

**BİSFENOL-A SULU ÇÖZELTİSİNİN GRAFİTİK KARBON NİTRÜR (g-C<sub>3</sub>N<sub>4</sub>)  
KATALİZÖRÜ İLE FOTOKATALİTİK OKSİDASYONU**

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**ÖZET**

Bisfenol-A (BPA) bileşiği polimer endüstrisinde yaygın olarak kullanılan bir bileşiktir. BPA, üretilen plastik ürünlerin sert ve şeffaf olmasına katkı sağlar. Endokrin yıkıcı maddeler sınıfında yer alan bu bileşik, yaygın arıtım yöntemlerine karşı dayanıklıdır ve bozunmadan çevreye deşarj edilir. İleri oksidasyon teknikleri, hidroksil radikali ( $\cdot\text{OH}$ ) ve sülfat radikali ( $\text{SO}_4^{\cdot-}$ ) gibi oksidasyon gücü yüksek kimyasal türlerin oluşumuna dayalı yöntemlerdir. Çözelti ortamında oluşan bu radikaller seçici olmaksızın hızla organik kirleticiler ile reaksiyona girer. Grafitik karbon nitrür (g-C<sub>3</sub>N<sub>4</sub>), altıgen karbon halka katmanlarından oluşur ve yapısında triazin ve heptazin grupları içerir. g-C<sub>3</sub>N<sub>4</sub>, yüksek termal ve kimyasal stabilite ve toksik olmayan özellikler sergilediğinden, çevresel gelişme ve enerji tasarrufu için en umut verici fotokatalizör olarak kabul edilir. Grafitik karbon nitrür (g-C<sub>3</sub>N<sub>4</sub>) metal içermeyen polimerik yarı iletken olduğu rapor edilmiştir. 2.7 eV'lik dar bant boşluğu, görünür ışığı doğrudan değişiklik yapmadan absorbe etmesine izin verir. g-C<sub>3</sub>N<sub>4</sub>, görünür ışık ışıması altında, organik kirletici bozunma ve su ayrışmasından kaynaklanan hidrojen üretimi için yüksek fotokatalitik aktivite sergiler. Bu çalışmada, grafitik karbon nitrür bazlı katalizörler kullanılarak BPA bileşiğinin sulu çözeltisinin ultrasonik destekli fotokatalitik oksidasyonu gerçekleştirildi. BPA giderimi ve mineralizasyonu sırasıyla yüksek performanslı sıvı kromatografisi (HPLC) ve toplam organik karbon (TOC) analizi ile takip edildi. g-C<sub>3</sub>N<sub>4</sub> sentezinde kısaca, üre tüp fırın içerisinde argon gazı ortamında 5°C/dak sıcaklık artışı ile ısıtılarak 550°C de 2 saat bekletildi. Sentezlenen g-C<sub>3</sub>N<sub>4</sub> üzerine ultrasonik hidrotermal yöntem ile CoFe<sub>2</sub>O<sub>4</sub> yüklenerek g-C<sub>3</sub>N<sub>4</sub>@CoFe<sub>2</sub>O<sub>4</sub> katalizörü hazırlandı. Ayrıca üreden grafitik karbon nitrür sentezi sırasında ortama farklı yüzdelere anataz formülde TiO<sub>2</sub> eklenerek g-C<sub>3</sub>N<sub>4</sub>@TiO<sub>2</sub> katalizörleri elde edildi. BPA'nın ultrasonik destekli fotokatalitik oksidasyonu persülfat oksidantı (PS) ve hazırlanan katalizörler kullanılarak gerçekleştirildi (UV/US/PS/Katalizör). Tek başına kullanıldığında persülfat, ultrasonik sistem, UV ( > 350 nm) ve katalizörlerin BPA gideriminde etkili olmadıkları görüldü. Buna rağmen hazırlanan tüm katalizörler ile UV/US/PS kombine sistemi ile %100 BPA giderimi sağlandı. Kullanılan katalizörlere bağlı olarak farklı mineralizasyon etkinlikleri elde edildi. Hazırlanan katalizörlerin karakterizasyonları için FTIR, SEM-EDS ve XRD analizleri gerçekleştirildi.

