



Photocatalytic degradation of textile dye direct orange 26 by using $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$

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ARTICLE INFO

Article history:

Received 4 May 2016

Received in revised form

19 November 2016

Accepted 3 December 2016

Keywords:

Photocatalyst

Degradation

Magnetic ferrite

CoFe_2O_4

Ag_2O

ABSTRACT

The magnetic and recyclable nanoparticles of CoFe_2O_4 were synthesized by a reverse co-precipitation process. Sonication was used to couple the CoFe_2O_4 surface with Ag_2O . The characteristics and optical properties of the catalyst were studied by powder X-ray diffraction, UV–visible reflectance spectroscopy and scanning electron microscopy analyses. Pure CoFe_2O_4 and $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$ were utilized to determine the visible light photocatalytic degradation of Direct Orange 26. The effects of pH, the initial concentration of catalyst and initial dye concentration on the photocatalytic process were investigated. It was found that the presence of Ag_2O remarkably improved the photocatalytic adsorption capacity and degradation efficiency of $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$ when compared with the pure CoFe_2O_4 . Moreover, due to the magnetic behavior of CoFe_2O_4 , these coupled nanoparticles can be easily separated from the aqueous solution by applying an external magnetic field. The prepared Ag_2O -modified CoFe_2O_4 exhibited much higher (about 40%) photocatalytic activity than the unmodified one. The results showed that the loading of the Ag_2O significantly improved the photocatalytic performance of the CoFe_2O_4 in which the Ag_2O acted as a charge carrier to capture the delocalized electrons.

1. Introduction

The wastewater from textile industries is a major hazard for the aquatic environment. Some dyes are released into the environment which leads to detrimental effects. Hence, these dyes must be removed or degraded before being discharged into the environment. Different methods have been used for degradation, removal or discoloration of dyes from the wastewater such as adsorption, zonation, precipitation, flocculation, reverse osmosis, ultra-filtration, and biodegradation. Conventional methods are costly. Additionally, it is difficult to dispose of them as they produce numerous side effects. Advanced oxidative processes (AOPs) can be used for the degradation of organic pollutants such as dyes and sometimes inorganic wastewater pollutants by oxidation through reactions with hydroxyl radicals. Hydroxyl radicals are strong and non-

selective oxidant species that react with many organic compounds. This technique is promising because of its

efficiency in their mineralization and the production of ideal end products such as carbon dioxide, water, and inorganic mineral [1-3]. Semiconductor photocatalysts are well-known for this process (AOPs), and it has been proven that they are useful in the degradation of dyes, pesticides and other contaminants [4]. Most of the common semiconductor photocatalysts need UV irradiation due to their wide bandgap excitation whereas the UV light of incoming sunlight is only 4% compared with visible light that is 45%. Therefore, it is a great challenge to explore photocatalysts for the degradation of dyes that are active in the region of visible light (400-700 nm). In past decades, the photocatalytic degradation of pollutants with spinel ferrites (AFe_2O_4 , A = Mg, Co, Ni or Zn) have been extensively studied due to their excellent properties, which include excellent magnetic performance, good chemical stability and narrow

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band gap (2.0 eV or lower). On the other hand, fast photogenerated electron-hole recombination leads to a reduction in photocatalytic performance of ferrites. In recent years, great efforts have been made to improve the photocatalytic performance of semiconductors, such as loading a metal, combining with other semiconductors and doping a metal ion [5]. Additionally, silver based heterogeneous catalysts have been extensively investigated in recent years due to their unique catalytic properties for various catalytic reactions, including partial oxidation of ethanol, catalytic reduction of 4-nitrophenol to 4-aminophenol, combustion of volatile organic compounds, etc. for CO oxidation. It is worthy to note that the catalytic activity of Ag catalysts depends highly on the properties of the supports; therefore, many researchers have attempted to deposit Ag on different metal oxide supports such as Fe_2O_3 to increase the photocatalytic activity, which can enhance the separation of electron-hole pairs and photocatalytic activity [6]. Moreover, it has been reported that Ag_2O also exhibits high acidity, so it could be a potential material to enhance adsorption capacity [7]. On the other hand, a nanocomposite heterostructure system using two semiconductor materials with different band gaps is a novel strategy to enhance photocatalytic activity [8]. In the present paper, the influence of Ag_2O substitution on the structural, magnetic and electrical properties of CoFe_2O_4 nano-ferrite were studied and their photocatalytic efficiency for the degradation of Direct Orange 26 (DO26) dye was determined.

