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ORIGINAL RESEARCH PAPER

Photodegradation of Human Serum Albumin by Fe_3O_4/ ZnO/Ag Nanocomposite

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ABSTRACT

Fe_3O_4/ ZnO/Ag magnetic nanocomposite was synthesized for the first time and its ability was evaluated for photocatalytic degradation of albumin in aqueous solutions under UV-A light. The resulting nanoparticles were then characterized using X-ray diffraction (XRD), scanning electron microscopy (FESEM), vibration magnetometer (VSM), and Fourier infrared (FTIR). The effects of some parameters such as pH, initial albumin concentration, catalyst concentration, and temperature were also investigated in the photodegradation of albumin. The results showed that the maximum removal of albumin was obtained at pH 9, catalyst concentration of 0. 5 g/l, initial albumin concentration of 150 mg/l, and room temperature in 90 min. Under the optimum conditions, the total amount of organic carbon (TOC) was 56%. Kinetic degradation experiments followed the pseudo-first-order kinetic model with a constant rate (k) of 0.0255 min^{-1}. Therefore, due to the high performance of Fe_3O_4/ ZnO/Ag magnetic nanocomposite in the degradation of albumin as well as its easy synthesis and separation with an external magnetic field, it can be used as a suitable and environmentally friendly catalyst for the degradation of organic and resistant pollutants in the wastewater.

Keywords: *Emerging contaminants, wastewater, Photocatalyst, UV radiation*

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INTRODUCTION

The high population growth rate, limited water resources, and pollution of resources due to various biological, agricultural, and industrial activities alarmed the threat of a water crisis. Therefore, maintaining the physical, chemical, and biological quality of water resources in good and standard conditions is one of the most priorities of the governments [1]. Water pollution due to the discharge of municipal and industrial wastewater effluents, toxic pollutants, and improper management of solid waste, seriously affect human health and other organisms [2]. Protein and its derivative, such as albumin are a large portion of organic pollution in wastewater. Based on the scientific reports, the percentage of protein in raw wastewater is 40-60% of organic matter. Human serum albumin (HSA) is one of the most important contaminants in water. HSA is formed in the liver, and its normal serum concentration is 3.5 - 5 g / dL; thus, it is the most abundant protein [3]. It plays a significant role as a transport molecule because many endogenous molecules (bilirubin) and exogenous molecules (e.g. pharmaceutical molecules) can conjunct to one or more of its several conjunction sites. Interactions with albumin greatly affect the pharmacokinetics of many therapeutic factors. The distribution and removal of different matters can also be regulated by the conjunction of albumin [4]. With a large amount of wastewater produced

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annually, more efforts are needed for the safe and proper disposal of wastewater to the environment. Conventional treatment methods, including chemical oxidation, membrane processes, sediment extraction, and biological treatment have low efficiency in removing protein and its derivatives [5]. Advanced oxidation processes (AOPs) as alternative methods have been applied to remove emerging pollutants and refractory organic matter from wastewater. Amongst the different AOPs processes, the use of semiconductor photocatalysts as a "green chemistry" technology, due to its efficient degradation rate, high mineralization efficiency, and low toxicity has been considered as an ideal and effective candidate for degradation of different types of pollutants.

Zinc oxide (ZnO), a popular semiconductor photocatalyst with a bandgap of 3.2 eV, has been widely used in the photocatalysis process due to its high chemical stability and high photocatalytic activity, low cost, photosensitivity, and environmental friendliness [6]. However, with a large band gap, ZnO can only respond to UV light, which means less efficiency under visible light and high electron-hole recombination [7]. The separation of photocatalysts after their application in wastewater is another drawback. Due to these limitations, the photocatalytic applications of ZnO have decreased. Researchers have proposed doping different materials such as metal or non-metallic ions with ZnO or use of it with other semiconductors [8] and noble metals [6] to overcome these limitations; for example, the presence of magnetic nanoparticles, including Fe_3O_4, in the structure of the ZnO, reduces its bandgap. Moreover, using Fe_3O_4 causes magnetic properties in the photocatalyst, which facilitates the separation of the catalyst from the aquatic environment.

