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Highly effectual photocatalytic degradation of tartrazine by using Ag nanoparticles decorated on Zn-Cu-Cr layered double hydroxide@ 2D graphitic carbon nitride (C3N5)

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Research Article

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Abstract

Pollution of water resources is one of the main concerns of many countries. This issue originates from the entry of diverse pollutants, including dye compounds, into water sources. In this work, ternary Zn-Cu-Cr layered double hydroxides (LDH) supported on graphitic carbon nitride (g-C_3N_5) decorated by silver nanoparticles (C_3N_5-LDH-Ag) was first prepared. Application of various characterization techniques such as SEM, XRD, and FT-IR revealed that the synthesized nanocomposite was composed of Zn-Cu-Cr LDH nanoparticles, g-C_3N_4 nanosheets, and Ag nanoparticles. The prepared nanomaterials were employed for the photodegradation of tartrazine in aqueous solutions. It was found that the C_3N_5-LDH-Ag catalyst outperformed their pure g-C_3N_5, Zn-Cu-Cr LDH, and C_3N_5-LDH composite in photocatalytic degradation of tartrazine under visible light irradiation. Tartrazine (20 mg/L) can be entirely removed by 0.25 g/L C_3N_5-LDH-Ag photocatalyst under one h visible light irradiation (200W) at pH 6 with a rapid degradation rate constant (*k*) that is 4.4, 3.9, and 2.6 times higher than that of pure C_3N_5, Zn-Cu-Cr LDH, and C_3N_5-LDH component, respectively. The formation of hydroxyl radicals on the surface of C_3N_5-LDH-Ag as the main active species was approved by the capturing experiment. The finding results approved the stability and reusability of C_3N_5-LDH-Ag in four photocatalytic degradation cycles. In general, our findings revealed that the synthesized nanocomposite could be employed as an efficient photocatalyst in environmental remediation.

Introduction

The widespread issue of water pollution is endangering human health so that every year the human death due to polluted waters are more than war. Toxic substances from agriculture, urban, and industry readily enter and cause water pollution. Almost every industry utilizes dyestuffs to dye their products and it's estimated 10–15% of the dye is lost into the effluent during the process (Gupta et al. 2011). There is number of coloring agents that are commonly used in pharmaceutical, texture and food industries, among which tartrazine is most widely used. Tartrazine is a yellow to orange colored synthetic azo-dye, which is also known as FD&C Yellow 5 and/or E102. Tartrazine is a water-soluble colorant used in many food products like cotton candy, corn flakes, soft drinks, foodstuffs, pickles, chewing gum, and drugs (Mehedi et al. 2009). Tartrazine has been known to show side effects like hyperactivity, asthma, migraines, eczema, thyroid cancer (Skinner et al. 2020), and also lupus chromosomal aberration in somatic cells of rats (Elhkim et al. 2007). Despite such toxic effects observed on tartrazine exposure, this azo-dye is still cheaply available worldwide and has been observed to be used. Accordingly, it is necessary to develop efficient and sustainable methods to remove tartrazine from wastewater. Consequently, eliminating organic and inorganic contaminants from contaminated water is of crucial significance. Several techniques, including adsorption (Gautam et al. 2017; Goscianska & Ciesielczyk 2019; Grover et al. 2022; Kumar Biswal et al. 2022), photocatalytic degradation (Balu et al. 2019; Dalponte et al. 2019; Alcantara-Cobos et al. 2020; Cubas et al. 2020; Dalponte Dallabona et al. 2021; Abd-Ellatif et al. 2022), electrochemical and sonochemical oxidation (Donoso et al. 2021), electro-Fenton reaction (Zhang et al. 2019) have been employed in the treatment of tartrazine.

Graphitic carbon nitrides (CNs) are exciting materials with unique properties such as high hardness, semi-conductivity, and adsorption properties, which are mainly controlled by the structure, composition, and crystallinity of the CN framework. According to the C/N ratio, carbon nitride materials ranging from 0.4 to 3 have been synthesized and denominated as C_3N_2, C_3N_4, C_3N_5, C_3N_6, C_3N_7, and so on. Graphitic carbon nitrides have attracted growing attention as a semiconductor polymeric photocatalyst because of their facile synthesis procedure, attractive electronic band structure, easy functionalization, light absorption in the visible spectrum, and high physicochemical stability (Vadivel et al. 2020). The catalytic properties of a material are often related to its electronic structures. Chemical doping on CNs is an effective method to regulate the electronic structures, ionic conductivity, and surface properties. It has been found that the addition of extra nitrogen-rich moieties in the CNs framework to increase the C/N ratio can reduce the band gap significantly due to a more extended conjugated network. For example C_3N_5 in comparison with C_3N_4 displayed improved photosensitization properties at longer wavelengths and solar cell devices fabricated using low band gap C_3N_5 demonstrated improved power conversion efficiency and open-circuit voltage (Kumar et al. 2019).

Layered double hydroxides (LDHs) constitute a class of stacked inorganic sheets with simple abbreviation formula $M^{II}M^{III}$-X where M^{II} and M^{III} represent divalent and trivalent cations, respectively, within the layer of hydroxides. Their layered structure, high adsorption capacity, comprehensive chemical composition, variable layer charge density, ion-exchange properties, reactive interlayer space, tunable acidity-basicity surface, and environment-friendly property make it a promising material for various applications (Forano et al. 2013). Besides, LDHs are prospective candidate catalysts for water treatment owing to their excellent structural and physicochemical properties interacting with pollutants in aqueous solutions (Karim et al. 2022). The catalytic activity and further application of LDHs are limited owing to the lack of functional groups and structural components in pure LDHs. To overcome these drawbacks, modification of LDHs have been performed by introducing functional groups or structural components. Modifications of LDHs has been caused to design and yield novel functional LDHs-based catalysts. Meanwhile, various modification strategies of LDHs, such as polyoxometalates, metal nanoparticles, metal oxide, carbon-based nanomaterials, have been proposed (Chen et al. 2022; Li et al. 2022a; Li et al. 2022b; Qiu et al. 2022; Salem et al. 2022; Yang et al. 2022).

Herein, we report a novel Zn-Cu-CrLDH@C_3N_5/AgNPs (C_3N_5-LDH-Ag) composite for the first time, which was synthesized step by step. Zn-Cu-Cr ternary layered double hydroxide was synthesized by the co-precipitation method (Liu et al. 2018). Graphitic carbon nitride g-C_3N_5 was synthesized by hydrothermal method from melamine (Liu et al. 2020). Solvothermal method was used to prepare Zn-Cu-CrLDH@C_3N_5, and at the last step, silver nanoparticles were decorated onto the Zn-Cu-CrLDH@C_3N_5 nanocomposite. The photocatalytic activity of (C_3N_5-LDH-Ag) nano-composite in the degradation of tartrazine azo dye was investigated. Tartrazine can completely be degraded by 2% (C_3N_5-LDH-Ag) in 60 min and pH 6.0. Compared with pure Zn-Cu-CrLDH, g-C_3N_5, and C_3N_5-LDH, the as-prepared C_3N_5-LDH-Ag photocatalyst has improved photocatalytic activity for the removal of tartrazine in such a way the degradation rate

constants *k* are 4, 3, and 2 times higher than that of pure C_3N_5, Zn-Cu-CrLDH and C_3N_5-LDH, respectively. The structure of C_3N_5-LDH-Ag and the applicability of the improved photocatalytic performance were systematically investigated.

