1;92(10):2304-47

19. Hong Y, Li C, Meng Y, Huang C, Shi W (2017 Oct) In situ synthesis of a nanoplate-like Bi-based heterojunction for photocatalytic degradation of ciprofloxacin. Materials Science and Engineering: B 1:224:69–77

20. Hu C, Chu YC, Wang MS, Wu XH Rapid synthesis of g-C3N4 spheres using microwave-assisted solvothermal method for enhanced photocatalytic activity. Journal of Photochemistry and Photobiology A: Chemistry. 2017 Nov1;348:8–17

21. Ismael M, Wu Y (2019) A mini-review on the synthesis and structural modification of g-C3N4 based materials, and their applications in solar energy conversion and environmental remediation. Sustainable Energy & Fuels 3(11):2907–2925

22. Jensen F (1985 Jan) Activation energies and the Arrhenius equation. Qual Reliab Eng Int 1(1):13–17

23. Jin Z, Zhang Q, Yuan S, Ohno T (2015) Synthesis high specific surface area nanotube gC 3 N 4 with two-step condensation treatment of melamine to enhance photocatalysis properties. RSC Adv 5(6):4026–9

24. Kumar A, Kumar P, Joshi C, Manchanda M, Boukherrour R, Jain SL (2016 Apr) Nickel decorated on phosphorous-doped carbon nitride as an efficient photocatalyst for reduction of nitrobenzenes. Nanomaterials 6(4):59

25. Liu C, Dong X, Hao Y, Wang X, Ma H, Zhang X (2017) A novel supramolecular preorganization route for improving gC 3 N 4/gC 3 N 4 metal-free homojunction photocatalysis. New J Chem 41(20):11872–80

26. Liu X, Ma R, Zhuang L, Hu B, Chen J, Liu X, Wang X (2021) Recent developments of doped g-C3N4 photocatalysts for the degradation of organic pollutants. Critical Reviews in Environmental Science and Technology. Apr 18;51(8):751-90

27. Luo D, Duan W, Liu Y, Chen N, Wang Q (2019 Apr) Melamine cyanurate surface treated by nylon of low molecular weight to prepare flame-retardant polyamide 66 with high flowability. Fire Mater 43(3):323–331

28. Marcos-Hernández M, Villagrán D Mesoporous composite nanomaterials for dye removal and other applications. InComposite Nanoadsorbents 2019 Jan 1 (pp. 265-293). Elsevier

29. Park H, Choung YK (2007) Degradation of antibiotics (tetracycline, sulfathiazole, ampicillin) using enzymes of glutathion S-transferase. Human and Ecological Risk Assessment: An International Journal. 18:1147–1155

30. Pattnaik SP, Behera A, Martha S, Acharya R, Parida K (2019 Apr) Facile synthesis of exfoliated graphitic carbon nitride for photocatalytic degradation of ciprofloxacin under solar irradiation. J Mater Sci 54(7):5726–5742

31. Rastogi R, Kaushal R, Tripathi SK, Sharma AL, Kaur I, Bharadwaj LM Comparative study of carbon nanotube dispersion using surfactants. Journal of colloid and interface science. 2008 Dec15;328(2):421–8
32. Ren X, Meng X, Ren J, Tang F (2016) Graphitic carbon nitride nanosheets with tunable optical properties and their superoxide dismutase mimetic ability. RSC Adv 6(95):92839–44
33. Rodriguez-Narvaez OM, Peralta-Hernandez JM, Goonetilleke A, Bandala ER (2017 Sep) Treatment technologies for emerging contaminants in water: A review. Chem Eng J 1:323:361–380
34. Sangeetha V, Kanagathara N, Sumathi R, Sivakumar N, Anbalagan G (2013) Spectral and thermal degradation of melamine cyanurate. Journal of Materials. ; 262094
35. Shi H, Fu J, Jiang W, Wang Y, Liu B, Liu J, Ji H, Wang W, Chen Z (2021 Apr) Construction of g-C3N4/Bi4Ti3O12 hollow nanofibers with highly efficient visible-light-driven photocatalytic performance. Colloids Surf, A 20:615:126063
36. Singh M, Goyal M, Devlal K Size and shape effects on the band gap of semiconductor compound nanomaterials. Journal of Taibah University for Science. 2018 Jul 4;12(4):470-5
37. Smith RA, M’ikanatha NM, Read AF Antibiotic resistance: a primer and call to action. Health communication. 2015 Mar;30(3):309–14
38. Thomas A, Fischer A, Goettmann F, Antonietti M, Müller JO, Schlögl R, Carlsson JM (2008) Graphitic carbon nitride materials: variation of structure and morphology and their use as metal-free catalysts. J Mater Chem 18(41):4893–4908
39. Vasei HV, Masoudpanah SM, Adeli M, Aboutalebi MR, Habibollahzadeh M (2019 Sep) Mesoporous honeycomb-like ZnO as ultraviolet photocatalyst synthesized via solution combustion method. Mater Res Bull 1:117:72–77
40. Wang A, Wang C, Fu L, Wong-Ng W, Lan Y (2017 Oct) Recent advances of graphitic carbon nitride-based structures and applications in catalyst, sensing, imaging, and LEDs. Nano-micro letters 9(4):1–21
41. Wang F, Feng Y, Chen P, Wang Y, Su Y, Zhang Q, Zeng Y, Xie Z, Liu H, Liu Y, Lv W (2018 Jul) Photocatalytic degradation of fluoroquinolone antibiotics using ordered mesoporous g-C3N4 under simulated sunlight irradiation: kinetics, mechanism, and antibacterial activity elimination. Appl Catal B 5:227:114–122
42. Wang Q, Li P, Zhang Z, Jiang C, Zuojiao K, Liu J, Wang Y (2019 Jun) Kinetics and mechanism insights into the photodegradation of tetracycline hydrochloride and ofloxacin mixed antibiotics with the flower-like BiOCl/TiO2 heterojunction. J Photochem Photobiol, A 378(1):114–124
43. Wang X, Sø L, Su R, Wendt S, Hald P, Mamakhel A, Yang C, Huang Y, Iversen BB, Besenbacher F (2014) The influence of crystallite size and crystallinity of anatase nanoparticles on the photo-degradation of phenol. Journal of catalysis. Feb 1;310:100-8
44. Xin G, Meng Y (2013 Jan) Pyrolysis synthesized g-C3N4 for photocatalytic degradation of methylene blue. Journal of Chemistry. 1;2013.
45. Yadav AA, Hunge YM, Mathe VL, Kulkarni SB (2018 Sep) Photocatalytic degradation of salicylic acid using BaTiO 3 photocatalyst under ultraviolet light illumination. J Mater Sci: Mater Electron 29(17):15069–15073
46. Yan SC, Li ZS, Zou ZG. Photodegradation performance of g-C3N4 fabricated by directly heating melamine. Langmuir. 2009 Sep 1;25(17):10397-401