Recombination of the electron-hole is under deficiency of some photocatalysts. One of the practical solutions to reduce the amount of recombination is the use of noble metal nanoparticles such as silver in the photocatalyst structure. The binding of ZnO/Fe_3O_4 semiconductors to noble metals such as silver (Ag) has attracted the attention of many researchers. Ag has high electrical conductivity, remarkable physical and chemical properties, and antibacterial activity[9]. The presence of Ag nanoparticles in the structure of ZnO/Fe_3O_4 forms a compound with a high surface-area-to-volume ratio with less recombination rate [10]. In addition, the surface plasma resonance (SPR) effect of these Ag nanoparticles can increase the degradation efficiency in the visible light region [11]. Moreover, some studies have shown an interaction between nanoparticles and protein components such as albumin and hemoglobin [12-14]. In a study by Alavi and Karimi (2020), it was observed that hemoglobin was aggregated under Ag nanoparticles. This phenomenon was based on the charge-transfer complex and potential electron transfer from hemoglobin to Ag^+ ions. Moreover, the aggregation of albumin in the vicinity of Ag^+ ions was observed in another research[14]. Therefore, it can be hypothesized that the synthesis of a nanocomposite containing Ag^+ might have better ability to degrade albumin. This study aimed to synthesize $Fe_3O_4/ZnO/Ag$ magnetic composite to remove albumin from aqueous solutions.

MATERIALS AND METHODS

Materials

Ferric chloride ($FeCl_3 . 6H_2O$), ethylene glycol (EG), sodium acetate (NaAc), sodium lauryl sulfate (SLS), dimethyl-formamide (DMF), zinc nitrate hexahydrate ($ZnNO_3 . 6H_2O$), hydroxy Na (hydroxide) Alcohol (C_2H5OH), tetraethyl orthosilicate (TEOS), silver nitrate (AgNO3), Hcl, NaOH, polyvinyl pyrrolidone (PVP), concentrated ammonia solution (25% by weight) were purchased from Merck (Germany). All chemicals used in this study had analytical grades used without purification. Deionized water was also used during the experiments in this study.

Synthesis of Fe_3O_4 nanoparticles

The Solvothermal synthesized Fe_3O_4 nanoparticles[1]. Initially 2.14 g of $FeCl_3. 6H_2O$ was dissolved in 80 ml of ethylene glycol (EG) for 1 hour to prepare an obvious yellow solution. Then 0.34 g of NaAc and 0.5 g of SLS were added to the above solution and dissolved under a strong magnetic stirrer for 1 hour. After this step, the mixture was transferred to an autoclave for 10 hours at 120 ° C. Afterward the sample was placed at room temperature, and the resulting black nanoparticles were washed several times with deionized water and ethanol and dried in an oven at 70 ° C for 6 h.

Synthesis of Fe_3O_4 / ZnO nanoparticles

Fe_3O_4/ZnO nanoparticles were synthesized using a co-precipitation method. 0.3 g of $ZnNO_3 .6H_2O$ was dissolved in 50 ml of DMF and then 0.04

g of NaOH was dissolved in 2 ml of deionized water to create a 0.5 M solution. Then, Fe_3O_4 nanoparticles were sonicated for 30 min for dispersion. The dispersed solution was added to zinc nitrate solution and stirred for 30 min. Afterward, 0.5 M NaOH was added to the prepared solution. After precipitation, the resulting nanoparticles were filtered and washed several times with distilled water and ethanol and then dried at 60 ° C for 7 h.

Synthesis of Fe_3O_4 /ZnO /Ag nanoparticles

Fe_3O_4/ZnO/Ag nanoparticles were prepared by wet chemistry with some modifications [15]. Initially, 0.12 g of Fe_3O_4/ZnO microstructures were dispersed in the 30 ml of ethanol and sonicated. After 30 min of sonication, $[Ag(NH_3)^{2}]^{+}$ ions were added. In the next step, 0.2 g of PVP and 30 ml of ethanol were added to the solution. Then the resulting mixture was washed several times with distilled water and ethanol and dried at 60 ° C for 8 h.

Characterization of the nanoparticles

X-ray diffraction (XRD) patterns of Fe_3O_4/ ZnO/Ag samples were determined using Rigaku MiniFlex 600 (XRD) with Cu Ka irradiation (k = 0.154178 nm). The magnetic properties of the samples were measured using a vibrating sample magnetometer (VSM) (Lake Shore 7403) at ambient temperature. The morphology and shape of the magnetic composite were determined using the scanning electron microscope (FESEM) (TE-SCAN model MIRA3 FESEM). In addition, infrared Fourier transform spectroscopy (FTIR) (Shimadzu, FT_IR1650 spectrophotometer, Japan) was applied to identify the chemical features of the samples.