**Anahtar Kelimeler:** Bisfenol-A, karbon nitrür, fotokataliz, ultrasonik

**PHOTOCATALYTIC OXIDATION OF AQUEOUS SOLUTION OF BISPHENOL-A  
USING GRAPHITIC CARBON NITRIDE (g-C<sub>3</sub>N<sub>4</sub>) CATALYST**

## **ABSTRACT**

Bisphenol-A (BPA) is a compound commonly used in the polymer industry. BPA contributes to the hardness and transparency of the plastic products produced. This compound, which is a class of endocrine disruptors, is resistant to common treatment methods and is discharged to the environment without degradation. Advanced oxidation techniques are based on the formation of highly oxidizing chemical species such as hydroxyl radical ( $\cdot\text{OH}$ ) and sulfate radical ( $\text{SO}_4\cdot^-$ ). These radicals, which are formed in solution medium, react with organic pollutants rapidly without selective. Graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) is composed of hexagonal carbon ring layers and contains triazine and heptazine groups in its structure.  $\text{g-C}_3\text{N}_4$  exhibits high thermal and chemical stability and non-toxicity such that it has been considered as the most promising photocatalyst for environmental improvement and energy conservation. Graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) is reported metal-free polymeric semiconductor. Its narrow band gap of 2.7 eV permits it to absorb visible light directly without modification.  $\text{g-C}_3\text{N}_4$  exhibits high photocatalytic activity for organic pollutant degradation and hydrogen generation from water splitting, under visible light irradiation. In this study, ultrasonic assisted photocatalytic oxidation of aqueous solution of BPA compound was performed by using graphitic carbon nitride based catalysts. BPA removal and mineralization were followed by high performance liquid chromatography (HPLC) and total organic carbon (TOC) analysis, respectively. Briefly, a known amount of urea in a covered crucible was heated to 550 °C in a muffle furnace at a heating rate of 5 °C/min and then retained at 550 °C for 2h. The  $\text{g-C}_3\text{N}_4@\text{CoFe}_2\text{O}_4$  catalyst was prepared by loading  $\text{CoFe}_2\text{O}_4$  onto the synthesized  $\text{g-C}_3\text{N}_4$  by ultrasonic hydrothermal method. Furthermore, during the synthesis of graphite carbon nitride from the urea,  $\text{g-C}_3\text{N}_4@\text{TiO}_2$  catalysts were obtained by adding  $\text{TiO}_2$  in different percentages in the anatase formula. Ultrasonic-assisted photocatalytic oxidation of BPA was performed by using persulphate oxidant and prepared catalysts (UV / US / PS / catalyst). When used alone, persulphate, ultrasonic system, UV ( $> 350$  nm) and catalysts were found to be ineffective in BPA removal. However, 100% BPA removal was achieved with UV / US / PS combined system with all prepared catalysts. Different mineralization activities were obtained depending on the catalysts used. FTIR, SEM-EDS and XRD analyzes were performed for characterization of prepared catalysts.

