

Photocatalytic removal of Pb ions from aqueous solution using Fe_2O_3 doped in $\text{G-C}_3\text{N}_4$ nanocomposite under visible light

Baeissa ES*

Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

Abstract

A pyrolysis technique of urea and dicyandiamide in an air atmosphere was used to prepare graphitic carbon nitride, and a modified precipitation technique was used to prepare Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ nanocomposites. Different techniques, such as UV-Vis, XPS, FT-IR, XRD, PL and BET surface area, were used to characterize the prepared materials. The results reveal that the wt% of Fe_2O_3 plays an important role in the control band gap of Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ nanocomposite. The photocatalytic performance of $\text{g-C}_3\text{N}_4$ and Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ nanocomposites was studied by measuring its photocatalytic reduction of Pb ions under visible light. Photocatalytic parameters such as the wt% of Fe_2O_3 , photocatalyst dose and Pb ion concentration were also studied. The photocatalytic activity of doped on $\text{g-C}_3\text{N}_4$ is smaller than that of Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ nanocomposites. This can be attributed to the fact that the addition of Fe_2O_3 to doped on $\text{g-C}_3\text{N}_4$ decreases the electron-hole recombination rate and shifts the absorption of $\text{pg-C}_3\text{N}_4$ to a higher wavelength or alternatively due to the transfer of electrons between doped on $\text{g-C}_3\text{N}_4$ and Fe_2O_3 .

Introduction

Industrialization technologies lead to many benefits for humans but also cause many environmental problems, such as water pollution. One of the most dangerous problems is pollution by heavy metals, as heavy metals are very difficult to remove from wastewaters. The Agency for Toxic Substances and Disease Registry considers Pb ions to be the second top water hazard that requires critical treatment [1]. Many sources can cause lead contamination of water, including natural or industry sources. The presence of Pb ions causes many problems to human health, such as brain damage from prolonged exposure to Pb ions. The maximum safe level of Pb ions in drinking water is 10 and 15 ppb according to the World Health Organization and the Environmental Protection Agency, respectively [2,3]. The treatment of Pb ions in water has been carried out by many methods [4,5], but these methods are not effective due to the presence of harmful by-products [7], high cost [8] and the fact that pretreatment and a long residence time are needed [9,10]. Therefore, the photocatalysis process is a very effective method due to its very easy and effective execution. The most efficient photocatalyst is titanium dioxide due to its high stability and activity. The disadvantage of using titanium dioxide as a photocatalyst is its absorption in the UV region and fast recombination of electron and hole [11-13]. Many methods have been used to solve these two problems. The first method is doping by metal, and the second one is coupling by another semiconductor [14-21]. The third one is the synthesis of a novel photocatalyst working under visible light irradiation such as bismuth vanadate and bismuth oxychloride [22-25]. Currently, researchers prepare polymer-like semiconductor materials that are considered to be an efficient photocatalyst using visible light for environmental purification and hydrogen production [26-30]. Polymer-like semiconductor materials have many properties, such as high stability, low cost and a controllable surface. Therefore, a polymer-like semiconductor material can be considered as a new

material for solar energy and environmental applications. There are three drawbacks for using it as a commercial photocatalyst: a small surface area, high recombination rate of electron-hole pairs and a lack of absorption above 460 nm. Researchers have overcome these drawbacks by three methods. One of them is to control the texture of polymer-like semiconductor materials, which increases adsorption ability and photocatalytic activity [31-38]. The second one is to extend the absorption range of polymer-like semiconductor materials by changing their electronic structure via metal and nonmetal doping [39-44]. The third one is to extend the absorption range of polymer-like semiconductor materials by changing their electronic structure by coupling with another semiconductor photocatalyst such as Bi_2WO_6 , TaON , TiO_2 [45-47] and so on. In this work, a new Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ photocatalyst was synthesized and characterized. The photocatalytic reduction of Pb ions using Fe_2O_3 doped on a $\text{g-C}_3\text{N}_4$ photocatalyst using visible light was studied.

