Research Article

Photocatalytic removal of ceftriaxone from aqueous solutions using g-C_3N_4

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Ceftriaxone is a pharmaceutical compound that causes the pollution of water. In this research, g-C_3N4 photocatalyst was synthesized and its efficiency in removal of ceftriaxone was studied. The synthesized g-C3N4 was analyzed using XRD, FTIR, FESEM, EDS, and dot mapping. The effect of the initial concentration of ceftriaxone, dosage of photocatalyst, irradiation time, and pH was studied, and based on these results, the highest removal efficiency of ceftriaxone from the water was obtained at about 83.4% at the concentration of 20 mg/L, pH=2, 0.25 g/500 mL of g-C_3N_4 photocatalyst at 50 min of irradiation time. This study confirmed that the g-C3N4 photocatalyst can be efficiently removed ceftriaxone from water.

KEYWORDS

Ceftriaxone, g- C3N4, Photocatalyst, Recovery, Removal.

I. INTRODUCTION

In recent years, due to the prevalence and appearance of various diseases, the use of antibiotics has increased in the world, hence there are many concerns due to their discharge into the environment, especially into receiving waters [1,2]. Today, excessive use of antibiotics has led to a series of environmental problems that seriously threaten human health and microbial populations [3]. Ceftriaxone, as a third-generation cephalosporin antibiotic, is widely used to treat various infections that accumulate in water and sewage and may create bio-environmental and health problems [4]. Although antibiotics are usually detected in very low concentrations, they may cause harmful physiological effects on humans and other living organisms, so effective and efficient techniques are necessary to remove them. Chemical oxidation, membrane processes, ion filtration, biological filtration, photochemical decomposition, and adsorption are the conventional methods to remove Ceftriaxone [5]. In recent years, advanced oxidation processes (AOPs) have been used to remove organic compounds [6]. The photocatalytic process is one of the advanced oxidation processes in which organic materials are decomposed in the presence of UV or Vis radiation and the presence of a photocatalyst [7].

Graphitic carbon nitride (g-C3N4) is a metal-free semiconductor and has unique electrical, optical, and physicochemical properties, which makes this material a new group of versatile nanomaterials for use in electrical and catalytical broad [8]. g-C3N4 is a two-dimensional material with a honeycomb structure and a band gap of about 2.7 eV [8]. The conduction band and valance band of g-C3N4 (using a standard hydrogen electrode as a potential reference) are equal to -1.15 and 1.48 eV, respectively [9]. Due to the negative potential of the conduction band, it has the necessary ability to reduce air oxygen and form superoxide anion. Also, due to the position of the energy bands, it will be possible to produce hydrogen fuel and oxygen during photocatalytic processes. In general, this photocatalyst is used in various fields, including the degradation of organic pollutants and fuel production [10, 11]. For the first time, the use of graphite carbon nitride in photocatalytic activity was reported by Wang in the photocatalytic splitting of water and the production of molecular oxygen and hydrogen [12].

This study aims to use graphite carbon nitride (g-C3N4) as a photocatalyst in the photocatalytic process of ceftriaxone (CFT) removal. The effect of pH, irradiation time, photocatalyst dosage, and different concentrations of ceftriaxone on the process efficiency has been investigated.

II. Materials and Methods

A. *Materials*

Melamine($C_3H_6N_6$), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were purchased from Merck company. Ceftriaxone ($C_{18}H_{18}N_8O_7S_3$) was prepared from Daana Pharma, Iran.

Synthesis of g-C_3N_4

The polycondensation method was used for g-C_3N_4 synthesis. For this purpose, 5 g of melamine was poured into a half-closed crucible and placed inside the oven at 520 °C for 6 h with a flow rate of 4 °C/min. The resulting g-C3N4 sample was yellow [9].