**Keywords:** Bisphenol-A, carbon nitride, photocatalysis, ultrasonic

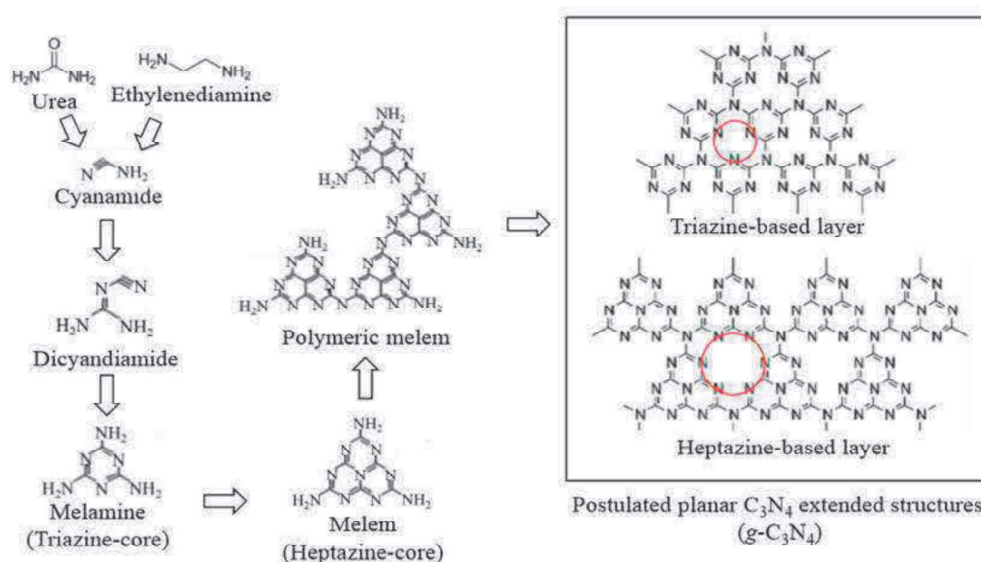
## **1.INTRODUCTION**

Due to the increase in population and technology, chemical types and concentrations in wastewaters are increasing. Some of these pollutants are released to the environment without being treated since they are resistant to common treatment methods. Bisphenol-A (BPA) is a compound commonly used in the polymer industry. BPA contributes to the hardness and transparency of the plastic products produced. This compound, which is a class of endocrine disruptors. The definition of endocrine disrupting compound is made by the United States Environmental Protection Agency (US EPA) as an "external agent that interferes with the synthesis, secretion, transport, metabolism, binding action or elimination of natural blood-derived hormones found in the body and responsible for homeostasis, reproduction and developmental processes" (Diamanti-Kandarakis et al., 2009). Bisphenol A (BPA) can be passed from the exposed mother to the fetus as well as through canned food, baby food or breast milk (Vom Saal et al., 2007). BPA was found in 92.6% of urine samples taken in a study conducted by the Centers for Disease Control over 2500 people in the USA (Calafat et al.,

2008). In that study, BPA concentrations in children and adolescents were higher than in adults. Recent studies have demonstrated that food is not the only source of exposure and that the half-life of BPA in humans is longer than expected (Stahlhut et al, 2009).

Advanced oxidation techniques (AOTs) include Fenton systems (photo and electro), photocatalytic oxidation, wet air oxidation, ozone, sono-catalytic oxidation and their combination are increasingly adopted to the destruction of organic pollutants because of high efficiency, simplicity, and applicability (Benjwal et.al., 2015).

Recent studies have shown that heterogeneous semiconductor photocatalysts (etc.  $\text{TiO}_2$ ,  $\text{ZnO}$ ) will be an alternative in wastewater treatment. When the semiconductors are illuminated with a suitable light source, the electron / hole pair is formed when the electron in the valence band is excited and passed to the conductivity band. The resulting electron / hole pair oxidizes the organic pollutant after a complex series of reactions.



**Figure 1.** The structures of  $g\text{-C}_3\text{N}_4$  (Dong et al., 2014).

Recently, graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ), a polymeric semiconductor material composed of mainly C, N and H atoms with a band gap of 2.7 eV (454 nm), has gained great attention in photocatalytic applications (Masih et al., 2017).  $g\text{-C}_3\text{N}_4$  has the advantageous features of including its low cost, nontoxicity, prominent stability, and effectiveness under both visible and ultraviolet light (Huang et al., 2015; Yao et al., 2016; Fagan et al., 2016).

Among spinel ferrites, cobalt ferrite  $\text{CoFe}_2\text{O}_4$  has attracted considerable attention due to their large magnetocrystalline anisotropy, high coercivity, moderate saturation magnetization, large magnetostrictive coefficient, chemical stability and mechanical hardness (Patil et al., 1990).  $\text{CoFe}_2\text{O}_4$  has an inverse spinel structure where oxygen atoms make up an FCC lattice and with one half of  $\text{Fe}^{3+}$  ions occupied the tetrahedral A sites and the other half, together with  $\text{Co}^{2+}$  ions located at the octahedral B sites (Pham et al., 2005). It is involved in magnetic, electrochemical and photocatalytic applications (Pui et al, 2011).