Experimental

Synthesis of graphitic carbon nitride ($\text{g-C}_3\text{N}_4$)

A pyrolysis technique of urea and dicyandiamide in an air atmosphere was used to prepare graphitic carbon nitride as follows: 6 g of dicyandiamide was added to 10 g of urea and mixed carefully. The

Correspondence to: Elham Baeissa, Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203 Jeddah 21589, Saudi Arabia, Tel.: +966-6400000; Fax: +966-2-6952292. **E-mail:** elhambaeissa@gmail.com

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resulting mixture was heated for 4 h at 550°C by a Muffle Furnace. The resulting materials were washed several times by deionized water to confirm that there is residue adsorbed on the graphitic carbon nitride surface, which was then dried at 100°C for 12 h.

Preparation of Fe₂O₃@g-C₃N₄ nanocomposites

A modified precipitation technique was used to prepare Fe₂O₃ doped on g-C₃N₄ nanocomposites as follows: 1 g of g-C₃N₄ was dispersed by sonication in 60 ml of deionized water. Then, 0.15 g of iron nitrate was added dropwise to the g-C₃N₄ dispersed solution. Ammonia solution was also added, and the obtained materials were stirred for 3 h at room temperature. The obtained materials were dried and washed several times by ethanol and deionized water and dried at 80°C for 12 h under a vacuum drier. Fe₂O₃ doped on g-C₃N₄ nanocomposite was obtained by the calcination of the materials at 550°C for 2 h. The obtained Fe₂O₃ doped on g-C₃N₄ nanocomposite was labelled as Fe₂O₃ doped on g-C₃N₄ - 1 wt%. Fe₂O₃ doped on g-C₃N₄ - 2 wt%, Fe₂O₃ doped on g-C₃N₄ - 3 wt% and Fe₂O₃ doped on g-C₃N₄ - 4 wt% nanocomposites were prepared by the same method for Fe₂O₃ doped on g-C₃N₄ - 1 wt% by changing only the amount of iron nitrate required.

Characterization of g-C₃N₄ and Fe₂O₃ doped on g-C₃N₄ nanocomposites

Nanostructure morphology and sample dimensions were measured using JEOL-JEM-1230 transmission electron microscopy (TEM). Samples were suspended in ethanol and ultrasonicated for 30 m. A small amount was then dried on a carbon coated copper grid and loaded into the TEM. In addition, N₂-adsorption measurements were taken on treated samples (2 h under vacuum at 100°C) with a Nova 2000 series Chromatech apparatus at 77K to calculate surface area. The crystalline phase was determined by powder X-ray diffraction (XRD) using Bruker axis D8 with Cu K α radiation ($\lambda=1.540 \text{ \AA}$) at room temperature. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-ALPHA spectrometer. Band gap performance was determined from an ultra violet-visible diffuse reflectance spectra (UV-Vis-DRS), which was measured using a UV-Vis-NIR spectrophotometer (V-570, Jasco, Japan) in air at room temperature to detect absorption over the range of 200 to 800 nm. Lastly, photoluminescence emission spectra (PL) were obtained with a Shimadzu RF-5301 fluorescence spectrophotometer.

Photocatalytic activity

The photocatalytic performance of g-C₃N₄ and Fe₂O₃ doped on g-C₃N₄ nanocomposites was studied by measuring its photocatalytic reduction of Pb ion under visible light. The experiments were conducted using a horizontal cylinder annular batch reactor. The photocatalyst was irradiated with a blue fluorescent lamp (150 W), and the reactor was doubly covered with a UV cut filter. In a typical experiment, the weight of the catalyst was suspended into a 300-ml, 100 mg/L lead nitrate solution. The reaction was carried out isothermally at 25°C, and samples of the reaction mixture were taken at different intervals for a total reaction time of 1 h. The lead concentration in the samples was estimated by Atomic absorption. The adsorption efficiency of Pb has been measured by applying the following equation:

$$\% \text{ adsorption efficiency of Pb} = (C_0 - C)/C_0 \times 100$$

where C_0 is the initial concentration of lead in solution and C is the remaining concentration of lead in solution.

Results and discussion

Photocatalyst characterization

XRD examination: The XRD patterns of g-C₃N₄ and Fe₂O₃ doped on g-C₃N₄ nanocomposites are shown in Figure 1. The results demonstrated that g-C₃N₄ and Fe₂O₃ doped on g-C₃N₄ nanocomposites consist from the signal phase of g-C₃N₄. In addition, we noticed that there is no peak for Fe, Fe₂O₃ or Fe₃O₄ due to strong dispersion of Fe₂O₃ above the g-C₃N₄ surface or the amount of g-C₃N₄ is the low detection limit of XRD. Additionally, the characteristic peak of g-C₃N₄ at 27.4° was broad by the addition of Fe₂O₃. Broadening was increased by increasing the weight percent of Fe₂O₃, which means that the crystallite size decreased as the weight percent of Fe₂O₃ increased.