Experimental Section

Chemicals and reagents

All of the materials were used in this study, such as melamine, hydrazine, $Zn(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$, $Cr(NO_3)_3.6H_2O$ $Ag(NO_3)$, were purchased from Merck (Darmstadt, Germany). All chemicals were analytical grade reagents and were used as received without further purification. Double distilled water was used for the preparation of solutions. A stock solution of 1000 ppm tartrazine was prepared and other working solutions were obtained by successive dilution of stock solutions.

Synthesis procedures

Synthesis of Melem

To synthesis melem (2,5,8 -triamino-s-heptazine), 6 gr of melamine was added in an alumina crucible covered with a lid and heated at an oven with a heating rate 20 ºC/min and holding at a final temperature of 425 ºC for 12. The obtained yellowish tinge powder was crushed and suspended in 100 ml DI water in an ultrasonic bath for 10 min. The obtained suspension was refluxed for 5 hours to remove unreacted melamine and other impurities. The resulting white product was collected by centrifugation at 7000 rpm for 12 min and dried at room temperature.

Synthesis of melem hydrazine

A hydrothermal reaction between melem and hydrazine was used to synthesize the monomeric unit of melem hydrazine or 2,5,8-trihydrazino-s-heptazine. In brief, 1.6 g of melem was dispersed in 15 mL of hydrazine hydrate solution (55%) by an ultrasonic probe and sealed in a 25 mL stainless steel reactor with Teflon liner and heated at 140 ºC for 24 h. After cooling the reactor to room temperature, the obtained yellowish solution suspension was transferred to a beaker and pH was adjusted 1–2 by adding 10% HCl solution. Then the solution was filtered to remove unreacted solid, and the filtrate was precipitated by adding 10% NaOH solution to maintain pH in the range of 7.5–8.5. The obtained solid was filtered and dissolved in HCl, filtered and reprecipitated in NaOH. This procedure was repeated three times.

Finally, the obtained white solid was washed three times with DI water and ethanol, centrifuged at 5000 rpm for 5 min, and dried at room temperature.

Synthesis of C_3N_5 polymer

The as-prepared melem hydrazine was heated at 450 ºC for 2 h (heating rate of 2 ºC) to synthesize C_3N_5 polymer. The obtained orange powder was used for subsequent experiments to modify by LDH and

Synthesis of Zn-Cu-Cr-LDH

The co-precipitation method, which is a common technique for direct synthesis of double-layer hydroxides, was used in this study. For the synthesis of Zn-Cu-Cr-LDH at first, 12 mmol $Zn(NO_3)_2.6H_2O$, 4 mmol $Cu(NO_3)_2.3H_2O$ and 8 mmol $Cr(NO_3)_3.6H_2O$ was dissolved in 200 ml of ultrapure water. Then 50 ml of an alkaline solution containing NaOH (2 M) and Na_2CO_3 (1 M) was prepared. The alkaline solution was then slowly added dropwise to the solution of metal cations under a magnetic stirrer until the pH of the solution reached 10. The resulting suspension is stored at 700°C for 24 h. After cooling, the resulting precipitate was filtered and washed with ultra-pure water until the pH of the filtrate was neutralized. Finally, the product was dried in an oven at 650°C for 24 hours. To compare, Zn-Cr-LDH, Zn-Cu-LDH, and Cu-Cr-LDH double layer hydroxides were synthesized similarly. It is worth to mention, the chloride salts of metals were used for the two-component synthesis of LDH.

Synthesis of Zn-Cu-Cr-LDH@g-C_3N_5 Composite

Zn-Cu-Cr-LDH@g-C_3N_5 (C_3N_5-LDH) composite was prepared by solvo-thermal method. For this purpose, 0.4 g of graphite nitride carbonate (g-C_3N_5) and 2 g of sodium hydroxide were added to 35 Ml of ethylene glycol and stirred. 12 mmol $Zn(NO_3)_2.6H_2O$, 4 mmol $Cu(NO_3)_2.3H_2O$ and 8 mmol $Cr(NO_3)_3.6H_2O$ (molar ratio 2: 1: 3) was solved into another 35 mL of ethylene glycol. The two ethylene glycol solutions were then mixed and stirred for 1 h. The suspension was transferred to a stainless steel reactor with Teflon liner and heated at 120 ° C for 24 hours. The obtained solid was collected by centrifugation, washed twice with ethanol and three times with ultra-pure water, and dried in an oven at 80 ° C for 24 hours.

Synthesis of Zn-Cu-Cr-LDH@g-C_3N_5 /AgNPs Composite

In order to synthesize Zn-Cu-Cr-LDH@g-C_3N_5/AgNPs (C_3N_5-LDH-Ag) nanocomposite, 50 mg of the as-synthesized C_3N_5-LDH was dispersed in 50 ml of DI water in an ultrasonic bath for 1 hour. Then 15 mL of silver nitrate with a concentration of 0.25 M was added drop-wise and stirred for 1 hour. Then 15 mL of sodium hydroxide (2 g/L) was added to the suspension, which changed the color from brown to black. The suspension was stirred for 6 h and then centrifuged at 6000 rpm for 10 min. The precipitate was first washed with water and then with ethanol and dried for 12 hours at 60°C.

Photocatalytic Degradation

To investigate the photocatalytic degradation of tartrazine in the presence of synthesized nanocomposite, a 500 mL photocatalytic reactor was used. 300 mL of 20 mg/L solution of tartrazine was poured into a photocatalytic reactor. 5 mL of 0.25 g/L well-dispersed synthesized nanomaterials were added to the photo-reactor. The mixture was stirred for 1 hour in the absence of light to balance the possible adsorption of tartrazine on the photocatalyst (It was considered as time 0 in all graphs). After 1 hour the reactor lamp was turned on and the photocatalytic degradation of tartrazine was followed under

the radiation of visible light. All experiments were conducted at room temperature (22 ± 2ºC). During each experimental process, 2.0 mL samples were withdrawn from the photoreactor at 10-minute intervals and centrifuged to remove the photocatalyst. UV-Vis spectrum of each samples was recorded in the range of 700 – 200 nm to evaluate the concentration of tartrazine, and the percentage of degradation was obtained using Eq. 1.

$$\%Removal = \frac{C_0 - C_t}{C_0} \times 100$$

1

Where C_0 and C_t are initial and instantaneous concentration of tartrazine at time t.

Results And Discussion

Characterization of nano-composite

The Morphology of the prepared nano-photocatalyst was evaluated by FE-SEM technique. The FE-SEM images of C_3N_5, Zn-Cu-Cr-LDH, C_3N_5-LDH and C_3N_5-LDH-Ag have been shown in Fig. 1. The rough and tumbled carbon nitride (C_3N_5) layered structure toward irregular thickness has been clearly remarked in Fig. 1a. The FE-SEM images of Zn-Cu-Cr-LDH are exhibited in Fig. 1b. A hexagonal layer structure was observed in Zn-Cu-Cr-LDH. Moreover, in Fig. 1b, the layers collapse due to thermal treatment upon calcination and material accumulated can be viewed. In the case of C_3N_5-LDH, good interaction between double layered hydroxide and C_3N_5 is apparent from the growth of particle-shape LDH configuration grown on the C_3N_5 sheets of C_3N_5-LDH composite. As can be seen in Fig. 1d, after Ag nanoparticles doping, the surface of C_3N_5-LDH is uniformly deposited by metallic Ag NPs as well as shown.