In this study, photocatalytic oxidation of bisphenol A was performed using graphitic carbon nitride,  $\text{TiO}_2$ ,  $\text{CoFe}_2\text{O}_4$ , and modified graphitic carbon nitride.

## **2. MATERIAL AND METHOD**

### **2.1. Preparation of graphitic carbon nitride**

Five grams of urea were placed in a quartz tube furnace in ceramic. It was heated to 550°C at 5°C / min with argon gas flow and held at this temperature for 2 hours.

### **2.2. Preparation of modified graphitic carbon nitride structures**

#### **2.2.1. Synthesis of graphitic carbon nitride@TiO<sub>2</sub>**

Five grams of urea and TiO<sub>2</sub> (1.2 and 5%) were placed in the quartz tube furnace in ceramic. It was heated to 550°C at 5°C/min with argon gas flow and held at this temperature for 2 hours.

#### **2.2.2. Synthesis of graphitic carbon nitride @CoFe<sub>2</sub>O<sub>4</sub>**

0.16 g of the prepared g-C<sub>3</sub>N<sub>4</sub> was taken and dispersed in 150 mL of water in ultrasonic bath.

0.3969 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 1.106 g Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were dissolved in 10 mL of water to a solution of g-C<sub>3</sub>N<sub>4</sub> such that the ratio of g-C<sub>3</sub>N<sub>4</sub>: CoFe<sub>2</sub>O<sub>4</sub> was 1: 2. The pH was adjusted to 11 using 3.5 M NaOH and kept for 5 hours in an ultrasonic bath.

### **2.3. Photocatalytic oxidation experiments**

Catalyst and persulfate were added to 50 mL of 12.5 mg/L BPA solution. Vis-LED (blue) lamp placed 15 cm above the solution was switched on and photocatalytic oxidation processes were performed in the ultrasonic bath. Samples were taken at certain times and HPLC and TOC analyzes were performed.

### **2.4. High performance liquid chromatography analysis**

Concentrations of BPA solution were carried out using the C-18 column 45% acetonitrile: 55% water mobile phase, Agilent HPLC with a diode array detector at 215 nm at a flow rate of 0.8 mL / min.

### **2.5. Total organic carbon analysis**

TOC analysis of samples taken after oxidation was performed with Shimadzu TOC analyzer.