XPS examination: The XPS spectra Fe₂O₃ doped on g-C₃N₄ -3 wt% sample is shown in Figure 2. The results demonstrated that the presence of two peaks of C1s at binding energy equal to 287.6 and 284.5 eV confirms the presence of carbon as C=N, as shown in Figure 2A. The presence of a peak of N1s at a binding energy at 398.5 eV confirms the presence of nitrogen as C=N-C (sp² hybridized nitrogen), as shown in Figure 2B. The presence of two peaks of Fe_{2p} at a binding energy equal to 710.2 and 724.8 eV confirms the presence of Fe³⁺ ion, as shown in Figure 2C. The presence of two peaks of O1s at a binding energy equal to 529.6 and 532.1 eV confirms the presence of an O²⁻ ion, as shown in Figure 2D. Therefore, the XPS spectra of C, N, Fe and O confirm that the structure of the nanocomposite is Fe₂O₃ doped on g-C₃N₄.

FT-IR examination: Figure 3 shows the FT-IR spectra of the g-C₃N₄, Fe₂O₃ and g-C₃N₄/Fe₂O₃. The results reveal that the formation of g-C₃N₄ was confirmed by the existence of a graphite-like sp²-bonding state and adsorption at 810 cm⁻¹, which corresponds to the breathing mode of triazine. The characteristic stretching vibration of the tri-s-triazine heterocyclic rings is apparent in the range of 1200 to 1600 cm⁻¹. The bands observed at 1317 and 1610 cm⁻¹ are related to the C(sp²)-N and C(sp²)=N stretching modes, respectively. The broad band from 2900 to 3400 cm⁻¹ is generally related to the stretching and deformation modes of the residual N-H groups and their intermolecular hydrogen bonding. For the g-C₃N₄/Fe₂O₃ composite, the weak peaks of g-C₃N₄ appeared in the spectrum of the sample with a low quantity of g-C₃N₄. The peaks at 1200 cm⁻¹ and 3000 cm⁻¹ are attributed to the C-N

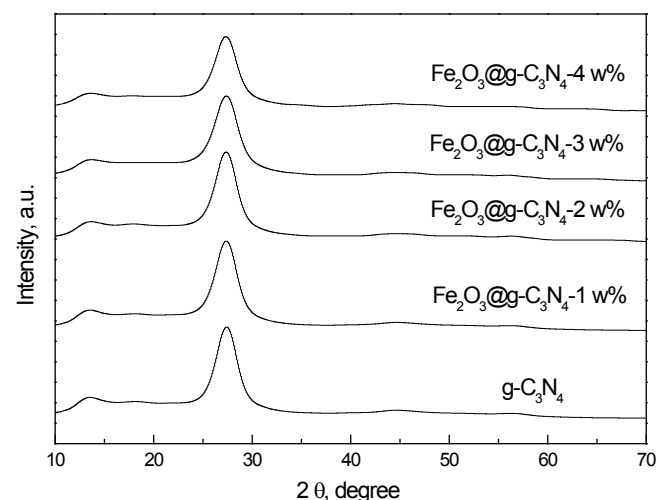


Figure 1. XRD patterns of g-C₃N₄ and Fe₂O₃@ g-C₃N₄ nanocomposites.