Figure 1

Energy dispersive spectroscopy (EDS) analysis was performed to determine the elemental composition of the synthesized compounds (Fig. 2a & b). The EDS spectrum demonstrated the presence of C, O, N, Cr, Cu and Zn in the structure of C_3N_5-LDH composite. C and N elements come from g-C_3N_5 and Zn, Cr, Cu and O attributed to LDH nanoparticles decorated on g-C_3N_5 sheets. In addition to the elements observed in Fig. 2a, silver is also identified in EDS spectrum of C_3N_5-LDH-Ag, which approves decoration of the silver layer on the surface of the synthetic nanocomposite.

Figure 2

Fourier transform infrared (FTIR) spectroscopy is used to identify structure vibration of the pure C_3N_5, pure Zn-Cu-Cr-LDH, C_3N_5-LDH, and Ag- doped C_3N_5-LDH material that has been shown in Fig. 3. The FT-IR spectrum of pure g-C_3N_5 has a specific broad peak at 3416 cm^{-1} which corresponds to stretching vibration -OH, -NH and the stretching modes of C = N and C-N bonds are located in the range of 1216–

1622 cm^{-1}. A featured sharp band at 808 cm^{-1} related to breathing bending modes of triazine units (Fig. 3) (Kumar et al. 2019). For LDH structure a broad absorbance peak at approximately 3416 cm^{-1} is due to stretching vibration of hydrogen bonding between LDH layers due to hydroxyl groups and water interlayers (Zhou et al. 2022). The emergence of CO_3^{2-} ions in the LDH interlayers proved a sharp band at 1358cm^{-1}. A peak around 1624 cm^{-1} can be correspond to water molecules bending vibration. The presence of metal-oxygen and metal- hydroxyl vibrational peaks is obviously confirmed in the 400–1000 cm^{-1} range(Prasad et al. 2019). C_3N_5-LDH exhibits the predominant characteristic peak for Zn-Cu-Cr-LDH and C_3N_5, indicating that both components are present in the composite as prepared. As can be seen, after doping Ag NPs in Ag-doped C_3N_5-LDH compound the characteristic peaks exhibited slight shifts toward lower wavenumbers. Furthermore, After the Ag nanoparticles were merged into the composite, the intensity was significantly decreased.

Figure 3

To verify the phase structure and identify phase impurities in the samples, the XRD patterns studied. XRD peak characteristics of pure C_3N_5, pure Zn-Cu-Cr-LDH, C_3N_5-LDH, and Ag-doped C_3N_5-LDH were ascertained in Fig. 4. A relatively strong diffraction peak 2θ = 26.94° is consistent with (002) nanosheets of conjugated aromatic structures in C_3N_5 (Kumar et al. 2019). A weak diffraction peak 2θ = 13.54° for (100) plane is attributed to in-plane repeating triazole units(Jigyasa *et al.* 2021). XRD diffraction patterns for pure Zn-Cu-Cr-LDH remarked at 2θ values of 12.04°, 23.54°, 34.19°, 38.99°, 46.64°, 59.84°, 60.84°. C_3N_5-LDH have similar XRD patterns to pure LDH and g-C_3N_5 samples. In the case of C_3N_5-LDH-Ag diffraction peaks related to (111), (200), (220) and (311) located at 38.44°, 44.69°, 64.64° and 77.89° (JCPDS no. 04-0783) are seen to confirm metallic silver doping condition.

Figure 4

The photocalalytic degradation of tartrazine

Photocatalytic degradation of tartrazine in the presence of pure g-C_3N_5, pure Zn-Cu-Cr-LDH, C_3N_5-LDH and C_3N_5-LDH-Ag was investigated, and the corresponded results were illustrated in Fig. 5. The degradation reaction was also followed by using no photocatalyst but under the same reaction conditions. However, no decolorization was detected in the absence of the photocatalysts. Figure 5a, b, c, and d shows the UV-Vis spectrum of tartrazine for all samples at different irradiation times. Before starting the catalyzed degradation reactions, the tartrazine solutions were stirred for 1h in the dark to establish an adsorption – desorption equilibrium between the photocatalyst particles and the tartrazine molecules. No significant adsorption of tartrazine onto the photocatalysts was observed. As shown in Fig. 5e, g-C_3N_5, Zn-Cu-Cr LDH and C_3N_5-LDH can respectively provide 63, 65 and 88% tartrazine degradation during 1 h, whereas the C_3N_5-LDH-Ag exhibit a greater photocatalytic activity over the same irradiation period. In other words, a combination of the two individual materials (g-C_3N_5 and Zn-Cu-Cr LDH) leads to the improved photocatalytic performance of the resultant composites and the presence of

Ag nanoparticles made the C_3N_5-LDH-Ag the best photocatalyst. Ag loading enabled the C3N5-LDH to absorb visible light effectively and improved charge separation ability during photocatalysis process. The C3N5-LDH-Ag composite exhibited enhanced performance toward tartrazine photodegradation, which could be ascribed to the fast separation and transfer of photogenerated electron-hole pairs and the modified band structure (Liu et al. 2021).

In order to confirm the effect of the catalyst on the photocatalytic activity, an experiment was conducted in the absence of C_3N_5-LDH-Ag. Without the photocatalyst, the concentration of tartrazine did not decrease under visible light irradiation. Accordingly, it was concluded that both light and the catalyst are important for the degradation of tartrazine. Kinetics of the photocatalytic degradation of tartrazine was explored using different catalysts and 2500 W visible light. A linear relationship between the natural logarithm of the changes in the tartrazine concentration, i.e., −ln(Ct/C0), and irradiation time (t) were observed. The observed linear relationship suggests that the degradation process can be described as a pseudo-first-order reaction. Its associated rate constant (k) can be calculated using − ln(Ct/C0) = kt. Accordingly, the rate constants of the photocatalysis processes of the dye degradation were obtained as 0.018, 0.020, 0.031 and 0.078 min^{-1}, for g-C_3N_5, Zn-Cu-Cr-LDH, C_3N_5-LDH and C_3N_5-LDH-Ag, respectively (Fig. 5f). It means that the photocatalytic degradation reaction in the presence of C_3N_5-LDH-Ag is 4.4, 3.9, and 2.6 times faster than the photocatalytic reaction in the presence of g-C_3N_5, Zn-Cu-Cr-LDH and C_3N_5-LDH, respectively.