### **2.6. Characterization of catalyst**

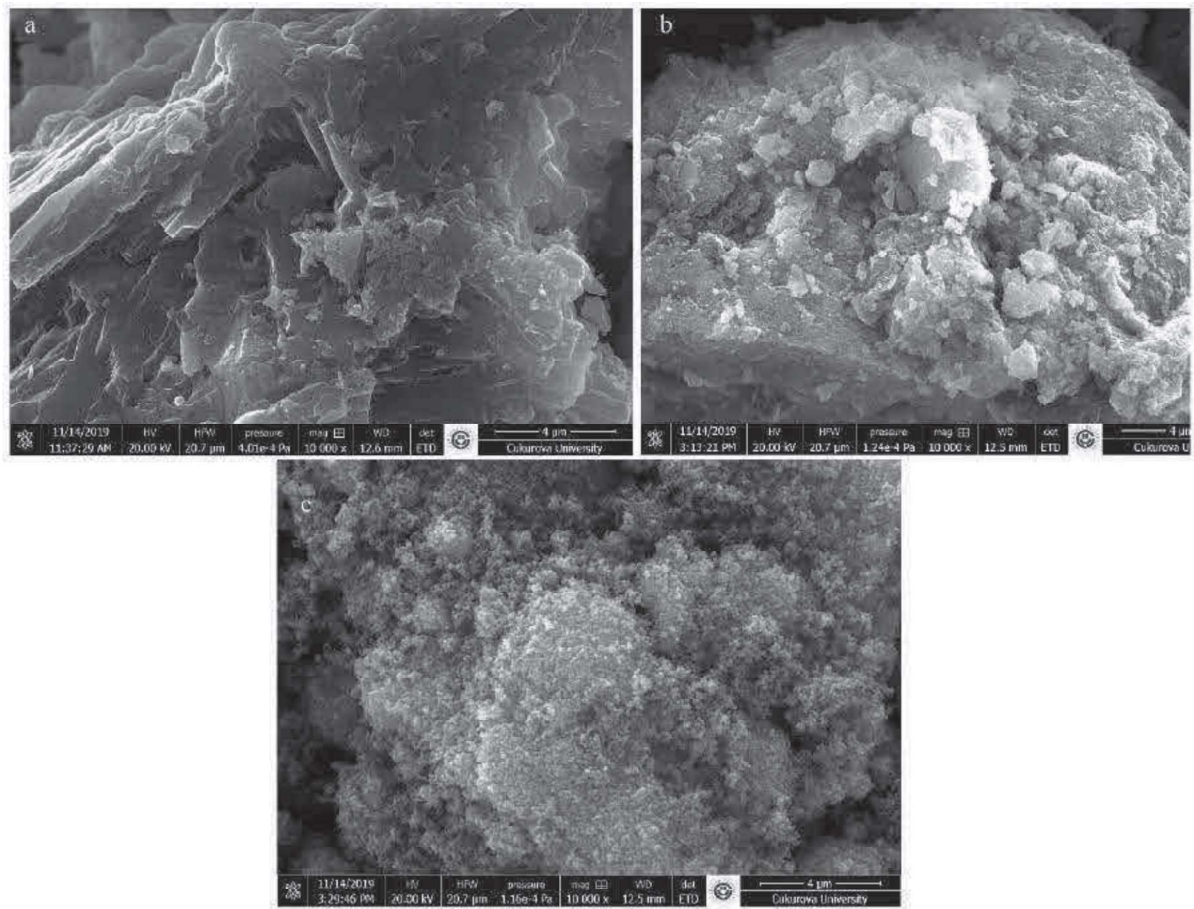
SEM-EDS (FEI Quanta FEG 650) was used for surface analysis and elemental analysis of catalysts.

## **3.RESULTS**

### **3.1. SEM-EDS Analysis of catalysts**

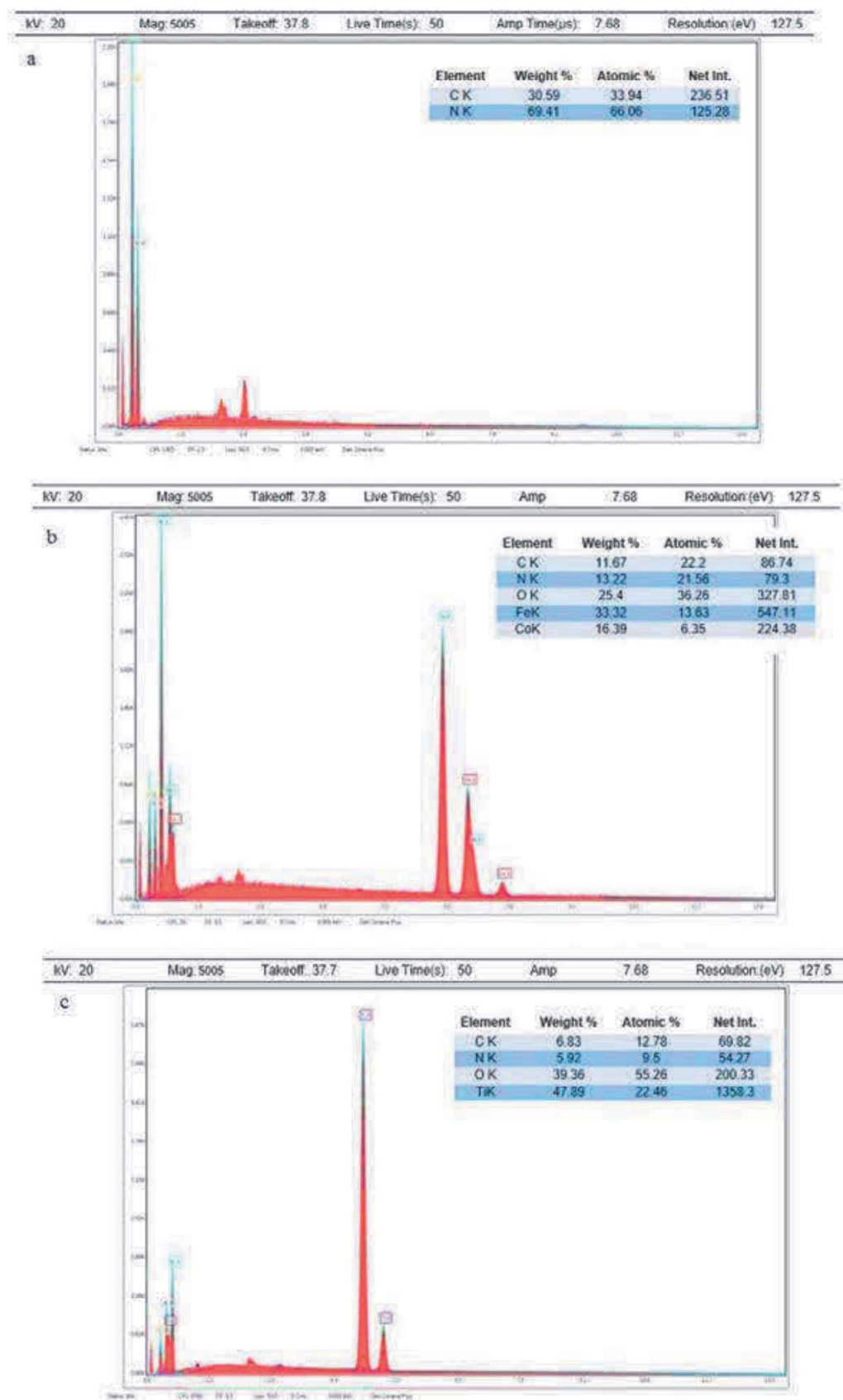
In Figure 2, SEM images are given after loading CoFe<sub>2</sub>O<sub>4</sub> and TiO<sub>2</sub> with bare form of graphitic carbon nitride synthesized from urea. It was observed that TiO<sub>2</sub> had a spherical and homogeneous distribution while coating the graphitic carbon nitride surface with both.