Photocatalytic experiments on albumin degradation

Photocatalytic experiments were performed in a 250 ml batch reactor containing 100 ml of albumin with a concentration of 150 mg/l and 0.2 g/l of Fe_3O_4/ZnO/Ag nanoparticles at room temperature. A UVA lamp (6 W) was used as the light source, an aeration pump was used to supply dissolved oxygen and a magnetic stirrer was used to mix the solution. It should be noted that the NaOH and HCl (0.1 N) were used to adjust the pH. Before irradiation, the solution containing the catalyst and the pollutant was stirred in the dark for 30 min to balance the adsorption/desorption. The adsorption-desorption equilibrium capacity was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where q_e are the metal ions adsorbed on the adsorbent, C_0 and C_e are the initial and final concentrations of the metal ions in solution at time t (mg/l), m is the weight of the adsorbent (g), and V is the volume of the solution (*l*). The solution was then exposed to light irradiation to optimize various parameters such as pH (3, 5, 7, 9, and 11), initial concentration of albumin (150, 300, and 500 mg/l), catalyst concentration (0.1, 0.2, 0.5, and 0.7 g/l), and different temperatures (25, 30, and 40 °C). After selected reaction intervals (5, 15, 45, 30, 75, 60, and 90 minutes), a 7 ml sample was extracted from the reactor. Samples were then centrifuged for 15 min at 2000 rpm to separate the nanoparticles. The final albumin concentration was measured using a spectrophotometer at 270 nm. The photocatalytic degradation efficiency of albumin was calculated using the following equation (Ahmadpour et al., 2019):

$$Photodegradation\ efficiency(\%) = \frac{C_0 - C_t}{C} \times 100 \quad (2)$$

Where, R, albumin degradation efficiency, C0, and Ct are the initial and final concentrations at time t.

RESULTS AND DISCUSSION

Characterization of magnetic nanoparticles Fe_3O_4 / ZnO /Ag

X-ray diffraction (XRD)

The crystal structure of magnetic nanoparticles Fe_3O_4, Fe_3O_4/ZnO, and Fe_3O_4/ZnO/Ag were determined using (XRD) in the range of 10-80 degrees (Fig. 1(a)). The observed peaks at 2θ = 30.4 °, 33 °, 35.5 °, 46.72 °, 57.65 °, and 63.25 ° belong to Fe_3O_4 on the surface of crystals (220), (002), (311), (102), (440) and (511), respectively (JCPDS no. 75-0449)[16]. As shown in the XRD pattern, the peaks at 2θ, 22.5, 34.65, and 36.36 correspond to (100), (002), and (102) diffraction planes of the ZnO structure (JCPDS. card no. 79-0206) (Lee et al., 2018). The XRD pattern of coated particles with Ag has several additional peaks. This indicates that Ag nanoparticles are loaded on the surface of the composites (JCPDS No. 04-0783) [17].

Magnetic properties (VSM)

The magnetic properties of Fe_3O_4, Fe_3O_4/ZnO, and Fe_3O_4/ZnO/Ag magnetic nanoparticles were

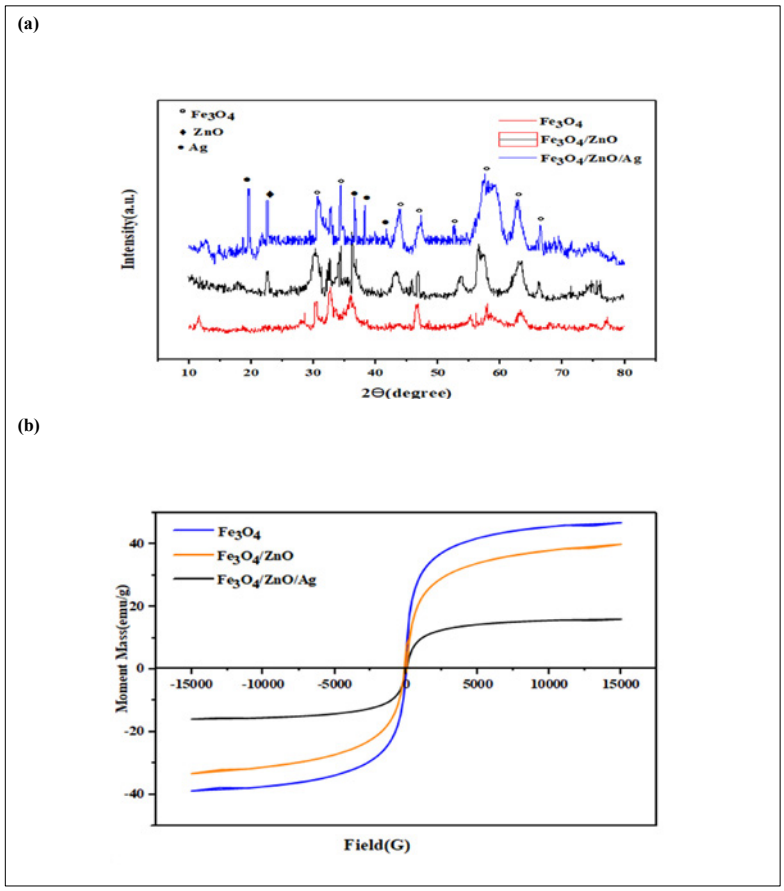

Fig.1. (a): XRD pattern of magnetic nanoparticles. (b): Magnetic properties (VSM) nanoparticles