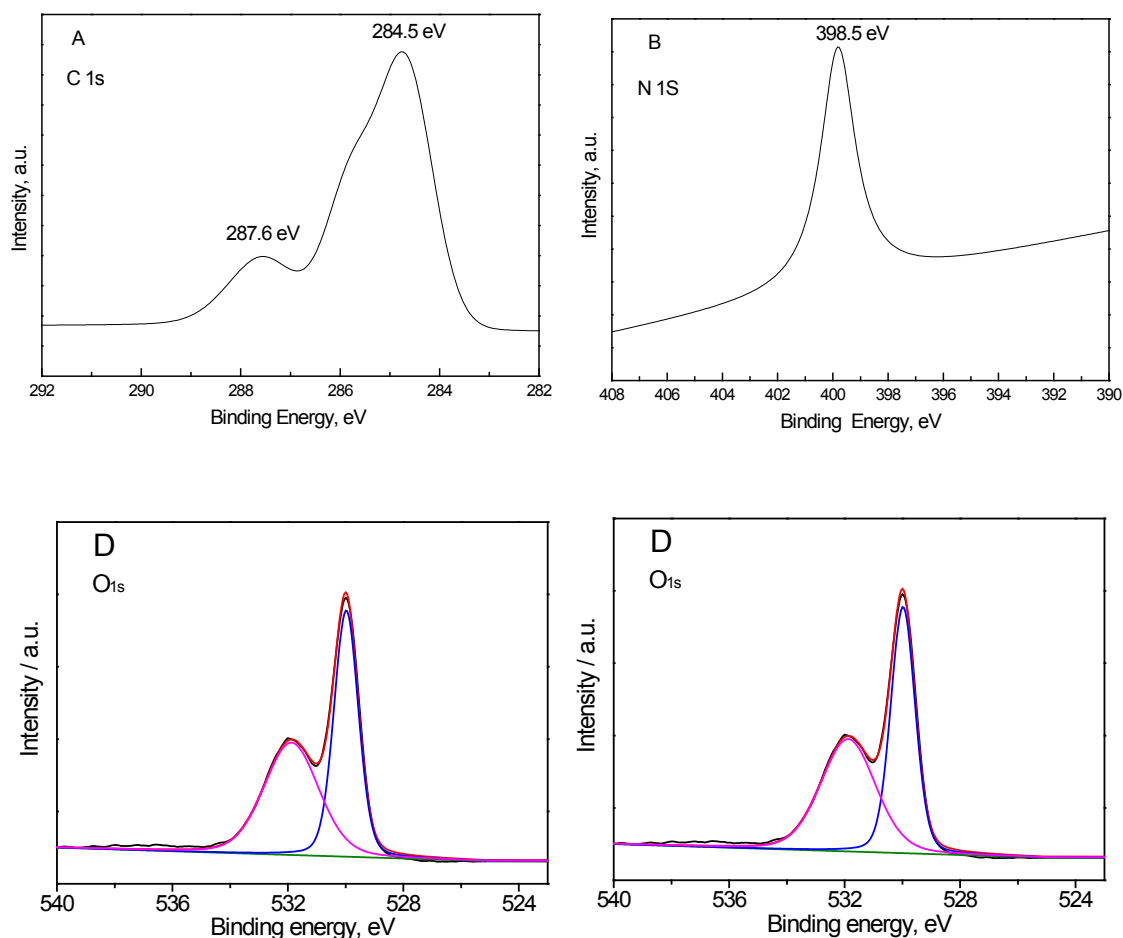


Figure 2. XPS spectra $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$ -3 wt% sample, where (A) C1s; (B) N1s; (C) Fe2p and (D) O1s.

stretching vibration and N–H stretching mode of $\text{g-C}_3\text{N}_4$ in the $\text{g-C}_3\text{N}_4/\text{Fe}_2\text{O}_3$ sample.

TEM examination: The TEM images of $\text{g-C}_3\text{N}_4$ and Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ nanocomposite samples are shown in Figure 4. The results demonstrated that the dispersion of Fe_2O_3 above the $\text{g-C}_3\text{N}_4$ surface was increased as the weight percent of Fe_2O_3 was increased from 1 to 3 wt%, as shown in Figures 4A to D. Additionally, we noticed that the agglomeration of Fe_2O_3 above the $\text{g-C}_3\text{N}_4$ surface increased as the weight percent of Fe_2O_3 increased above 3 wt%, as shown in Figure 4E.

BET surface area examination: The BET surface area of $\text{g-C}_3\text{N}_4$ and Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ nanocomposite samples is shown in Table 1. The results demonstrated that the surface area of Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ nanocomposites is almost similar to that of the $\text{g-C}_3\text{N}_4$ sample. Therefore, BET surface area is not an important factor for the enrichment of the photocatalytic activity of graphitic carbon nitride.