**Figure 2.** SEM image of (a) g-C<sub>3</sub>N<sub>4</sub> (b) g-C<sub>3</sub>N<sub>4</sub>@CoFe<sub>2</sub>O<sub>4</sub> (c) g-C<sub>3</sub>N<sub>4</sub>@TiO<sub>2</sub>

On the other hand, EDS analysis shows that loading has occurred (Fig 3). The coefficients between the elemental distribution ratios indicate that the coating process is carried out regularly.



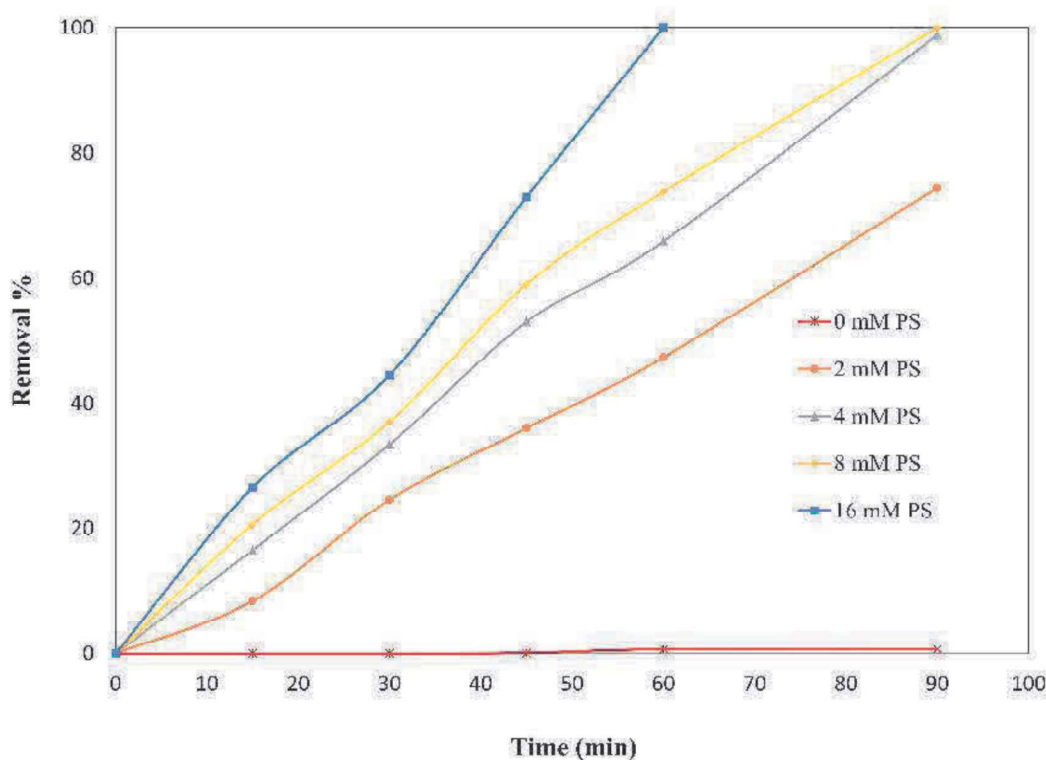
**Figure 3.** EDS results of (a) g-C<sub>3</sub>N<sub>4</sub> (b) g-C<sub>3</sub>N<sub>4</sub>@CoFe<sub>2</sub>O<sub>4</sub> (c) g-C<sub>3</sub>N<sub>4</sub> @TiO<sub>2</sub>