Figure 5

Figure 6

Effect of initial solution pH

The solution pH is a key parameter that affects the removal efficiency of tartrazine in the photocatalytic degradation process in the presence of C_3N_5-LDH-Ag. The effect of pH in the range 3–10 on tartrazine (20 mg/l) removal after 60 min visible light irradiation was investigated and the corresponded results were illustrated in Fig. 6a. As can be seen, increasing the initial solution pH from 3.0 to 6.0 increased the removal efficiency of tartrazine from 82% in pH 3.0 to more than 99% in pH 6.0 after 60 min reaction time. But the increasing in solution pH from 6.0 to 10 decreased the removal efficiency to 76%. In a similar pattern when the solution pH was raised from 3.0 to 6.0, increase in k_{obs} was seen in which the rate constant was increased from 0.028 min^{-1} to 0.078 min^{-1}, but the rate constant dropped with increasing pH from 6.0 to 10.0, (0.027 min^{-1}) Fig. 6b. The interpretation of pH effects on the dye photodegradation process is a challenging task due to its dependence on various physical and chemical phenonoma. First, the influence of pH on the rate of degradation can be explained by the processes of sorption–desorption in the semiconductor particle sheet (Chekir et al. 2017). Tartrazine is an anionic dye, because the sulphonate groups at the tartrazine (D-SO_3Na) were dissociated and converted into anionic dye ions (D-SO_3^-) Therefore, in acidic solution, the presence of hydronium ions in the solution attracted tartrazine

making it neutral or positive. This contributed to the higher removal efficiency of the dye. The same optimum pH has been reported by other authors (Abdul Rahman et al. 2018).

Effect of catalyst dosage

The effect of C_3N_5-LDH-Ag dosage (0.1–0.5 g/L) on the degradation of tartrazine (20 mg/L) was investigated in the photo-reactor. As demonstrated in Fig. 6c, the efficiency of tartrazine degradation an increased from 83% to more than 99% with increase in catalyst concentration from 0.1 to 0.25 g/L, but a decreasing trend was observed by increasing the photocatalyst dose beyond 0.25 to 0.5 g/l in such a way that tartrazine degradation dropped to 89% in catalyst dose 0.5 g/l. The increasing catalyst dose increased the amount of oxidizing radicals produced since, the active surface sites increased, more light was absorbed and caused the formation of more active species (Chekir et al. 2017). Therefore, the more tartrazine degraded by increasing photocatalyst from 0.1 to 0.25 g/L. When an excess amount of C_3N_5-LDH-Ag was added (more than 0.25 g/L), the percentage of degradation decreased because the photocatalyst suspension could notably inhibit the penetration of visible light into the solution, which leads to a decrease in the generation of oxidizing agents. Consequently, 0.25 g/L catalyst dose was chosen as the optimum dose for further experiments (Bouarroudj et al. 2021).

Effect of initial dye concentration

The initial concentration of the dye solution influenced the photocatalytic degradation of tartrazine as shown in Fig. 6d. Firstly, decolorization efficiency increased when the initial tartrazine concentration was increased from 10 to 20 mg/L. Then, increasing the concentration of tartrazine beyond 20 mg/L resulted in a decrease in the decolorization efficiency. The rate and amount of the degradation reaction is dependent on the rate of formation of the active species during photodegradation process as well as the probability of the radicals reacting with the tartrazine molecules. As the concentration of dye is increased, there will be more molecules of dye which could react with the oxidizing radicals, consequently resulting in an enhancement of the rate of the degradation of tartrazine (Bouarroudj et al. 2021). However, as the concentration of dye is increased beyond 20 mg/L, the decolorization efficiency decreases, showing that the decrease in the formation of active species on the surface of the photocatalyst has been taking place. The reason could be that the active sites on the catalyst surface are occupied by layers of dye molecules (Faramarzpour et al. 2009). On the other side, at a high concentration of dye, a significant amount of the visible radiation could be absorbed by the dye molecules rather than the photocatalyst particles and this could reduce the efficiency of the decolorization process (Shanthi & Kuzhalosai 2012).

Effect of scavengers

The radical scavenger experiment was conducted to highlight the roles of oxidizing radicals during the tartrazine photodegradation process. Typically, tri-ethanol amine (TEOA), Isopropanol (IP), and benzoquinone (BQ) were selected as the scavenger of holes, •OH and $•O_2^-$, respectively (Liu et al. 2018). Figure 7a shows the removal efficiency of tartrazine decrease from > 99% to 59.7, 82.1 and 33.2% in the presence of TEOA, IP, and BQ, respectively. We could find that the addition of BQ made an impediment on photocatalytic efficiency, suggesting the key roles of $•O_2^-$ played in tartrazine photodegrdation. On other

word, the radical scavenging experiment revealed that $\bullet O_2^-$was the main oxidizing radicals to degrade tartrazine in the presence of C_3N_5-LDH-Ag as photocatalyst.

The photocatalysis reaction begins with the photogeneration of active radicals. Absorption of radiation can lead to the transfer of the holes from the valence band of the C_3N_5-LDH-Ag to the conductance band in its surface, oxidation of the adsorbed hydroxide ions, and water molecules to the •OH and $\bullet O_2^-$radicals took place, and finally, degradation of dye molecules occurred. The capturing experiment showed $\bullet O_2^-$radicals was the main active species to degrade dye molecules, and after, that holes and •OH were responsible for degradation of tartrazine. The corresponding reactions follow Eq_s 2–5.

$$(2) C_3N_5 - LDH - Ag + h\vartheta \rightarrow h^+ + e$$

$$(3) O_2 + e \rightarrow O_2^{\bullet -}$$

$$(4) H_2O + h^+ \rightarrow {}^\bullet OH + H^\bullet$$

$$(5) OH^- + h^+ \rightarrow {}^\bullet OH$$

Catalyst reusability

To evaluate the practical applicability of the developed photocatalyst, the reusability and stability of the photocatalyst, C_3N_5-LDH-Ag, has been assessed by performing four consecutive catalytic cycles. The photocatalyst was recovered by centrifugation after each reaction cycle, washed with methanol and dried at 100 ◦C. Figure 7b depicts the tartrazine degradation efficiency over four sequential photocatalytic experiments. The photocatalytic activity decreased to some extent upon four successive cycles, from the 99% removal achieved in the first cycle to 80% at the 4th cycle. The observed loss of photocatalytic activity can be attributed to the loss of active particles during the washing and separation processes. However, the photocatalyst is able to conserve its activity after 4 catalytic runs and could be classified as a stable and durable catalyst.

Figure 7

Conclusion

In this study, g-C_3N_5 nanosheets, ternary Zn-Cu-Cr LDH nanoparticles, Zn-Cu-Cr LDH-C_3N_5 composite and their combination Zn-Cu-Cr LDH-C_3N_5- Ag nanocomposites with high purity were designed for the first time. Further, the architected nanocomposite were applied for photocatalytic removal of tartrazine from aqueous solutions under visible radiation. Among the synthesized materials, Zn-Cu-CrLDH-C_3N_5- Ag

(C_3N_5-LDH-Ag) exhibited the highest photocatalytic efficiency. The observed enhancement in the photocatalytic activity of these nanocomposites can be related to the synergistic effect between these components and restriction of electron – hole recombination. The C_3N_5-LDH-Ag nano-photocatalyst was found to be highly efficient and recyclable and therefore reusable. The excellent photocatalytic properties of C_3N_5-LDH-Ag for degradation of tartrazine have been found in 1 h light time. Therefore, this synthesized nanocomposite has potential and can apply as an efficient catalyst for the degradation of tartrazine in environment.