investigated using a vibrating sample magnet at ambient temperature. As Fig .1 (b) shows, the nanoparticles have super magnetic properties and the magnetic saturation (MS) $Fe_3O_4$was 46.8emu/g. When the ferrite magnetic nanoparticles were coated with ZnO, as can be seen, the magnetic saturation decreased to 17.96 emu/g. The lowest magnetic saturation was for Fe_3O_4/ZnO/Ag. However, the magnetic properties of synthesized nanocomposite were preserved; therefore, the catalyst was easily separated from the reactor using an external magnetic field [18].

Morphology and size of nanoparticles

The surface morphology of Fe_3O_4/ZnO/Ag magnetic nanoparticles was investigated using a field diffusion scanning electron microscope (FE-SEM). As shown in Fig. 2 the surface of the nanoparticles is almost uniform in size and shape, spherical, and to some extent, agglomerated. The agglomeration of nanoparticles is attributed to the magnetic properties between ferrite particles and the magnetic dipolar interaction [19] and the lack of sonication of nanoparticles before imaging [2].

FTIR analysis

The results of FTIR analysis of Fe_3O_4/ZnO/Ag, in the range of 400-4000 cm^{-1} are presented in Fig. 3. The bond vibrations at 448 cm^{-1} are related to the Fe – O tensile vibration, and the bond vibrations at 592 cm^{-1} to the Zn-O stretching vibrations [2]. In addition, the 892 cm^{-1} peaks were attributed to tensile vibrations C = C. The bond vibrations in 1106 cm^{-1} pertained to the C-O stretching vibrations. The two peaks of 1501 and 1630 cm^{-1} were related to the C-H and O-H coupling vibrations [20]. Peaks at 2853 and 2932 cm^{-1} correspond to C = O and C-H, respectively. The tensile strength of O-H was exhibited in 3452 and 3745 cm^{-1} [21]. After the coating process with Ag to obtain Fe_3O_4/ZnO/Ag, the vibrational tension in 1382 cm^{-1} indicates the Ag-O bond [22].