UV-Vis spectra examination: Figure 5 shows the UV-Vis spectra of $\text{g-C}_3\text{N}_4$ and Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ nanocomposite samples. The results demonstrated that the absorption edge of $\text{g-C}_3\text{N}_4$ was shifted to a longer wavelength as the weight percent of Fe_2O_3 was increased from 0 to 4 wt%. The band gap energy was calculated from the UV-Vis spectra, and the values obtained are 2.7, 2.6, 2.5, 2.3, and 2.2 eV, for $\text{g-C}_3\text{N}_4$, Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ -1 wt%, Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ -2

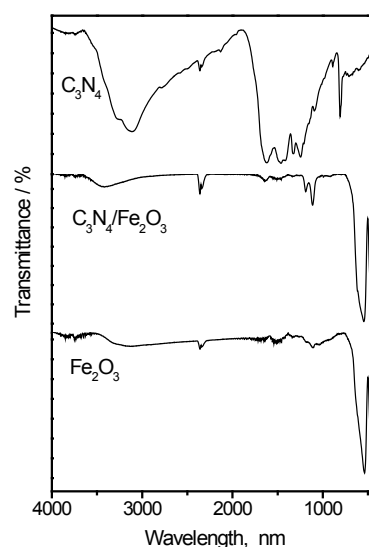


Figure 3. FT-IR spectra of $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$ nanocomposite.

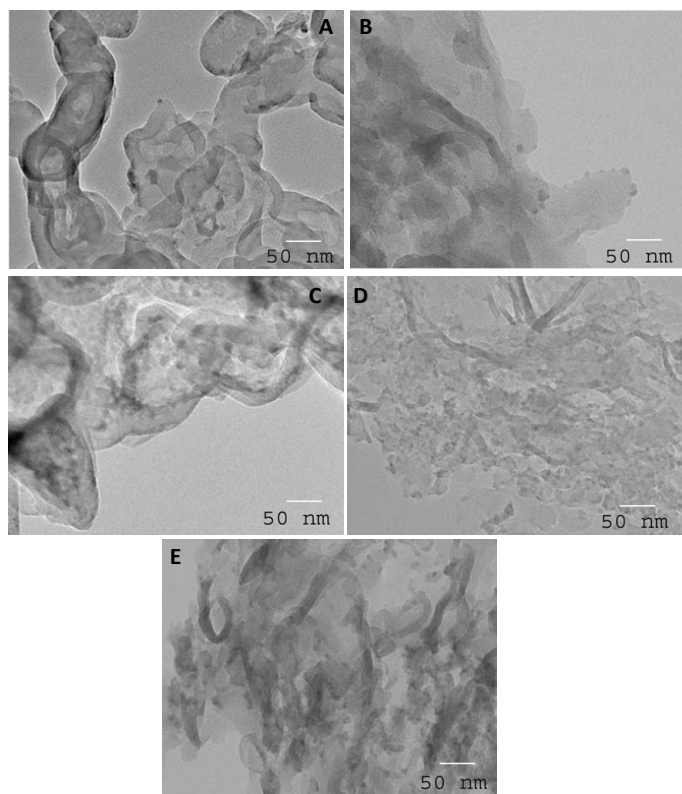


Figure 4. TEM images of g-C₃N₄ and Fe₂O₃@g-C₃N₄ nanocomposites, where (A) g-C₃N₄; (B) Fe₂O₃@g-C₃N₄-1 wt%; (C) Fe₂O₃@g-C₃N₄-2 wt%; (D) Fe₂O₃@g-C₃N₄-3 wt% and (E) Fe₂O₃@g-C₃N₄-4 wt% samples

Table 1. BET surface area of pg-C₃N₄ and Fe₂O₃ doped on pg-C₃N₄ samples.

Samples	Surface area (m ² /g)
g-C ₃ N ₄	80
Fe ₂ O ₃ @pg-C ₃ N ₄ -1 wt%	79.7
Fe ₂ O ₃ @pg-C ₃ N ₄ -2 wt%	79.6
Fe ₂ O ₃ @pg-C ₃ N ₄ -3 wt%	79.5
Fe ₂ O ₃ @pg-C ₃ N ₄ -4 wt%	79.4

wt%, Fe₂O₃ doped on g-C₃N₄-3 wt%, and Fe₂O₃ doped on g-C₃N₄-4 wt%, respectively.