Declarations

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Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contribution

Abbas Akbarzadeh: Conceptualization, Providing required facilities, Yeganeh khazani: Sample preparation, Synthesis, photocatalytic experiments, Shokooh Sadat Khaloo: Supervision, Conceptualization, characterization, data analysis and manuscript writing, Masoumeh Ghalkhani: Providing some required facilities.

Ethical approval and consent to participate

This proposal has the ethical code of IR. SBMU.PHNS. REC.1400.022 from ethical commission of Shahid Beheshti University of Medical Sciences. .

Consent for publication

Not applicable.

Consent for participate

Not applicable.

Availability of data and materials

Not applicable.

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Figures

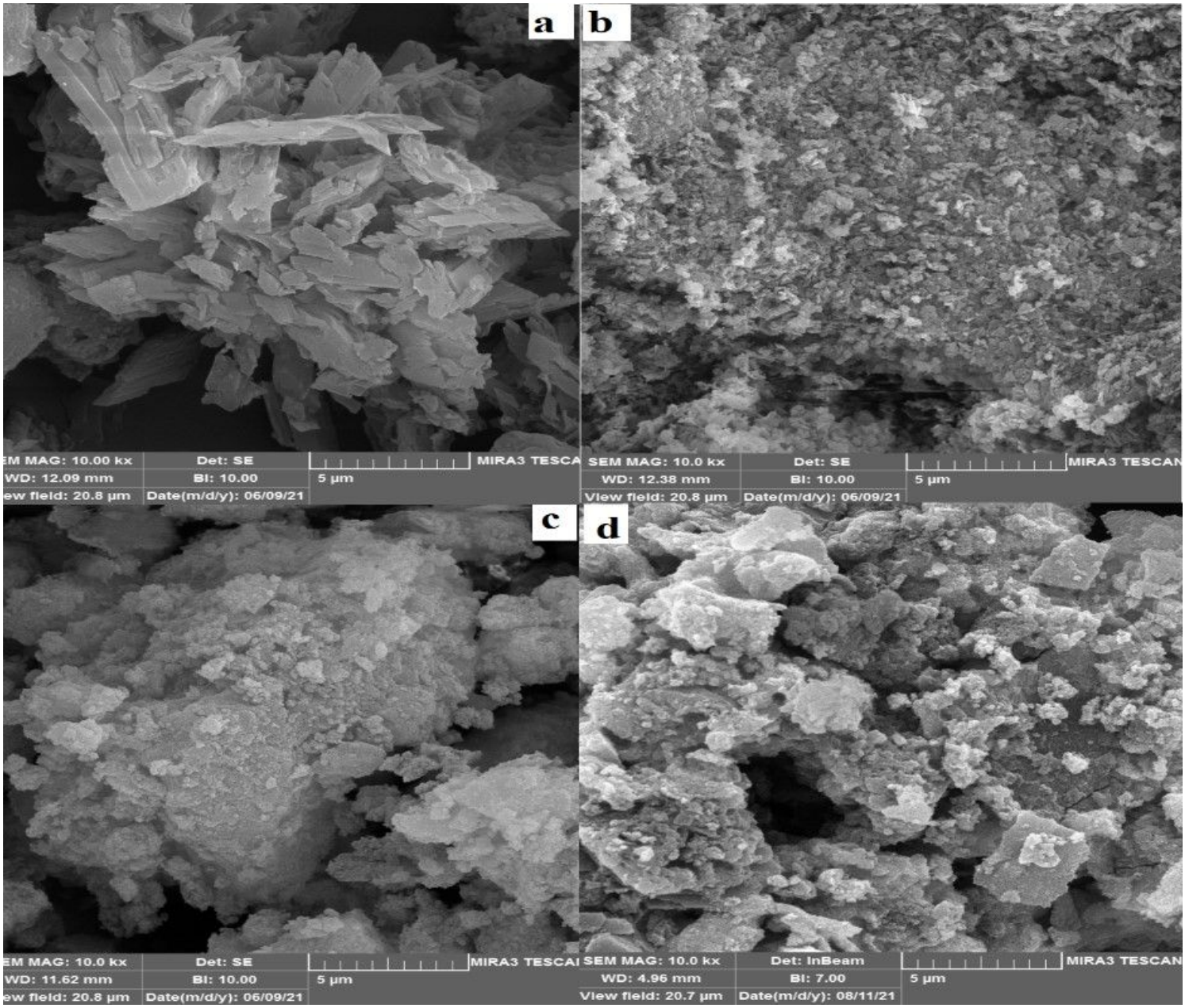

Figure 1

FE-SEM image of (a) C_3N_5, (b) Zn-Cu-Cr-LDH, (c) C_3N_5-LDH and (d) C_3N_5-LDH-Ag