### 3.2. Photocatalytic oxidation results

Individually persulfate, UV, US and catalyst were not effective in photocatalytic oxidation of aqueous solution of bisphenol A compound. It was determined that photocatalytic oxidation (UV/US/PS/Catalyst) provides effective removal efficiency of BPA.

#### 3.2.1. Effect of persulphate concentration

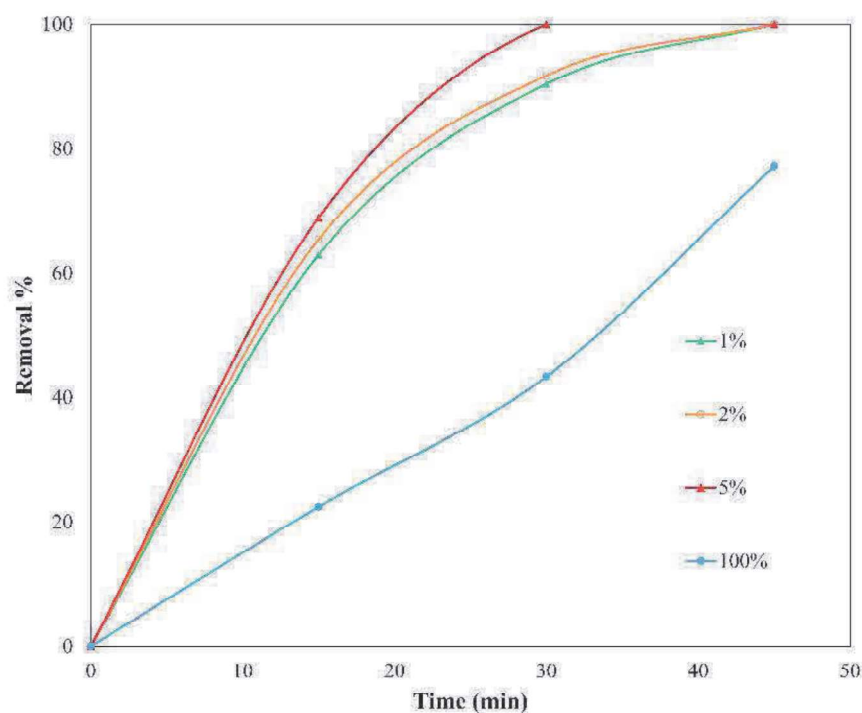
The removal of BPA was determined by HPLC by adding persulfate oxidant at different concentrations (0-16 mM) (Fig. 4). While no removal was possible in the absence of PS, BPA removal was increased due to increased PS concentration. When 16 mM PS was used, BPA was completely disrupted in 60 minutes.