2. Materials and methods

All reagents were of analytical grade, and they were used without additional purification. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and AgNO_3 were the cobalt, iron and silver precursors while NaOH acted as a precipitant for the preparation of CoFe_2O_4 . All solutions were prepared with distilled water. Sodium hydroxide and sulfuric acid were used to adjust the pH of the solutions.

2.1. Synthesis of CoFe_2O_4 nanoparticles

The CoFe_2O_4 nanoparticles were synthesized by reverse co-precipitation according to the previously reported technique. In a typical synthesis, a solution composed of 20 ml $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 M) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.0 M) were dropped into a 10 ml NaOH solution with a pH=12.5. During the precipitation process, the solution was vigorously stirred and the NaOH solution (0.1M) was added to adjust the pH to its initial value. The precipitate was aged for 1hr at a temperature of 92°C. Then it was separated and washed with distilled water several times. Subsequently, the precipitate was dried at 110 °C for 12h. The powders were calcined at 600 °C for 1hr in a furnace and cooled to the room temperature to produce CoFe_2O_4 nanoparticles [9].

2.2. Surface modification of CoFe_2O_4 nanoparticle by Ag_2O

For loading Ag_2O on the CoFe_2O_4 nanoparticles, silver nitrate was used to prepare the silver nanoparticles. In this section, 1gr of cobalt ferrite was dissolved in 10 ml of distilled water and 0.17 gr of silver nitrate was dissolved in 5 ml of distilled water. Then the silver nitrate solution was dropped in the cobalt ferrite suspension within the ultrasonic bath with a temperature of 60°C and frequency of 28 Hz for 40 minutes. Silver Oxide insemination on cobalt ferrite was done at this stage.

2.3. The photo reactor

A photo reactor was an important piece of equipment used throughout this study for photocatalytic tests. All of the photocatalytic tests were performed in the batch mode photo reactor. The reactor was double cylindrical shape made up of Pyrex. The total volume of this reactor was 500 ml. The geometry of the reactor was chosen to avoid the creation of dead space within the system and the catalyst was in thorough contact with the examined solution. Because of the strong magnetic properties of the catalyst, magnetic mixing was impossible; therefore, an air pump system was used for mixing. The reactor was designed in such a way that the whole process of system temperature remained constant by applying a jacket and positioning a light source in the reactor so that all the light reached the catalyst surface. The process was performed in the batch mode reactor. The liquid inside the jacket was tap water used to keep the temperature at a constant and specified value. Water was connected to the jacket by a pump and hoses (chamber of the reactor) in order to cool the reactor. In addition to the mixing system, and because oxygen played a role as the electron acceptor, the air was put into the solution from the head of the reactor through two hoses to prepare the required oxygen for the process.

2.4. Photocatalyst experiments

To evaluate the performance of the synthesized photocatalytic nanoparticles, DO26 color degradation was carried out with different concentrations of dye, concentrations of the catalyst, and pH values in each experiment in the reactor and under visible light irradiation. The effect parameters, including dye concentration, catalyst concentration, and pH of the solution, were evaluated in the photocatalytic process in this study. To check each parameter, other parameters were kept constant. The dye and catalyst solution were poured into the reactor. To prevent light from reaching the catalyst, the reactor wall was covered completely with aluminum foil. The catalyst solutions were kept in the dark for 30 minutes to achieve their absorption and desorption equilibrium. During this time, the air pump system was switched on for the purpose of mixing. Then samples of 5 ml solution were taken, and the concentrations were determined by spectrophotometer. Then two visible lamps

(60 Watt-Philips Model) were placed into the reactor and water pumps were turned on to prevent an increase in the temperature. The photocatalytic reaction was examined at a specified time Sampling was taken every ten minutes to determine the dye concentration.