PL spectra examination: The PL spectra of g-C₃N₄ and Fe₂O₃ doped on g-C₃N₄ nanocomposite samples is shown in Figure 6. The results demonstrated that the PL peak intensity of g-C₃N₄ decreased as the weight percent of Fe₂O₃ was increased from 0 to 4 wt%. Thus, the presence of Fe₂O₃ on the g-C₃N₄ surface prevents electron-hole recombination by trapping photogenerated electrons.

Photocatalytic activities

Effect of weight percent of Fe₂O₃ on the photocatalytic activity of g-C₃N₄ nanocomposites for the removal of Pb ions: The effect of weight percent of Fe₂O₃ on the photocatalytic activity of g-C₃N₄ nanocomposites for the removal of Pb ions is shown in Figure 7. The results reveal that increasing the weight percent of Fe₂O₃ from 0 to 3 wt% increases the photocatalytic activity of g-C₃N₄ from 66 to 100%, respectively. In addition, we noticed that increasing the weight percent of Fe₂O₃ above 3 wt% has no significant effect on the photocatalytic activity of g-C₃N₄. Therefore, the weight percent of Fe₂O₃ plays an

important role in the control band gap and the photocatalytic activity of the g-C₃N₄ photocatalyst. Fe₂O₃ doped on the g-C₃N₄-3 wt% photocatalyst has the highest photocatalytic activity.

Effect of dose of Fe₂O₃ doped on g-C₃N₄-3 wt% photocatalyst on the photocatalytic activity of g-C₃N₄ nanocomposites for the removal of Pb ions: The effect of the dose of Fe₂O₃ doped on g-C₃N₄-3 wt% photocatalyst on the photocatalytic activity of g-C₃N₄ nanocomposites for the removal of Pb ions is shown in Figure 8. The results reveal that the photocatalytic activity of Fe₂O₃ doped on g-C₃N₄-3 wt% photocatalyst increased from 85 to 100% by increasing the dose of Fe₂O₃ doped on g-C₃N₄-3 wt% photocatalyst from 0.5 to 1.0 g/L, respectively. Increasing the dose of Fe₂O₃ doped on g-C₃N₄-3 wt% photocatalyst from 1.0 to 1.5 to 2.0 g/L decreases the reaction time required for the complete reduction of Pb ions from 60 to 50 to 40 min, respectively. This can be attributed to the fact that an increased dose of Fe₂O₃ doped

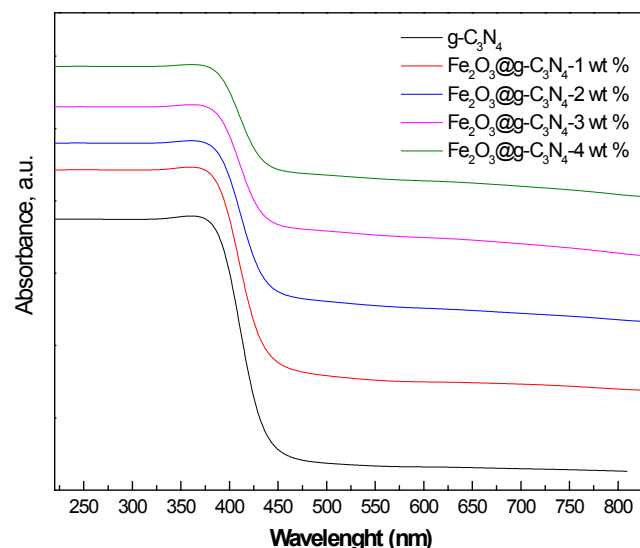


Figure 5. UV-Vis spectra of g-C₃N₄ and Fe₂O₃@g-C₃N₄ nanocomposites.

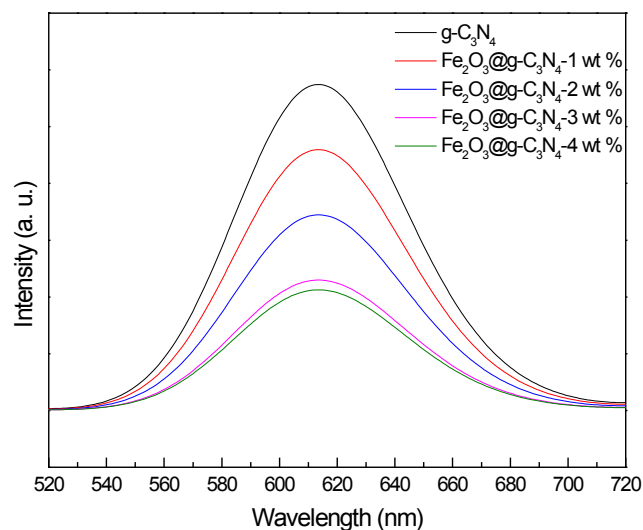


Figure 6. PL spectra of g-C₃N₄ and Fe₂O₃@g-C₃N₄ nanocomposites.