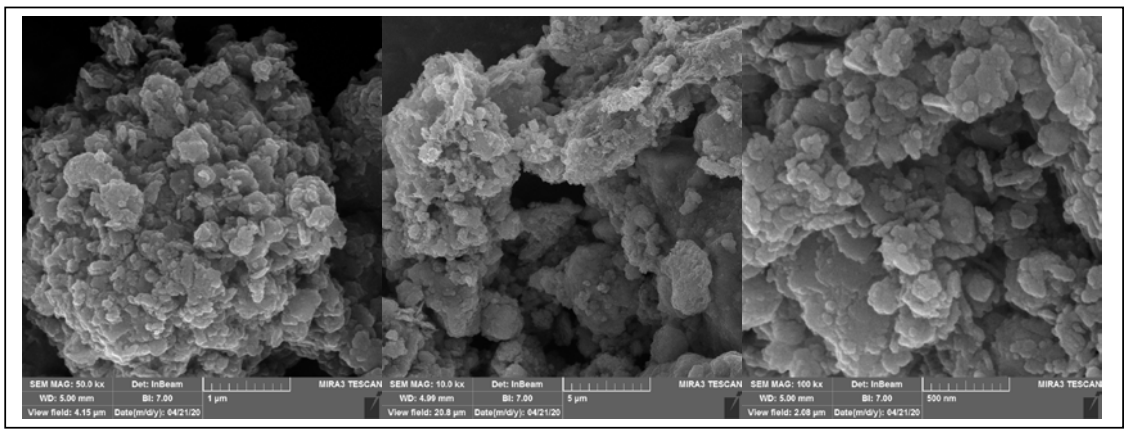

Fig. 2. FE-SEM images of Fe_3O_4/ZnO/Ag nanoparticle

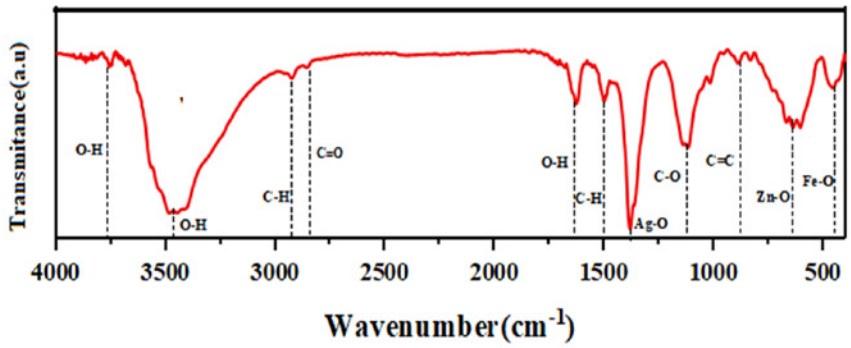

Fig. 3. FTIR spectrum of nanoparticles Fe_3O_4 / ZnO / Ag

Photocatalytic degradation of albumin

Effect of pH on the degradation of albumin

pH is one of the important factors in the photocatalytic process that impacts the efficiency of many chemical and biological reactions [23]. The results of different pH on the photocatalytic degradation of albumin using catalyst concentration of 0.2 g/l and albumin concentration of 150 mg/l in 90 minutes. are shown in Fig. 4. Before irradiation, the solution was placed in the dark for 30 min to balance the adsorption-absorption then the lamp was turned on. As shown in Fig 4, with increasing pH, photocatalytic degradation of albumin increases. The maximum removal was observed at pH 9. The photocatalytic degradation efficiencies of albumin at pH 3, 5, 7, 9, and 11 were 51, 54, 65, 89, and 79%, respectively. In an alkaline medium, the presence of a high concentration of OH° radical in the solution [24] increases the efficiency of the process. Because in photocatalysis, the production of hydroxide and peroxide radicals plays an important role in the degradation of pollutants [25]. Therefore, the higher production of these radicals caused more degradation of organic matter [23]. Since pH has an important impact on the surface charge of catalysts and pollutant molecules, it determines the production of hydroxyl radicals [26]. Under these conditions, the amount of hydroxyl radical production and the impact on photodegradation are based on the following reactions [27]:

$$Fe_3O_4/\ ZnO/\ Ag + hv\ (UV\ ) \rightarrow (Catalyst\ (e^- + h^+) \quad (3)$$

$$h^+ + OH^- \rightarrow OH^{\circ} \quad (4)$$

$$h^+ + H_2O \rightarrow H^+ + OH^{\circ} \quad (5)$$

$$e^- + O_2 \rightarrow O_2^{\circ -} \quad (6)$$

$$O_2^{\circ -} + H^+ \rightarrow 2HO^{\circ} \quad (7)$$

$$Albumin + OH^{\circ} \rightarrow Degradation\ products \quad (8)$$

$$Albumin + h^+ \rightarrow Oxidation\ products \quad (9)$$

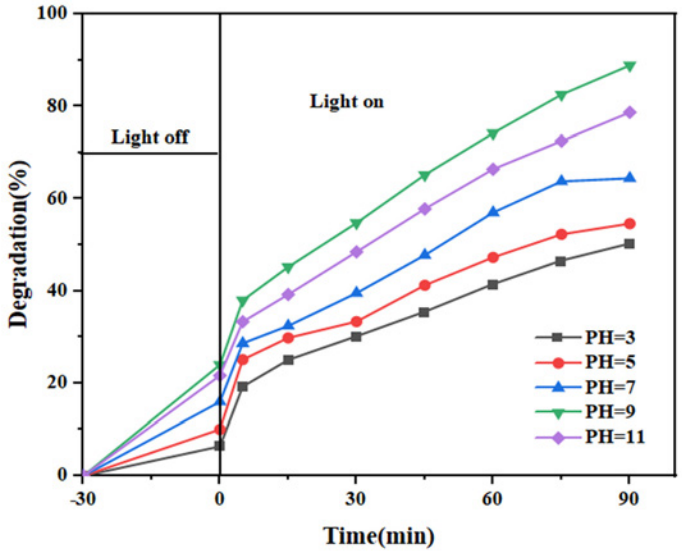

Fig. 4. Effect of pH on photocatalytic degradation of albumin

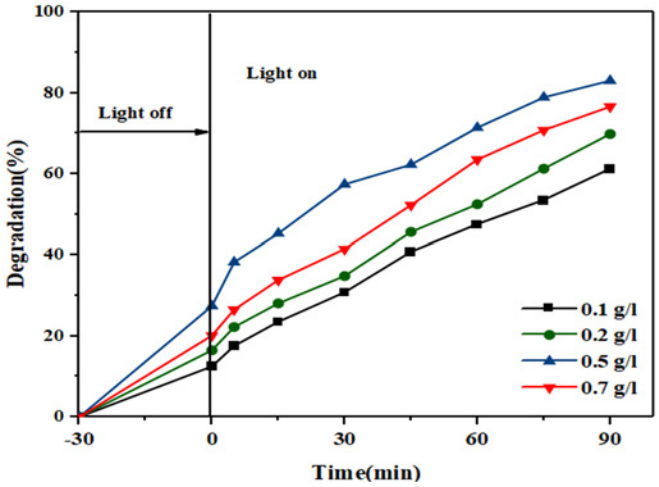

Fig. 5. Effect of nanocomposite concentration on photodegradation of albumin

Moreover, in the acidic condition, the synthesized composite nanoparticles tend to accumulate; and as a result, the degradation efficiency is reduced. Also, the absorption of photons with energy higher than the bandgap led to the transfer of electrons from the valence band to the conduction band. Since the produced holes have very strong oxidation potential with the water molecule, the hydroxide ions are adsorbed on the surface of the semiconductor to produce hydroxyl radicals[2].

Effect of nanocomposite concentration on photodegradation of albumin

The concentration of magnetic nanocomposites is another effective factor in photocatalytic processes [26]. The effect of various concentrations of Fe_3O_4/ZnO/Ag nanocomposite on the photodegradation of albumin was investigated. The experimental conditions were the albumin concentration of 150 mg/l and pH 9 at ambient temperature. Photolysis experiments in the presence of light and without the use of catalyst showed that the amount of degradation was very small. The results of photocatalytic experiments at different Fe_3O_4/ZnO/Ag concentrations are seen in Fig. 5. As shown, the albumin degradation was first enhanced by increasing the catalyst; however, it decreased with more nanocomposite concentration. The highest removal was obtained at a concentration of 0.5 g/l.

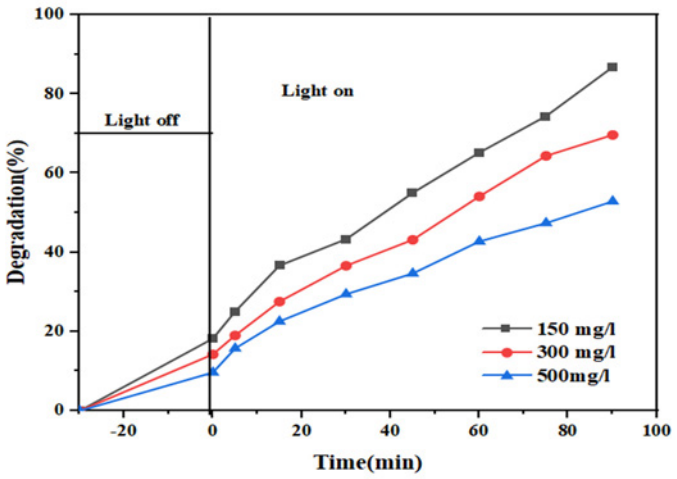

Fig. 6. Effect of initial concentration of albumin on photocatalytic degradation

By increasing the catalyst dose from 0.1 to 0.5 g/l the number of active sites was enhanced, increasing the probability of contact between the catalyst and the albumin. As a result, more hydroxyl radicals are available for degradation with increasing concentration [2]. On the other hand, increasing the catalyst concentration beyond 0.5 g/l led to increased absorbed photons and light penetration is limited. The higher concentrations of the catalyst are attributed to the turbidity in the solution, preventing light from penetrating the solution, consequently the removal of albumin decreases[29]. On the other hand, with the deposition and accumulation of catalysts in solution, the available sites for photon absorption are limited and thus the degradation efficiency is reduced[30].

Effect of initial concentration of albumin on photodegradation of albumin

Different concentrations of albumin (150, 300, and 500 mg/l) were used at pH 9 and 0.5 g/l of catalyst to investigate the effect of the initial albumin concentration on photocatalytic performance. As shown in Fig. 6, the degradation of albumin decreases strongly with increasing concentration. The maximum removal was 89% at an albumin concentration of 150 mg/l in 90 min. Increasing the concentration of albumin, the rate of degradation decreased so the minimum degradation of the pollutant was observed at a concentration of 500 mg/l (62%). As the concentration of the catalyst, the amount of light, and the duration of irradiation are constant, therefore, the number of hydroxyl radicals formed on the surface of the catalyst is constant. As a result, the degradation decreases in these conditions [2]. In addition, at higher concentrations, some parts of the emitted radiation are absorbed by the polluting molecules. Therefore, the degradation efficiency is greater than at higher concentrations. Higher degradation of albumin at lower initial concentrations is also due to the greater availability of hydroxyl free radicals. However, at higher pollutant concentrations, the amount of photons absorbed by albumin molecules decreases due to the limit of light penetration into the whole solution [28]. Moreover, as the concentration of albumin pollutants increases, its adsorption on the surface of magnetic nanocomposite also increases. Therefore, the efficiency of the catalyst against absorbed light is reduced.