3. Results and discussion

3.1. XRD analysis

XRD analysis was performed to determine the crystal structure of $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$ and pure ferrite. The XRD results of pure ferrite are shown in Figure 1. The entire characteristic peaks matched the standard peaks of CoFe_2O_4 in JCPDS CARD (NO.22-1086). The XRD results of

$\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$ are shown in Figure 2. The results showed the formation of Ag_2O . The peaks in the 2θ angle of 27, 34, 38, 55, 65 and 68 corresponded to the values of 311, 220, 200, 111, 110 and 222. These results proved the presence of silver oxide in the structure corresponding to standard JCPDS NO. 41-1140 [10-13]. The crystal size of the samples was calculated using the equation of Debye-Scherrer for which the calculated size of silver oxide/ CoFe_2O_4 nanoparticles was 36.147 nm. This value was 19.02 nm for pure CoFe_2O_4 . It was important that the catalyst was separated magnetically after synthesis. Ag_2O doesn't have magnetic properties. This could be an indication of doping Ag_2O on CoFe_2O_4 .

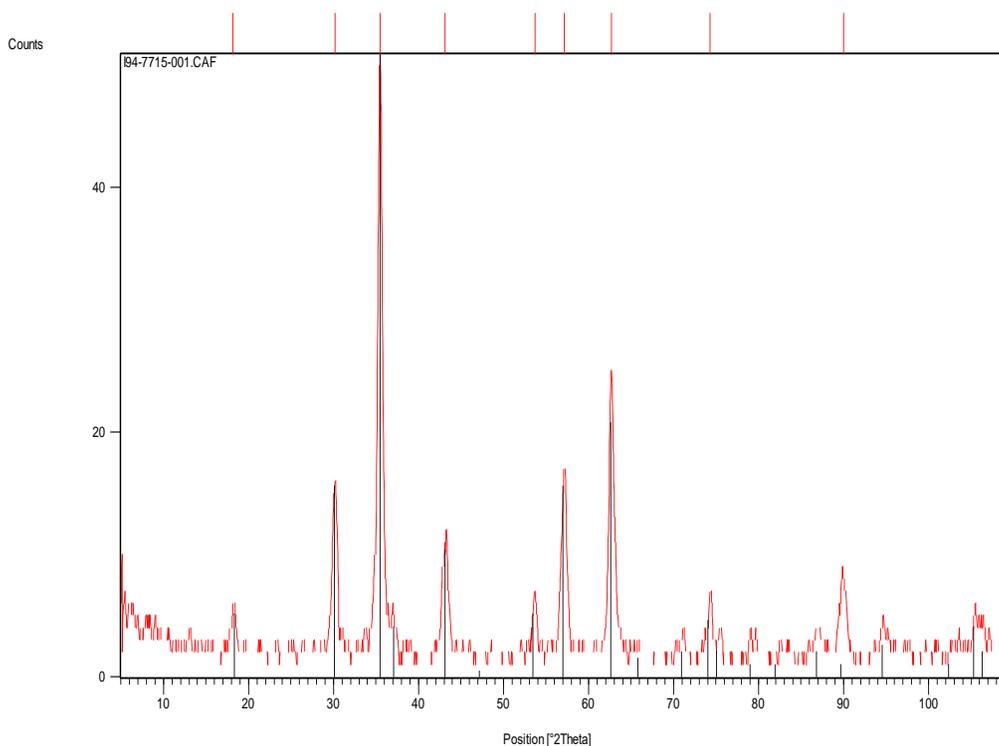


Fig. 1. XRD pattern of CoFe_2O_4

3.2. SEM analysis

Figures 3 and 4 shows the Electron Microscope SEM images of pure ferrite and $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$, respectively. As shown in Figure 3, the average size of CoFe_2O_4 obtained with both

spherical morphology and irregularly-shaped methods was 36.83 nm. Other studies conducted by researchers also reported similar morphology [14]. In addition, Figure 4 shows the morphology of $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$, which represents a spherical morphology with the average size of 49.31 nm.