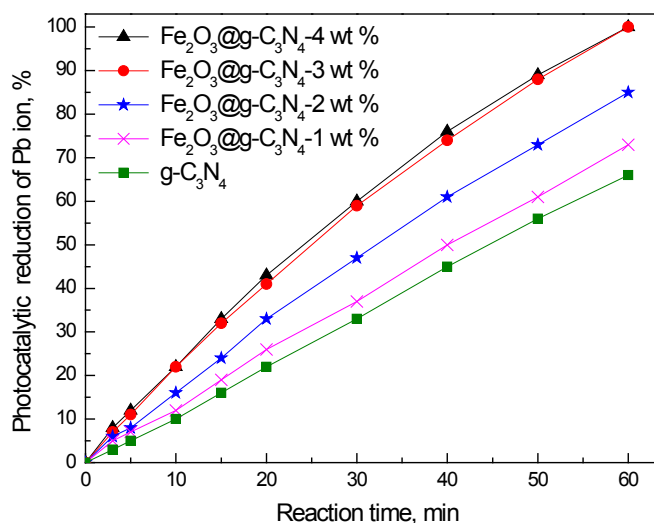


Figure 7. Effect of weight percent of Fe_2O_3 on photocatalytic activity of $\text{g-C}_3\text{N}_4$ nanocomposites for the removal of Pb ions.

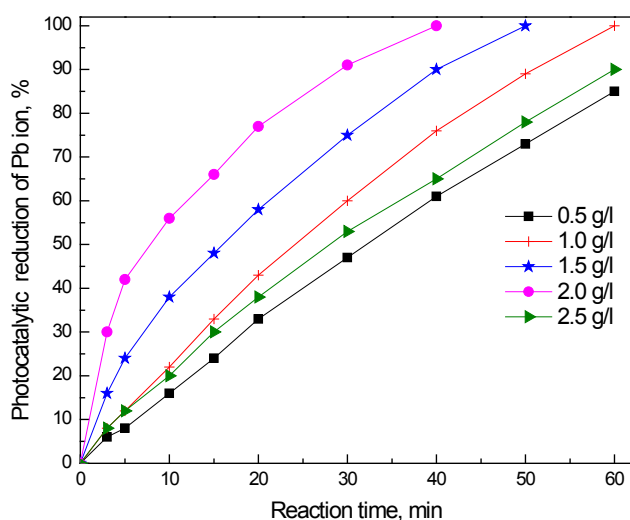


Figure 8. Effect of dose of $\text{Fe}_2\text{O}_3@ \text{g-C}_3\text{N}_4$ -3 wt % photocatalyst on photocatalytic activity of $\text{g-C}_3\text{N}_4$ nanocomposites for the removal of Pb ions.

on $\text{g-C}_3\text{N}_4$ -3 wt% photocatalyst will increase the number of active sites available for photocatalytic reduction. However, increasing the dose of Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ -3 wt% photocatalyst above 2.0 g/L increases the reaction time again from 40 to 60 min. Increasing the dose above a certain amount hinders the penetration of light to the surface of the photocatalyst and thus either decreases photocatalytic activity or increases reaction time.

Effect of initial concentration of Pb ions on the photocatalyst photocatalytic activity of $\text{g-C}_3\text{N}_4$ nanocomposites for the removal of Pb ions: The effect of initial concentration of Pb ions on the photocatalyst photocatalytic activity of $\text{g-C}_3\text{N}_4$ nanocomposites for the removal of Pb ions is shown in Figure 9. The results reveal that increasing the concentration of Pb ions from 25 to 100 ppm has no significant effect on the reaction time required to complete the

reduction of Pb ions (20 min). Increasing the initial concentration from 50 to 75 to 100 to 125 to 150 increases the reaction time from 20 to 30 to 40 to 50 to 60 min, respectively.