B. *Photocatalytic Experiments*

To perform photocatalytic experiments, a visible bubble lamp filled with tungsten halogen 300 w installed on top of a wooden box was used. All tests were performed on 50 mL samples using a crystallizer on a magnetic stirrer. HCl and NaOH were used to adjust the pH. To reach an adsorption-desorption equilibrium between the CFT solution and the catalyst, the mixture was stirred for 30 min in the dark. To perform the photocatalytic reaction, first, the solution containing CFT was poured into a crystallizer. A cut-off filter (> 420 nm) was used to prevent penetration of UV light into the solution. After sampling and filtering, the CFT concentration was recorded using a UV-Vis spectrophotometer at λ = 240 nm. In this work, the effect of different variables such as irradiation time, photocatalyst dosage, pH, and CFT concentration was investigated. To determine the percentage of CFT removal, R (%), Eq. 1 was used:

$$\mathrm{R}(\%) = \frac{[\mathrm{C}]_0 - [\mathrm{C}]_\mathrm{t}}{[\mathrm{C}]_0} \times 100 \tag{1}$$

Here, [C]0 and [C]t are the initial and final concentrations of CFT (mg/L), respectively.

III. Results and Discussion

A. *Characterization*

FTIR and XRD were used to characterize synthesized g-C3N4. In the FTIR spectrum, the band at 805 cm^{-1} is related to tri-s-triazine, broadband at 3155 cm^{-1} corresponds with the N-H bond at -NH2 and –NH and the bands at 1242–1639 cm^{-1} are related to CN heterocyclic typical stretching modes [13]. In the XRD spectrum, the spectra seen in 2θ= 12.99° (dimension of subunits in polymeric material) and 27.29° (interlayer spaces) confirmed the synthesis of g-C3N4[14].

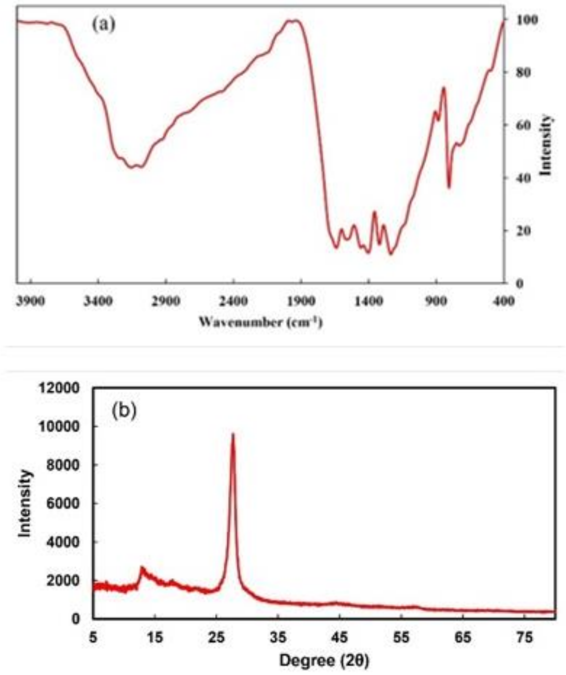

Fig. **1** FTIR and XRD of g-C3N4

FESEM images (Fig. 2) show that the synthesized g-C3N4 is uniform and cauliflower-shaped. The results of EDS and Dot mapping also show that synthesized g-C3N4 contains 49.5% carbon and 50.5% nitrogen, and carbon and nitrogen are uniformly distributed (Fig. 2).

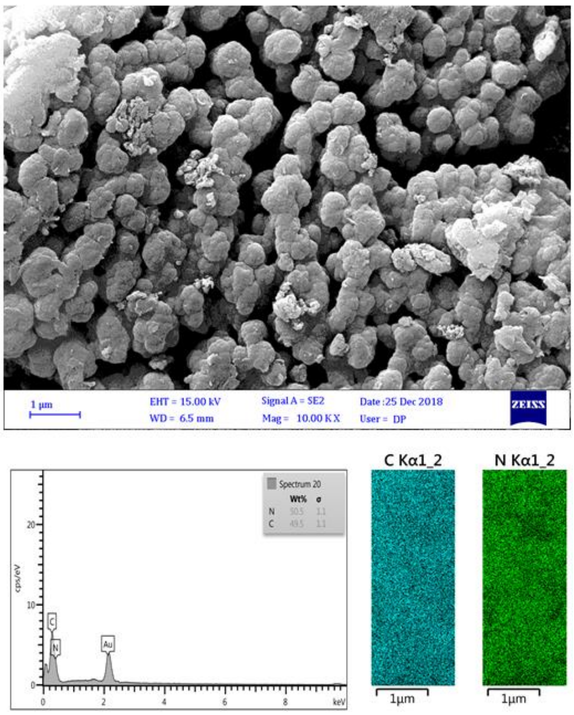

Fig. **2** FESEM, EDX, and DOT mapping of g-C3N4

B. *Photocatalytic degradation*

To investigate the effect of the main parameters in the process of photocatalytic degradation of ceftriaxone under visible light, four parameters affecting the degradation of ceftriaxone, including the initial concentration of ceftriaxone, amount of photocatalyst, time, and pH were investigated.