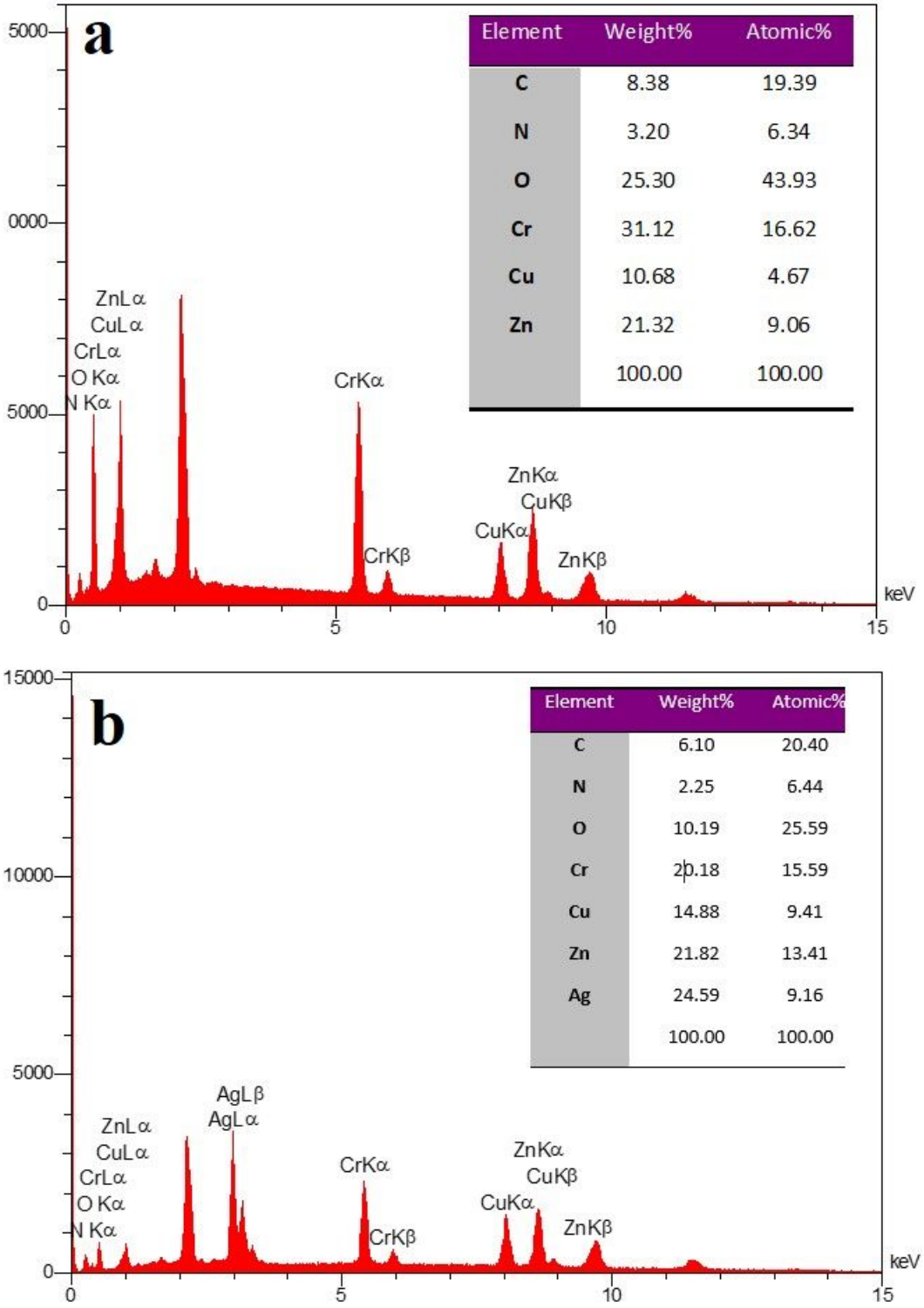

Figure 2

EDS pattern of (a) C_3N_5-LDH and (b) C_3N_5-LDH-Ag

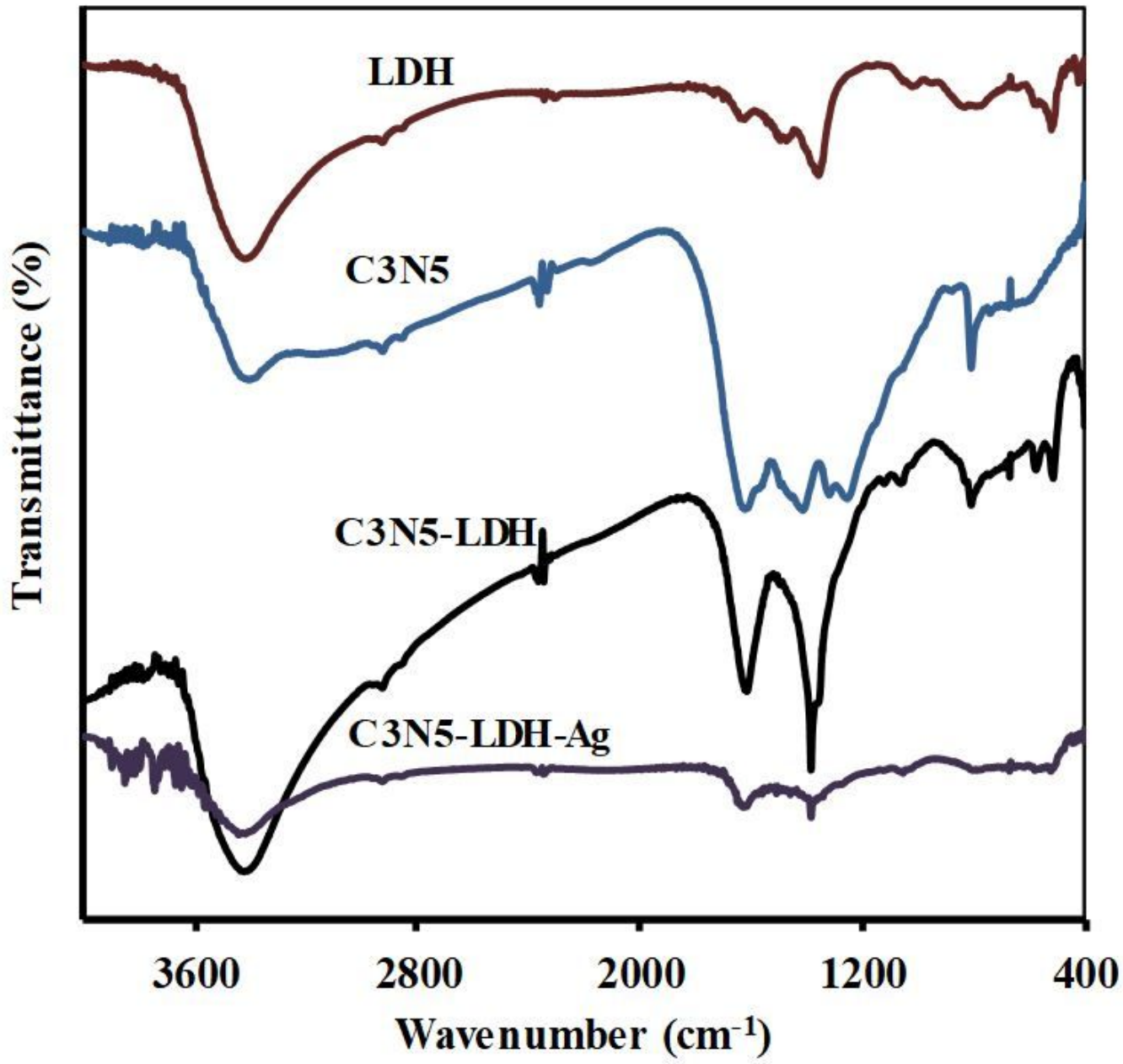

Figure 3

FT-IR spectra of C_3N_5, LDH, C_3N_5-LDH and C_3N_5-LDH-Ag

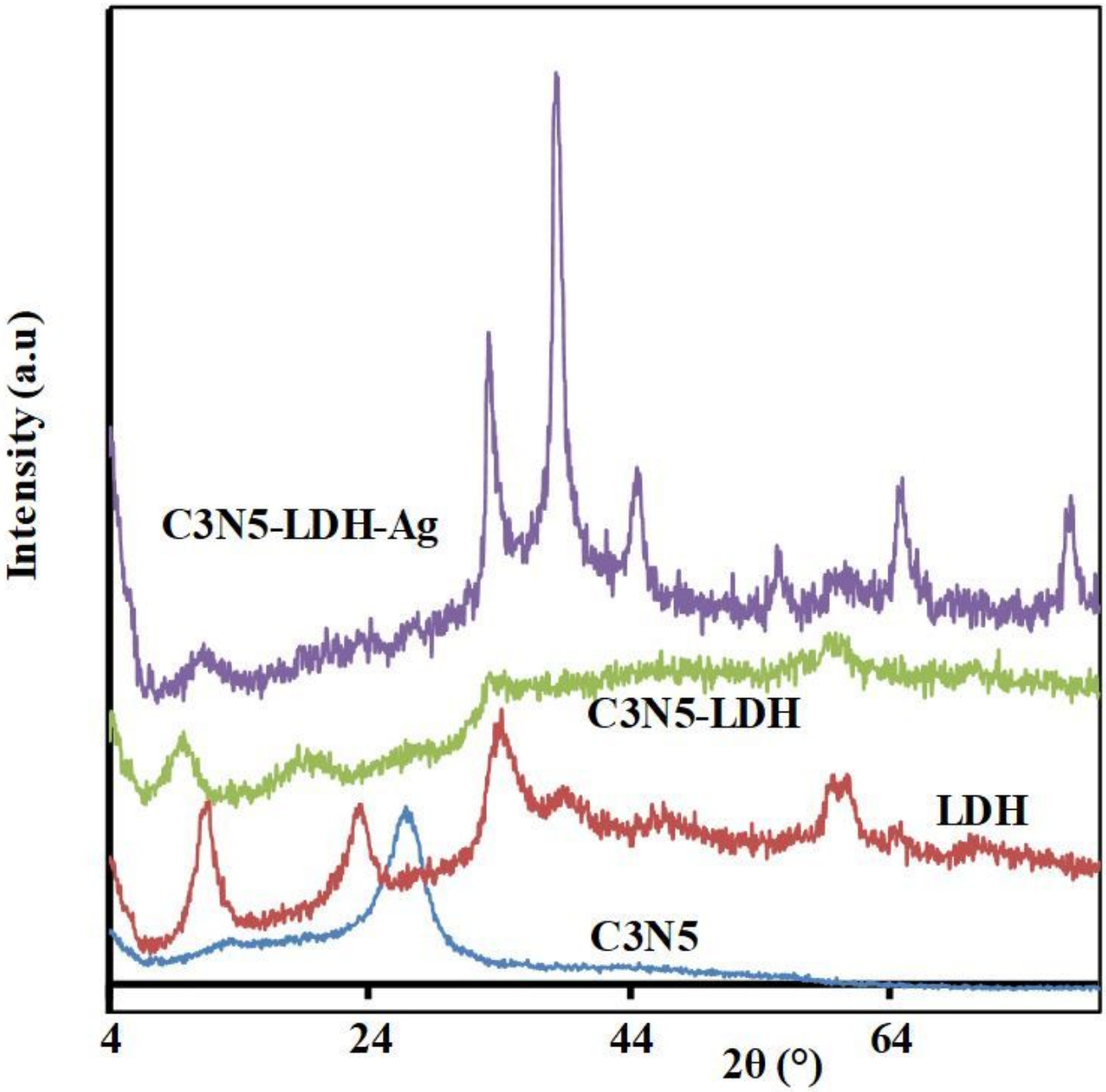

Figure 4

XRD pattern C_3N_5, LDH, C3N5- LDH and C_3N_5- LDH-Ag