Recycling and reuse of Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ -3 wt% photocatalyst for the removal of Pb ions: The recycling and reuse of Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ -3 wt% photocatalyst for the removal of Pb ions is shown in Figure 10. The results reveal that Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ -3 wt% photocatalyst has photocatalytic stability for the reduction of Pb ions for five times.

Conclusions

A pyrolysis technique of urea and dicyandiamide in an air atmosphere was used to prepare graphitic carbon nitride, and a modified precipitation technique was used to prepare Fe_2O_3 doped on $\text{g-C}_3\text{N}_4$ nanocomposites. Different techniques, such as UV-Vis, XPS, FT-IR, XRD, PL and BET surface area, were used to characterize the

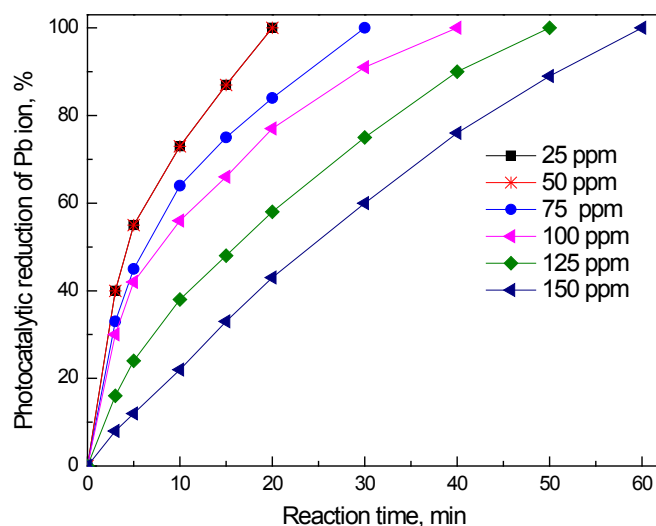


Figure 9. Effect of the initial concentration of Pb ions on the photocatalyst photocatalytic activity of $\text{g-C}_3\text{N}_4$ nanocomposites for the removal of Pb ions.

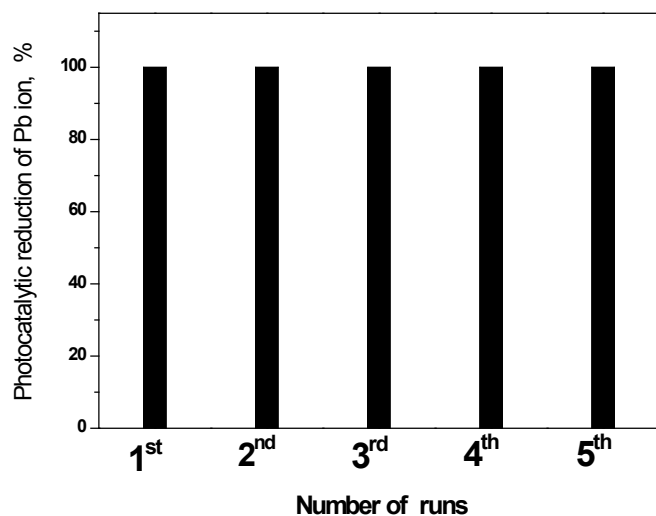


Figure 10. Recycling and reuse of $\text{Fe}_2\text{O}_3@ \text{g-C}_3\text{N}_4$ -3 wt % photocatalyst for the removal of Pb ions.

prepared materials. The results demonstrated that the band gap and photocatalytic activity of Fe₂O₃ doped on g-C₃N₄ nanocomposites can be controlled by controlling the weight percent of Fe₂O₃. The photocatalytic activity of Fe₂O₃ doped on g-C₃N₄ nanocomposites for the reduction of Pb ions is higher than that of the g-C₃N₄ photocatalyst. This can be attributed to the fact that the addition of Fe₂O₃ to g-C₃N₄ decreases the electron-hole recombination rate and shifts the absorption of g-C₃N₄ to a higher wavelength or alternatively due to the transfer of electrons between g-C₃N₄ and Fe₂O₃. Fe₂O₃ doped on g-C₃N₄-3 wt% photocatalyst has photocatalytic stability for the reduction of Pb ions for five times.

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