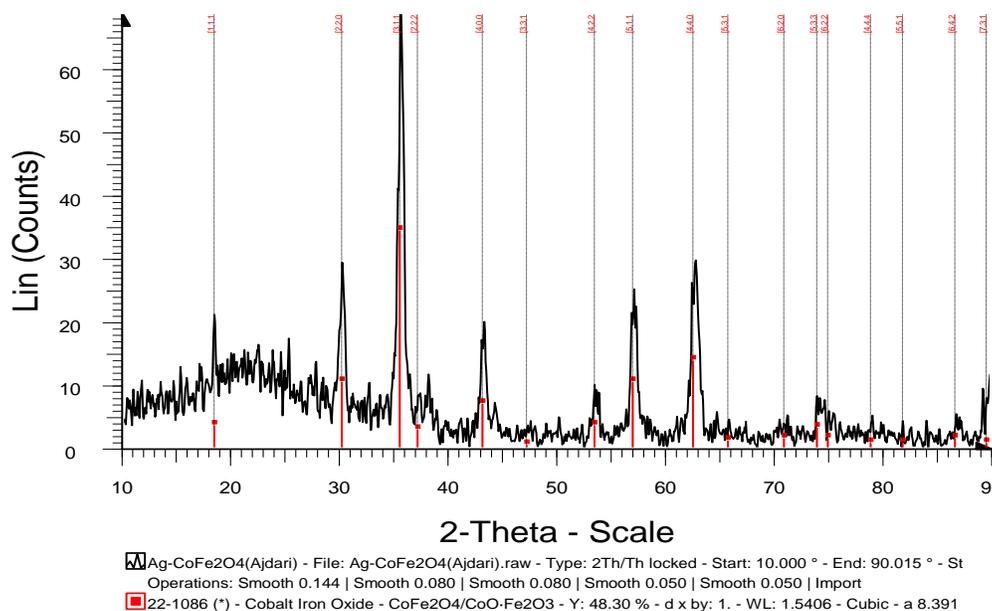


Fig. 2. XRD pattern of CoFe₂O₄/Ag₂O

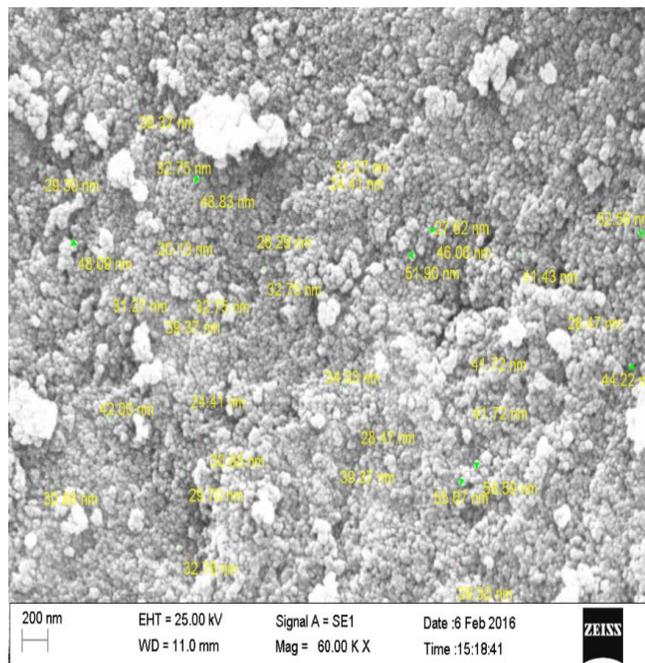


Fig. 3. SEM image of CoFe₂O₄

3.2.1. EDAX analysis

Figure 5 shows the analysis of elements in composite and pure ferrite. The ratio of iron to cobalt is very close to the ratio of iron to cobalt in the formula. In the second step of the synthesis, the ultrasonic system impregnated silver with a 9.61 weight percent (3 atomic percent) on cobalt ferrite,

where the ratio of iron to cobalt was approximately the same as the ratio of iron to cobalt in the formula.