Study of photocatalytic degradation kinetics of albumin

One of the most important factors in designing a photochemical process is to predict the rate of the reaction degradation process, which is controlled by the degradation kinetics of the pollutants. Experiments were performed under optimal conditions pH 9, catalyst concentration of 0.5 g/l, and different albumin concentrations (150, 300, 500 mg/l) for 90 min, to investigate the photocatalytic degradation kinetics of albumin. The kinetic study was followed according to the pseudo-first-order kinetic equation [31]:

$$Ln\left(\frac{C_0}{C}\right) = Kt \qquad (10)$$

Where k is the reaction rate constant and C_t

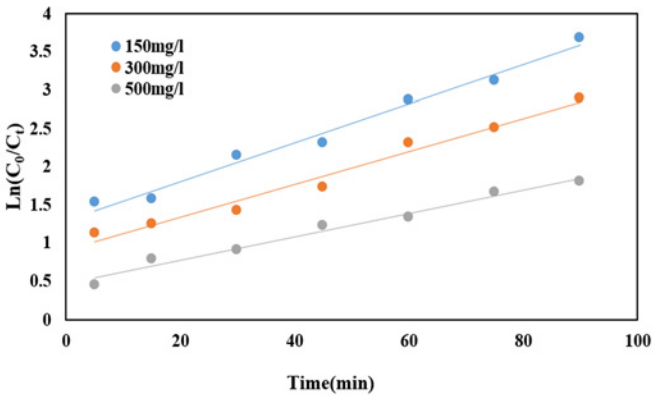

Fig. 7. Photocatalytic degradation kinetics of albumin

Table 1. Results of the kinetic study of albumin degradation

Albumin concentration(mg/l)	Equation	K	R^2
150	Y=0.0255x+1.2989	0.0255	0.984
300	Y=0.0216x+0.9034	0.0216	0.9764
500	Y=0.0154x+0.4661	0.0154	0.9809

and C_0 are the albumin concentration at time t (mg/l) and the initial albumin concentration (mg/l) at t reaction time (min), respectively. The plot ln (C_0/C_t) shows a linear relation with the irradiation time in which the slope is equal to the constant rate (k = 0.0255) and R^2 = 0.984 (Fig. 7). The kinetic results indicated that the reaction rate constant (k) decreased significantly with increasing albumin concentration. Therefore, the pseudo-first-order kinetic model is more appropriate to describe the kinetic of albumin photodegradation. As the concentration of albumin increases due to the increase in the concentration of intermediate products, the OH° radicals in the reaction decrease resulting in a decrease in constant rate (Table 1).

Effect of temperature on photodegradation of albumin

Numerous studies have studied the impact of reaction temperature on photocatalytic efficiency [32, 33]. Accordingly, in this study, the effect of temperature (25, 30, and 45 ° C) was investigated on the degradation of albumin under optimal conditions (pH 9, nanocomposite concentration of 0.5 g/l, albumin concentration of 150 mg/l). The results of this study are shown in Fig. 8. As can be observed, the highest removal was at room temperature (25 C). Albumin degradation efficiency decreased with the increase in temperature. Some factors such as desorption kinetic energy, the electron-hole pairs transfer and lifetime, and activity of the catalyst surface are related to temperature The increase in the temperature caused to escape dye molecules from the active zone of the catalyst surface before degradation [34]. One study found that due to photonic activation, heat is not required in photocatalytic reactors and can be done at room temperature [35], which is similar to this study.

Measurement of TOC in photodegradation of albumin

TOC was measured in photocatalytic degradation of albumin using Fe_3O_4/ZnO/Ag composite nanoparticles under optimal conditions. As observed in Fig. 9, the removal efficiency was 56. %.The decrease in TOC removal relative to albumin degradation can be explained by the formation of intermediate organic matter. In other words, some albumin compounds have not been completely mineralized and by-products have not been developed as indicated by TOC[36].