C. *Effect of initial concentration*

To investigate the effect of the initial concentration of ceftriaxone on the degradation, 10-50 mg/L concentrations of ceftriaxone were selected. The results showed that by increasing the initial concentration, photocatalytic degradation was decreased (Fig. 3). The decrease in the amount of degradation with the increase in the concentration of ceftriaxone can be justified by the fact that when the initial concentration of ceftriaxone increases, it prevents the passage of light into the solution and as a result, a smaller amount of oxidizing species is created [15].

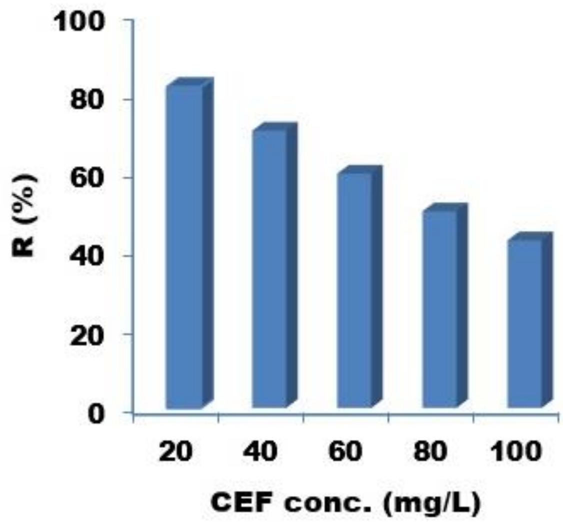

Fig. **3** The effect of ceftriaxone initial concentration

pH=2; Irradiation time=50 min., Dosage=0.25 g/500mL

D. *The effect of irradiation time*

The results showed (Fig.4) that as the irradiation time was increased, the percentage of ceftriaxone degradation increased. Over time, with the accumulation of ceftriaxone molecules in the empty and unoccupied places of the g-C3N4, the ceftriaxone concentration decreases, and therefore the percentage of removal increases [16].

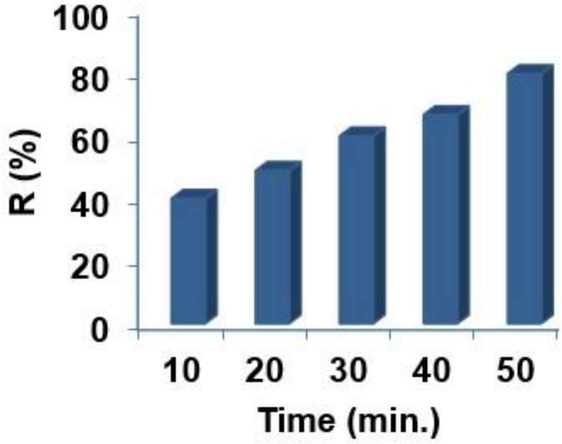

Fig. **4** The effect of Irradiation time

pH=2; Ceftriaxone initial concentration =20 mg/L; Dosage=0.25 g/500mL

E. *Effect of dosage*

Another important factor in the photocatalytic process is the amount of catalyst. According to the figure, with the increase in the amount of catalyst, the percentage of ceftriaxone degradation increases (Fig. 5). The reason for this phenomenon is due to the increase of empty and unoccupied positions with the increase in the amount of absorbent. In general, by increasing the amount of catalyst, more adsorption sites will be available, so the percentage of ceftriaxone removal will increase [24]. At low amounts of adsorbent, probably due to insufficient active sites and saturation of the adsorbent surface, the percentage of ceftriaxone removal decreases [17]. On the other hand, in the photocatalytic process, by increasing the amount of absorber, the availability of semiconductor particles to absorb protons increases, and as a result, more oxidizing sites are formed, which leads to more destruction of ceftriaxone [18].