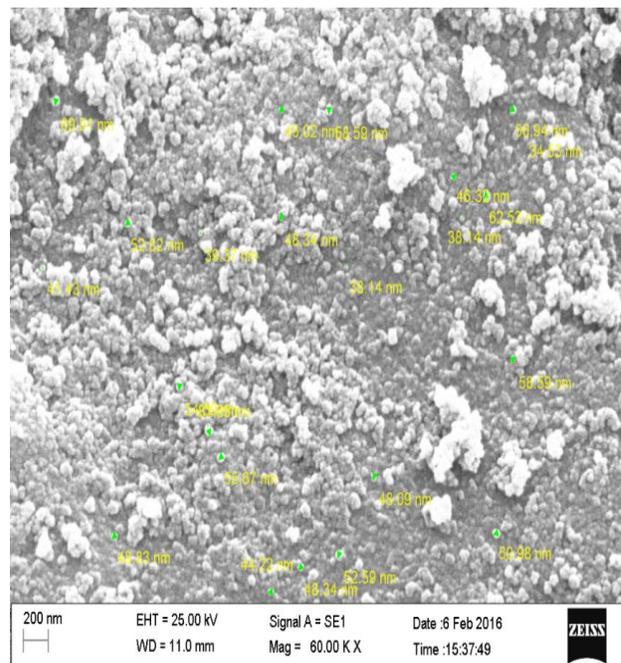


Fig. 4. SEM image of CoFe₂O₄/Ag₂O

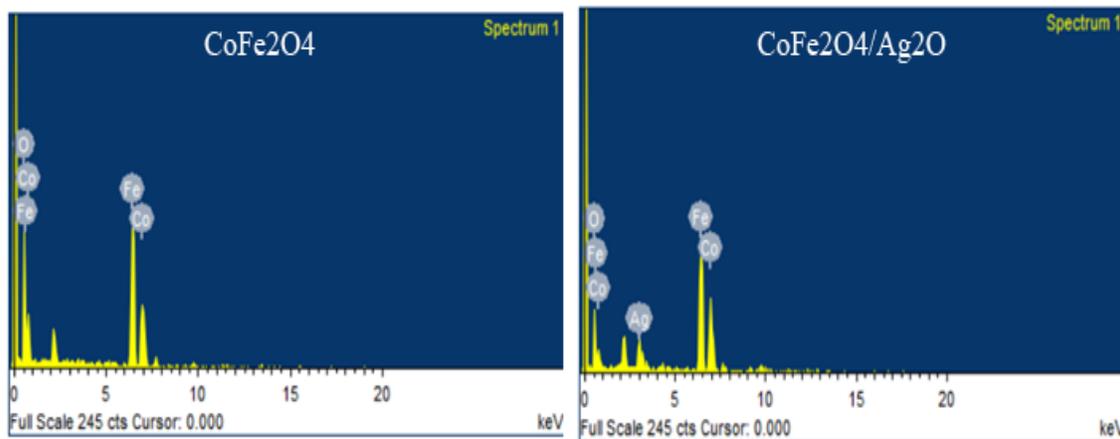


Fig. 5. EDAX image of CoFe_2O_4 and $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$

3.3. DRS analysis

The DRS sample of pure ferrite and ferrite silver oxide are shown in Figure 6. As shown, by adding silver, the visible light absorption was increased by 20%. The doping silver decreased the amount of the emission of light in the visible zone of the catalyst and enhanced the absorption of light in the visible light range.

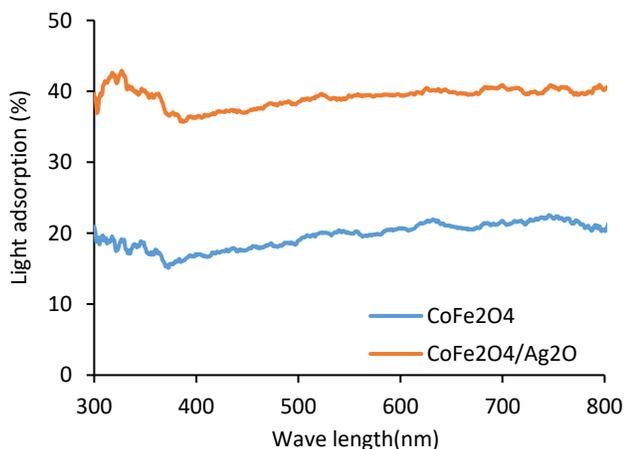


Fig. 6. Light adsorption of $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$ and CoFe_2O_4

3.4. Photocatalytic activity of CoFe_2O_4 and $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$

The combining of adsorption-degradation can increase the efficiency of the dye removal process. CoFe_2O_4 can be introduced as photocatalysts, adsorbents, and a silver doping. It helps to increase the photocatalytic properties. The molecules of DO26, which has a high absorption speed, were adsorbed on the surface of the catalyst. Then these molecules were degraded with a photocatalytic process. Figure 7 shows the dye concentration after the photocatalytic activity of silver oxide/cobalt ferrite and pure cobalt ferrite under visible light after 90 minutes.