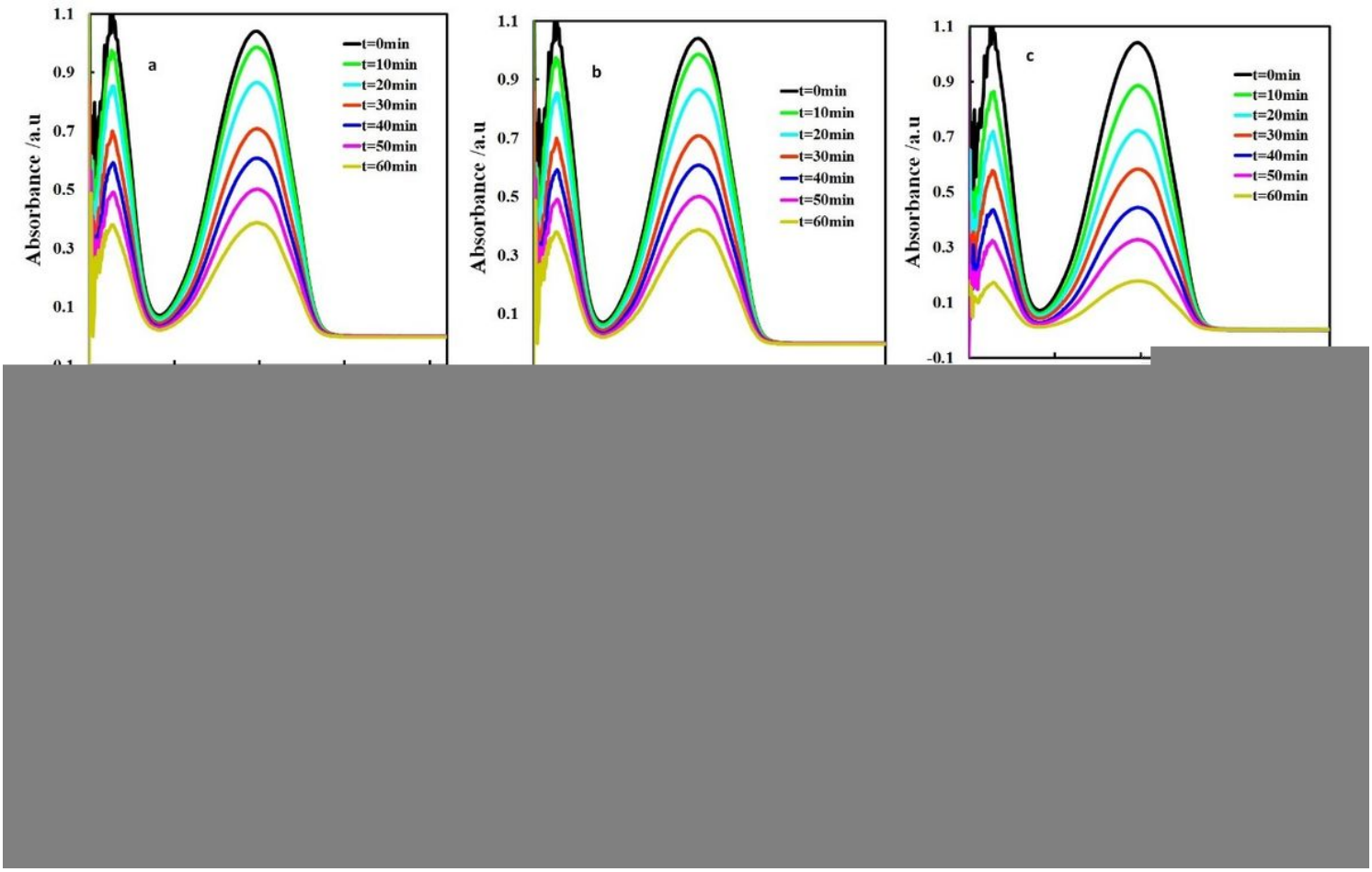

Figure 5

Absorption spectra of 20 mg/L of tartrazine in the presence of a) Zn-Cu-Cr-LDH, b) C_3N_5, c) C_3N_5-LDH and d) C_3N_5-LDH-Ag at different times at pH 6, e)removal efficiency and f) rate constant in the presence of different catalyst