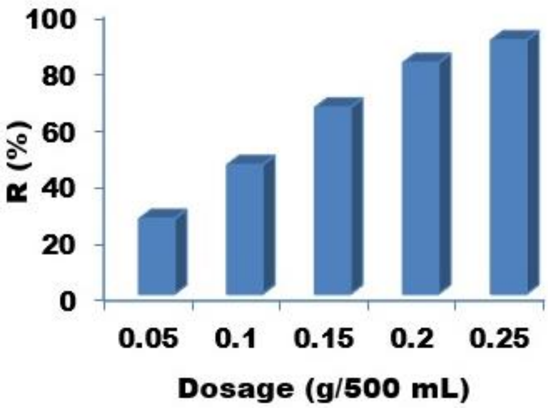

Fig. 5. Effect of dosage pH=2; Ceftriaxone initial concentration =20 mg/L; Irradiation time=50 min.

F. *Effect of pH*

As can be seen in the results, the highest removal efficiency occurs in acidic conditions, and with the increase in pH, the removal efficiency has decreased, which is due to the presence of more H + ions in the acidic environment, which produces more radicals and reacts with the oxygen in the solution. and produce radicals, which ultimately cause the production of radicals. In photocatalytic processes, free radicals cause an increase in the reaction rate because more radicals are produced in an acidic environment, as a result, the removal efficiency increases in an acidic environment [19,20].

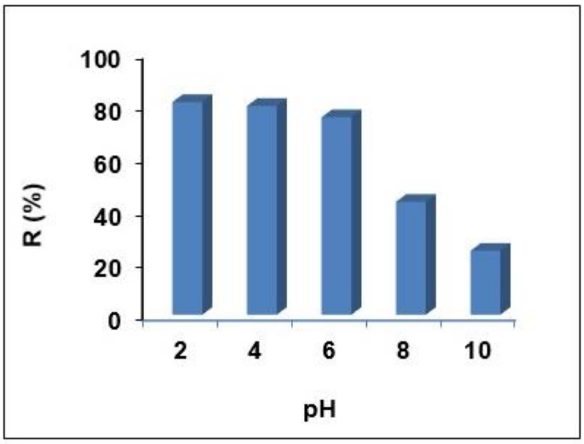

Fig. **6** Effect of pH Irradiation time=50 min.; Ceftriaxone initial concentration =20 mg/L; Dosage=0.25 g/500mL.

G. *Photocatalyst stability and recovery*

It is very important to evaluate the recovery and stability of the catalyst from an economic point. In this research, to estimate the chemical stability of g-C_3N_4, it was used in five consecutive experiments for the photocatalytic degradation of ceftriaxone. The results showed that after 5 times, the photocatalytic degradation efficiency of g-C_3N_4 decreased by about 16.24%, which can be related to the decrease in the amount of g-C_3N_4 in the washing process (Fig. 7).

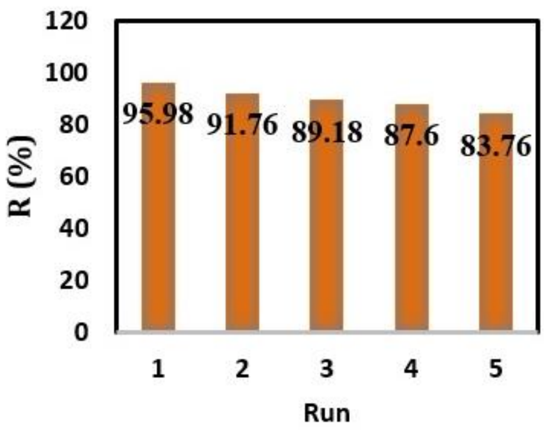

Fig.**7** Recovery of g-C3N4 pH=2; Ceftriaxone initial concentration =20 mg/L; Dosage=0.25 g/500 mL; Irradiation time=50 min.

IV.CONCLUTION

In this research, g-C_3N_4 was synthesized by a simple method and analyzed using XRD, FTIR, FESEM, EDS, and dot mapping. The potential of the synthesized g-C3N4 as a photocatalyst for the removal of ceftriaxone from aqueous solutions was evaluated under visible light. The effect of main factors such as initial ceftriaxone concentration, photocatalyst dosage, irradiation time, and pH showed that increasing the dosage and irradiation time increases the removal of ceftriaxone under visible light.

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