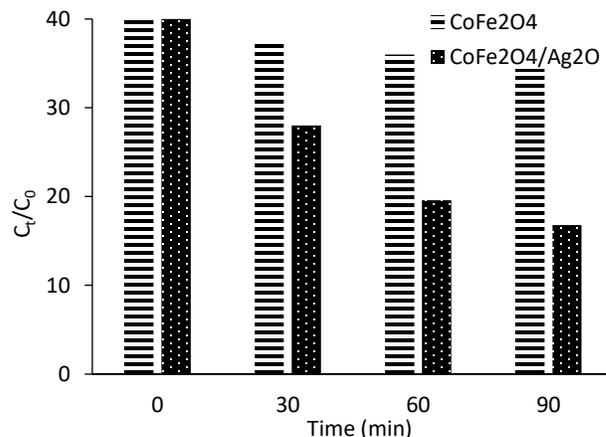


Fig. 7. Photocatalytic activity of $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$ and CoFe_2O_4 under visible light

As shown in Figure 7, $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$ had much higher dye degradation (about 40%) so that the $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$ can adsorb more molecules of dye on its surface. One explanation was that the Ag_2O can act as a bridge for reducing the recombination of electron and holes and the electronic interaction between $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$ nanocomposite; thus, the photocatalytic activity of $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$ was much higher than from CoFe_2O_4 .

3.5. Investigation of the factors affecting the process

3.5.1. The effect of initial concentration of catalyst on the photocatalytic degradation process

The effect of initial concentration of the catalyst on the photocatalytic degradation process was carried out by different values of initial concentration of catalyst as 0.5, 0.75, 1 and 1/25 g/L of catalyst. Figure 8 shows dechlorination with the different amounts of nanophotocatalyst at pH values ranging from 6.5-7 and at 20 ppm of dye concentration. One can see in Figure 8 that the decomposition of the dye increased when the amount of photocatalyst was less than 1 g/L catalyst. Then it decreased by increasing the amount of photocatalyst. The

rate of the photocatalytic reaction increased when the amount of catalysts increased. This led to an increase in active sites for reaction and subsequently an increase in hydroxyl radicals. However, more increase in the concentration of the photocatalysis led to scattering light and prevented the light from reaching the catalyst where a reduction in photocatalytic degradation occurred. Another reason is explained as follows. By increasing the catalyst, the agglomeration of catalyst particles' increases and it leads to a reduction of active sites of catalyst and photocatalyst efficiency [15, 16].

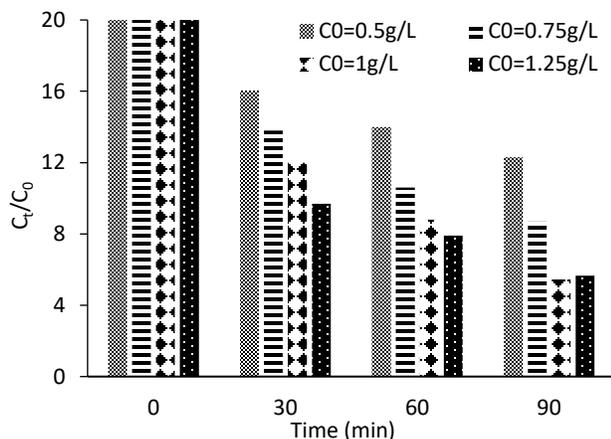


Fig. 8. Effect of initial concentration of catalyst on the degradation-adsorption process of $\text{Ag}_2\text{O}/\text{CoFe}_2\text{O}_4$

3.5.2. The effect of initial concentration of dye on photocatalytic process

To investigate the effect of initial concentration of dye on the photocatalytic process, the solution containing $\text{CoFe}_2\text{O}_4\text{-Ag}_2\text{O}$ and dye with concentrations of 10, 15 and 20 ppm were used. Figure 9 shows changes of dye concentration during the photocatalytic process by changing the initial concentration of dye. 1 g/L of the catalyst was kept constant. As it is shown, by increasing concentration of dye, removal of dye decreases within 60 minutes photocatalytic process and 30-minute adsorption process. This can be explained as follows. The amount of active species produced by the irradiation at the same conditions remains constant. By increasing dye concentration number, a number of active sites on photocatalyst are occupied with more dye. Therefore, the number of active species such as hydroxyl radicals will not be capable of degradation of the dye in different initial concentration at the same speed. In fact, when the initial concentration of dye increases, the dye adsorbed by the catalyst increased but the absorption of light photons by dye molecules cause some catalyst sites to stay inactive and diminished the degradation performance [17, 18].