**Figure 4.** Effect of persulphate concentration ( $[BPA]_0=12,5$  mg/L,  $[g-C_3N_4@CoFe_2O_4]_0=0,1$  g/L)

#### 3.2.2. Effect of $TiO_2$ percent

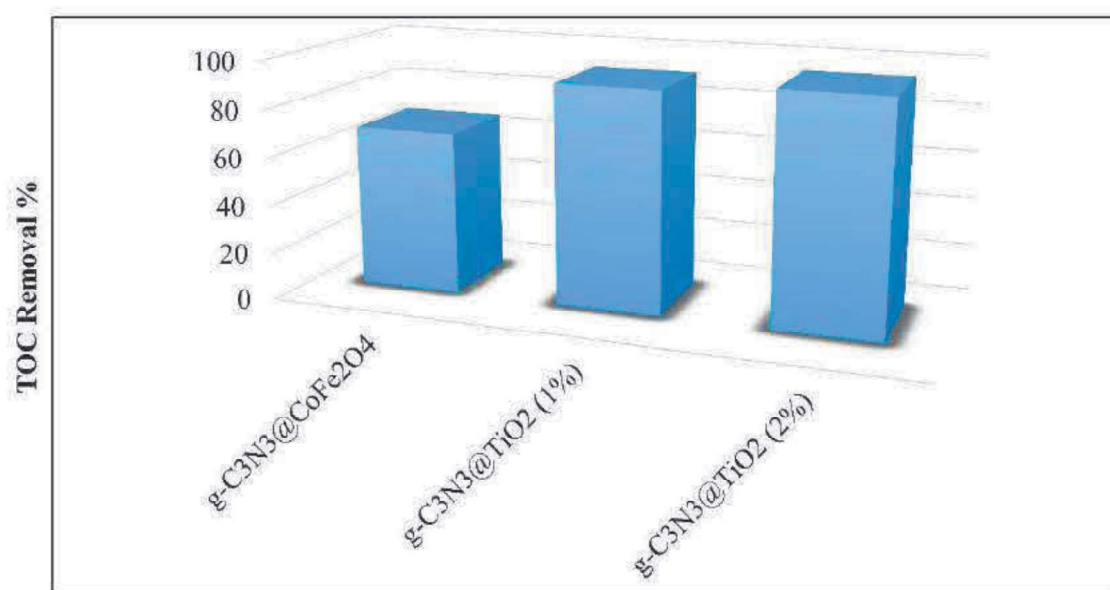
During the synthesis of graphitic carbon nitride,  $TiO_2$  was added at 1%, 2% and 5%. Photocatalytic oxidation of BPA using  $g-C_3N_4@TiO_2$  and bare  $TiO_2$  was performed and the results are given in Figure 5. The results show that the increase in the amount of  $TiO_2$  directly affects the time of oxidation.



**Figure 5.** Effect of  $\text{TiO}_2$  percent ( $[\text{BPA}]_0=12,5 \text{ mg/L}$ ,  $[\text{g-C}_3\text{N}_4@\text{TiO}_2]_0=0,1 \text{ g/L}$ ,  $[\text{PS}]_0=16 \text{ mM}$ )

### 3.2.2. Mineralization efficiency

After photocatalytic oxidation, the amount of Total Organic Carbon (TOC) of the solution was measured and TOC removal was determined.



**Figure 6.** TOC removal efficiency ( $[\text{BPA}]_0=12,5 \text{ mg/L}$ ,  $[\text{catalyst}]_0=0,1 \text{ g/L}$ ,  $[\text{PS}]_0=16 \text{ mM}$ )



#### 4. CONCLUSION

The synthesis of producing graphitic carbon nitride and TiO<sub>2</sub> loaded carbon nitride was carried out in the tube furnace. CoFe<sub>2</sub>O<sub>4</sub> loading was then performed in the ultrasonic bath hydrothermal. Photocatalytic activity was increased after CoFe<sub>2</sub>O<sub>4</sub> and TiO<sub>2</sub> loading to graphitic carbon nitride. Oxidation efficiency was not obtained in the absence of persulphate. Nearly 100% mineralization was performed especially with TiO<sub>2</sub> loaded graphitic carbon nitride.

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