47. Yin M, Jia F, Wu C, Zheng P, Fan Y, Li Z. (2017 Sep) Coupling g-C3N4 nanobelts and Cu (OH) 2 nanoparticles with TiO2 for visible-light photocatalytic H2 production. Materials Science and Engineering: B 1:223:35–42

48. Yu ZY, Zhao JN, Yang F, Tang XF, Wu YF, Ma CF, Song B, Yun L, Meng QW. (2020) Rose bengal as photocatalyst: visible light-mediated Friedel–Crafts alkylation of indoles with nitroalkenes in water. RSC Adv 10(8):4825–4831

49. Zhang Q, Jiang L, Wang J, Zhu Y, Pu Y, Dai W. Photocatalytic degradation of tetracycline antibiotics using three-dimensional network structure perylene diimide supramolecular organic photocatalyst under visible-light irradiation. Applied Catalysis B: Environmental. 2020 Nov15;277:119122

50. Zhang R, Zhang X, Liu S, Tong J, Kong F, Sun N, Han X, Zhang Y. (2021 Aug) Enhanced photocatalytic activity and optical response mechanism of porous graphitic carbon nitride (g-C3N4) nanosheets. Mater Res Bull 1:140:111263

51. Zhang YX, Jia Y. (2018 Feb) Synthesis of MgO/TiO2/Ag composites with good adsorption combined with photodegradation properties. Materials Science and Engineering: B 1:228:123–131

52. Zhao H, Chen XL, Jia C, Zhou T, Qu X, Jian J, Xu Y, Zhou T. WITHDRAWN: A facile mechanochemical way to prepare g-C3N4. Materials Science and Engineering: B. 2005 Sep25;122(3):226–30

53. Zhao X, Zhang Y, Zhao X, Wang X, Zhao Y, Tan H, Zhu H, Ho W, Sun H, Li Y. Urea and melamine formaldehyde resin-derived tubular g-C3N4 with highly efficient photocatalytic performance. ACS applied materials & interfaces. 2019 Jul18;11(31):27934–43

54. Zhu B, Xia P, Ho W, Yu J. (2015 Jul) Isoelectric point and adsorption activity of porous g-C3N4. Appl Surf Sci 30:344:188–195

Figures
Figure 1

FT-IR spectra of melamine-cyanuric acid (a), g-C3N4 NTs (b), and Ru(II)complex/g-C3N4 NTs (c).
Figure 2

The spectrum of a) UV-Vis spectrum b) curve of $(\alpha h \nu)^2$ versus $h \nu$ of g-C3N4 NTs to bandgap estimation.
Figure 3

XRD patterns of a) Melamine-Cyanuric acid, b) Ru(II)complex/g-C3N4 NTs
Figure 4

Scanning electron microscopy (SEM) photographs (a), energy-dispersive X-ray pattern (b) and element distribution map (c) of Ru(II)complex/g-C3N4 NTs photocatalyst.
Figure 5

TEM images of Ru(II) complex/g-C3N4 NTs photocatalyst.

Figure 6

a) Influence of temperature on the photocatalytic degradation of tetracycline, b) Plot of \( \ln(C/\text{C}_0) \) versus time to investigation of temperature effect on the degradation rate. Reaction conditions: drug concentration: 10 mg/L; irradiation time: 90 min; light intensity: 60 Watt; temperature: 25°C; pH: 7
Influence of irradiation time on the photocatalytic degradation of tetracycline in water. Drug concentration: 10 mg/L; Ru(II) complex/g-C3N4 NTs amount: 30 mg; light intensity: 60 Watt; temperature: 25 °C; pH: 7

Figure 8

a) Influence of temperature on the photocatalytic degradation of tetracycline in the first 30 minutes, b) Plot of $\ln(C/C_0)$ versus time to investigation of temperature effect on the degradation rate. Reaction
conditions: drug concentration: 10 mg/L; Ru(II) complex/g-C3N4 NTs amount: 30 mg; irradiation time: 90 min; light intensity: 60 Watt; pH: 7

Figure 9

Plot of Ln k versus 1/T to estimation of Ea.

Figure 10

a) Influence of pH on the photocatalytic degradation of tetracycline in the first 30 minutes, b) Plot of ln(C/C0) versus time to investigation of pH effect on the degradation rate. Reaction conditions: drug concentration: 10 mg/L; Ru(II) complex/g-C3N4 NTs amount: 30 mg; irradiation time: 90 min; light intensity: 60 Watt; Temperature: 25°C
Supplementary Files

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- Scheme1.png