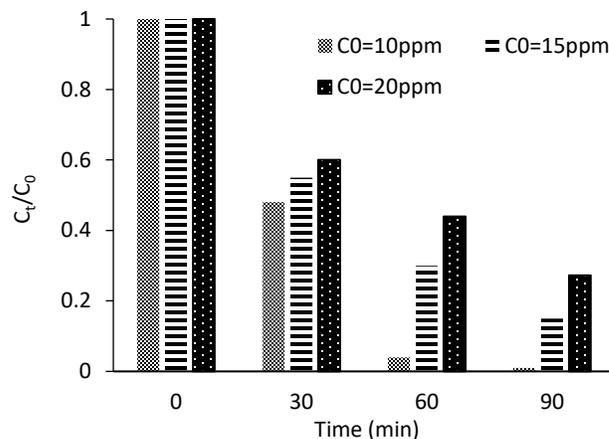


Fig. 9. The effect of dye initial concentration on the degradation-adsorption process of $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$

3.5.3. The effect of pH on the adsorption-degradation process

The pH value affects adsorption and oxidation of organic compounds. The electrostatic forces between the contaminant and the catalyst can affect the electrostatic interactions, the ionic properties and the molecular structure of the dye and catalyst. The pH value of the system, including the hydroxyl radical and these ions, can affect the oxidation process, so the value of pH can be effective in terms of the efficiency and absorption photocatalytic process. To evaluate the effect of pH on the adsorption, several tests with different pH were carried out. The experiments were performed with the pH values ranging from 4 to 10. The pH was set by using HCl and NaOH to carry out the process. The solution was kept in the dark for 30 minutes (to carry out the process of adsorption-desorption) and for 60 minutes under irradiation with visible light. The concentration of dye in the end of the process of degradation-adsorption was measured. The effect of pH on the process is shown in Figure 10. As shown, with the acidic pH (pH = 4), most of the adsorption-desorption process had occurred. This could be due to electrostatic interactions between the positively charged surface of the catalyst and negative ions of dye where solutions with a high pH made the catalyst surface negative. On the other hand, with an alkaline pH, hydroxyl anions will compete with negative ions of dye for adsorption on the surface of the catalyst which leads to a reduction in the adsorption of dye on the surface of the catalyst. At pH higher than 7 (alkaline region), interaction between the generated holes using light, converts hydroxyl ions to hydroxyl radicals. This facilitated and enhanced the photocatalytic process. In this study, in acidic pH, although adsorption was very high, the photocatalytic process was low. Therefore, the greatest amount of degradation was reached at a pH =6. It is noteworthy that the effect of pH on the photocatalytic degradation process was very

complicated because three reaction mechanisms could occur in a degradation process: hydroxyl radicals attack, the direct oxidation by and holes and direct reduction by electrons at the conduction bar. The pH on the photocatalytic process did not stay constant, thus it was difficult to measure the pH value [19-21].

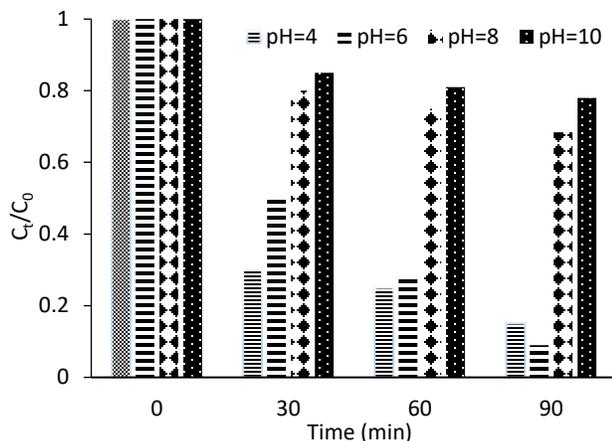


Fig. 10. Effect of pH on degradation-adsorption of $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$

4. Conclusions

A simple method was used to synthesize CoFe_2O_4 and it was modified by the loading of Ag_2O . The photocatalytic activities of the synthesized nanocomposites were then studied by applying them in the degrading of DO26 dye. The prepared Ag_2O -modified CoFe_2O_4 exhibited a much higher (about 40%) photocatalytic activity than the unmodified one. The results showed that the loading of the Ag_2O significantly improved the photocatalytic performance of the CoFe_2O_4 in which the Ag_2O acted as a charge carrier to capture the delocalized electrons. In addition, this work presented a simple method to prepare a magnetic composite of $\text{CoFe}_2\text{O}_4/\text{Ag}_2\text{O}$, which is a promising photocatalyst that is employable in environmental remediation applications.

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