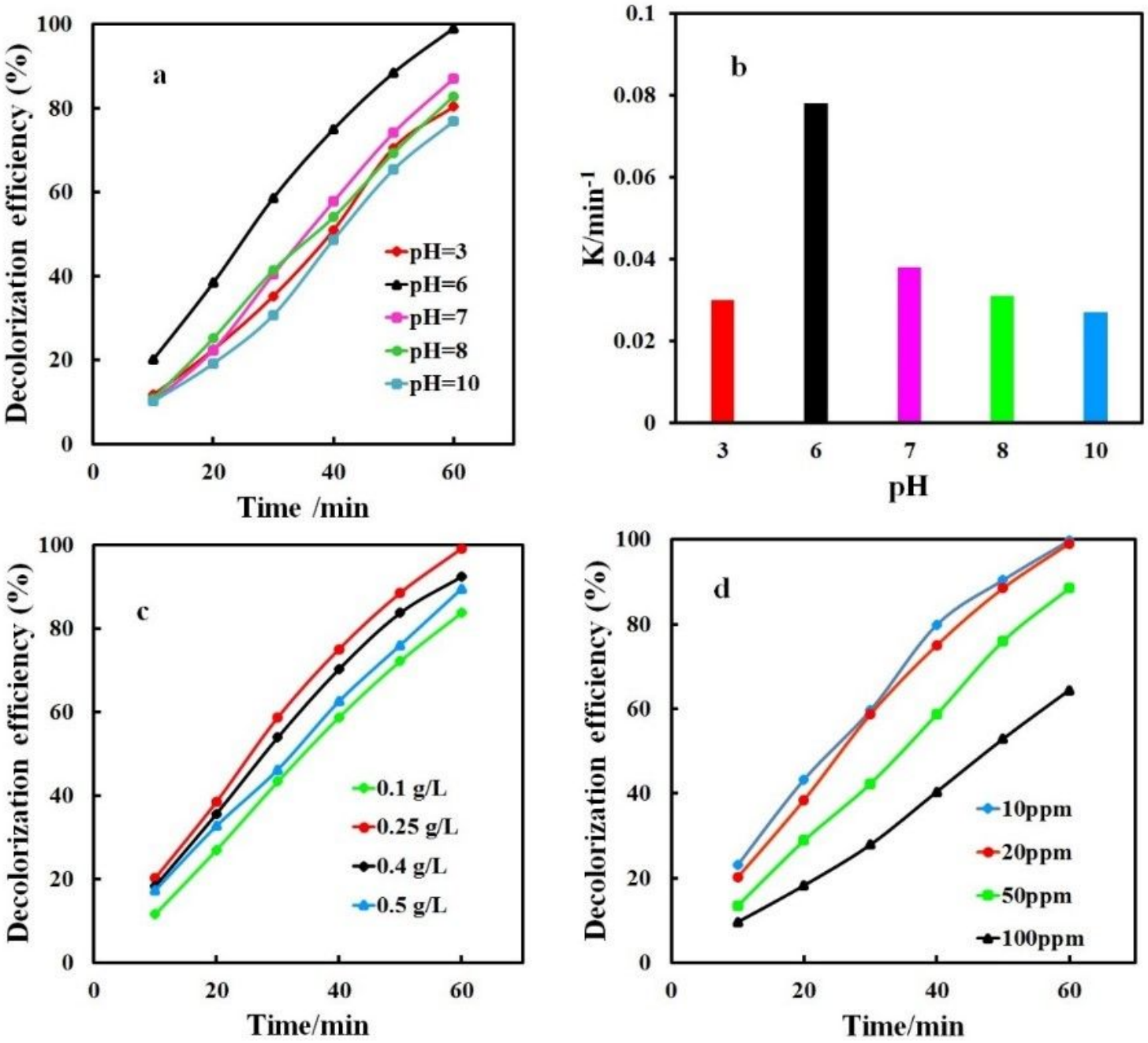

Figure 6

Evaluation of different parameters in photocatalytic degradation of 20 mg/L tartrazine in the presence of 0.25 g/L of C_3N_5-LDH-Ag a) Dosage of C_3N_5-LDH-Ag. b) The different initial Concentration of tartrazine c) The different initial pH d) Kinetic constant at different pH

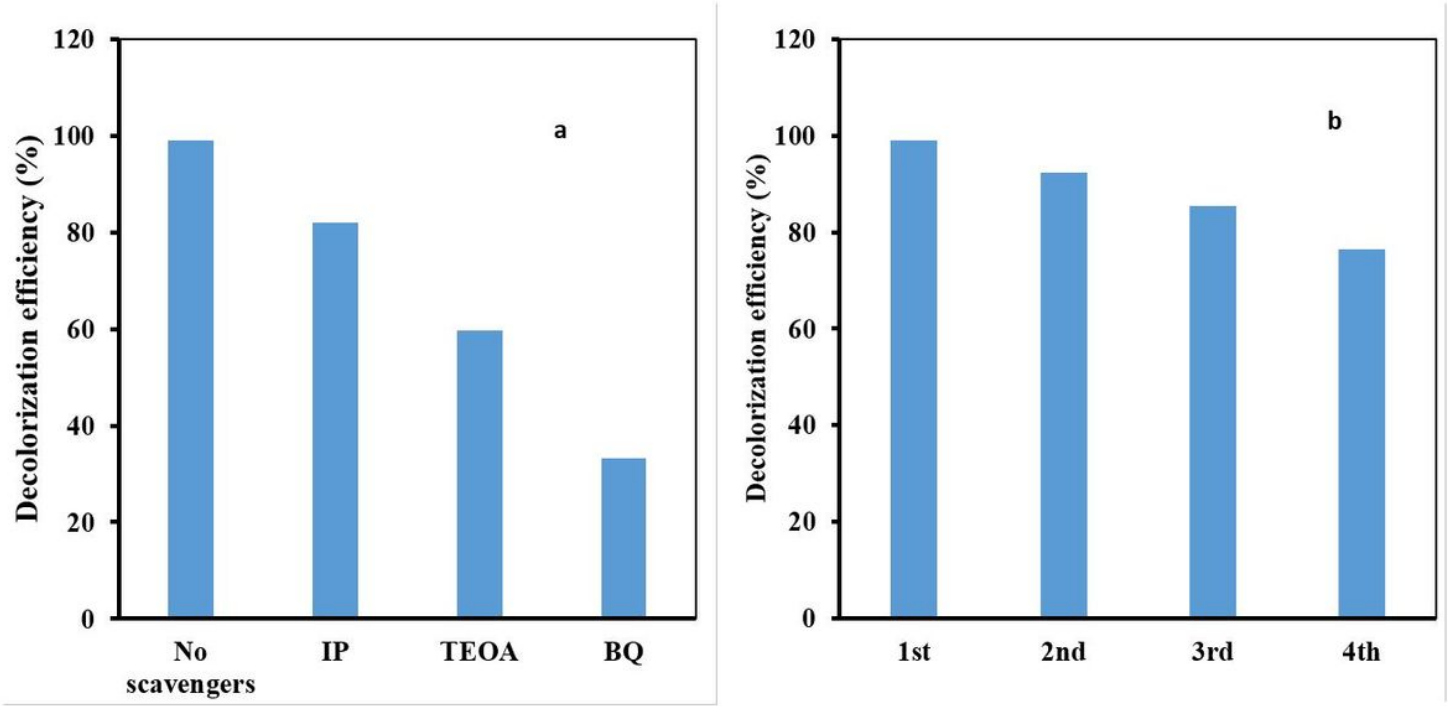

Figure 7

a) Effect of different scavengers on photocatalytic degradation, b) Reusability of C_3N_5-LDH-Ag in Degradation of 20 mg/L of tartarazine in the presence of 0.25 g/L of C_3N_5-LDH-Ag at pH 6