CONCLUSION

Fe_3O_4 / ZnO / Ag magnetic nanocomposite was synthesized and evaluated for photocatalytic degradation of albumin from aqueous solutions under UV-A light. Morphology and size of magnetic composite nanoparticles were studied by XRD, VSM, FE-SEM, and FTIR. XRD results revealed some peaks; moreover, FTIR analysis showed the

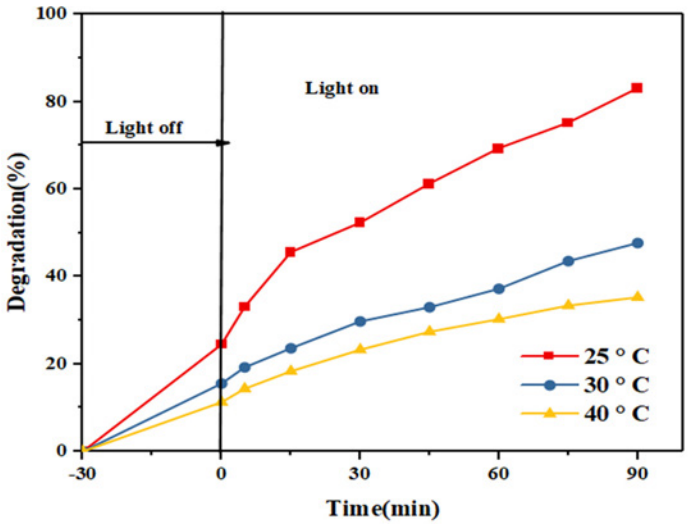

Fig. 8. Effect of temperature on photocatalytic degradation of albumin

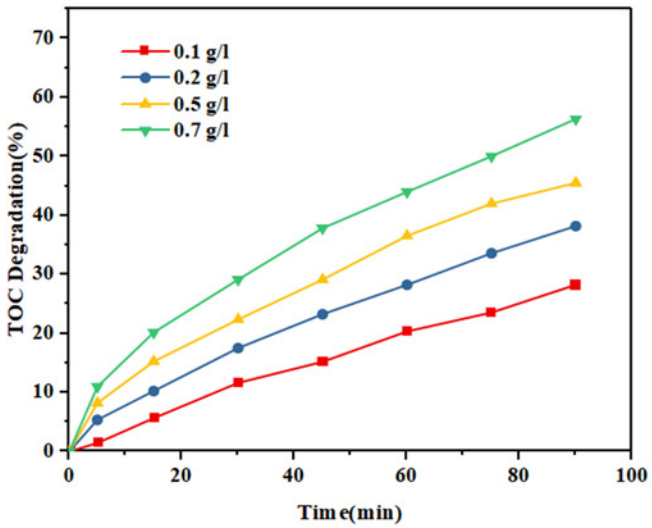

Fig. 9. The degradation of TOC using different Fe_3O_4 / ZnO / Ag composite nanoparticles concentration

bonding vibrations related to Fe3O4, ZnO, and Ag. While FE-SEM showed a uniform surface of nanoparticles, VSM proved the magnetic properties of the synthetized nanocomposite. The effects of various parameters such as pH, initial albumin concentration, nanocomposite concentration, and temperature on the photodegradation were also investigated. While the maximum degradation of albumin was observed at pH 9 (89 %), the worst removal (51%) was at pH 5. The maximum removal at pH 9 can be attributed to the catalyst surface charge and more produced hydroxyl radical. Using the different amounts of nanocomposite concentrations showed that 0.5 g/l of Fe_3O_4 / ZnO / Ag was the optimum amount of nanocomposite to degrade albumin in photocatalysis. In experimental conditions with pH 9 and 0.5 g/l of catalyst, the maximum removal (89%) was obtained with an initial pollutant concentration of about 150 mg/l amongst different concentrations of albumin. Investigation of different temperatures showed that as temperature increased the efficiency of photocatalysis decreased because dye molecules escaped from the surface catalyst. The maximum removal was observed at 25° C. The photocatalytic activity results showed that optimal conditions for

using Fe_3O_4 / ZnO / Ag nanocomposite in albumin degradation were pH 9, catalyst concentration of 0.5 g / l, and albumin concentration of 150 mg/ l at ambient temperature in 90 min. The degradation followed a pseudo-first-order model with a constant rate of 0.255 min^{-1} at 150 mg/l of albumin. TOC analysis showed that 56% of albumin was mineralized at optimum conditions. Therefore, due to the high performance of Fe3O4/ ZnO/Ag magnetic nanocomposite in the degradation of albumin, as well as its easy synthesis and separation with an external magnetic field, it can be used as a suitable and environmentally friendly catalyst for the degradation of other organic and resistant pollutants in the environment.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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