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Easy preparation of nano iron oxides@ZnO as a magnetic separable photocatalyst for degradation of acid orange 7 from aqueous solution under visible light

Ali Khani

Department of Chemistry and Chemical Engineering, Miyaneh Branch, Islamic Azad University, Miyaneh, Iran, Tel. +98 41 52229377; Fax: +98 41 52227290; emails: a.khani59@yahoo.com, a.khani@m-iau.ac.ir

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ABSTRACT

In order to improve the photocatalytic activity and easy separation of ZnO from aqueous phase, nano iron oxides@ZnO (nFeO-ZnO) as a magnetic separable photocatalyst was prepared. First, the solution of iron (III) and (II) sulfates (2:1 molar ratio) were stirred with ZnO powder in deionized distilled water for 2 h until ferric and ferrous sulfates adsorbed on ZnO, after which the suspension was heated to 323 K for 10 min. After heating, the solution was precipitated by ammonia solution with continuous stirring by mechanical stirrer at 373 K to produce nano iron oxides immobilized on ZnO (iron oxide@ ZnO). Results of detailed phase analysis by XRD and scanning electron microscopy (SEM) are discussed. XRD analysis revealed that the crystallite size (mean coherence length) of iron oxides (mainly Fe_2O_3) was 35 nm. In the next step, the degradation of acid orang 7 (AO7) from aqueous solution by prepared nFeO-ZnO in the presence of visible light was investigated. The results showed that the photocatalytic activity of prepared magnetic separable photocatalyst compared with ZnO powder as a standard photocatalyst was increased in same operational condition. Also, photocatalyst can be separated easily from the aqueous solution by a magnet. The result showed the photodegradation followed pseudo first order kinetic and the activation energy of reaction was 3.89 KJ.mol^{-1}.

Keywords: Photocatalyst; ZnO; Magnetic separation; Degradation; Water treatment; Visible light

1. Introduction

Organic pollutants especially azo dyes are being increased in environment because of wide use in various industries. Their toxic effects by producing aromatic amines and low degradation rate has convinced the researchers to focus on finding an efficient and low cost method for their treatment [1]. So many procedure such as adsorption [2], coagulation/flocculation [3], reduction [4], some advanced oxidation processes (AOPs) [5,6], etc., have been developed to treat organic pollutants, but not all of them had great efficiency and leading to full degradation or removal of pollutants. Semiconductor photocatalysts such as TiO_2 and ZnO are developed AOP, which can be conveniently applied to remove different organic pollutants [6].

In order to improve the efficiency further, the researchers focused their research on mixed oxide semiconductors due to an efficient charge separation can be obtained by coupling two semiconductor particles with different energy levels and also to increase the efficiency of photocatalytic reactions as a result of a vectorial transfer of photogenerated electrons and holes from a semiconductor to another [7–14]. In numerous investigations, an aqueous suspension of the catalyst particles has been used [15–17]. However, the use of suspensions requires separation and recycling of the ultra-fine catalyst from the treated liquid and can be an inconvenient, time-consuming and expensive process. The key to the problem of industrializing the technology seems to be simple and low cost immobilization of catalysts on solid media suitable for the treatment

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process [6] and or using the magnetic particles [18–20]. Kurinobu et al. have studied decomposition of pollutants in wastewater using magnetic photocatalyst particles that had been prepared by coating Fe_3O_4 core particles on SiO_2 and TiO_2 [20]. Mahesh and Kuo studied the photocatalytic activity of Ni nanoparticles decorated SiO_2/ TiO_2 magnetic spheres in degradation of an azo dye [21].

In the present work, we used the visible light compared with UV light because of its harmful and costly aspects and magnetic kind of photocatalyst. In addition, it is expected that the loading of other metal oxide such as iron oxides may improve photocatalytic activity of ZnO in the visible region and leads to preparation of magnetic separable photocatalyst.

2. Experimental

2.1. Materials

Acid orange 7 (AO7) as a target pollutant was purchased from Boyakhsaz Co. (Iran). $Fe_2(SO_4)_3.5H_2O$, $FeSO_4.7H_2O$ and ZnO were obtained from Merck (Germany). Deionized distilled water was used in all the experiments and all the experiments were repeated triple (variance (σ^2) = 0.01).

2.2. Preparation of nFeO-ZnO

The Fe_3O_4 immobilized on ZnO, prepared from pyrolysis of the previously composed iron (II, III) hydroxide on ZnO. The solution of iron (III) and (II) sulfates (2:1 molar ratio) were stirred with ZnO powder in deionized distilled water for 2 h until ferric and ferrous sulfates adsorbed on ZnO, after which the suspension was heated to 323 K for 10 min. After heating, the solution was precipitated by ammonia solution with continuous stirring by mechanical stirrer at 323 K. These particles were then separated from the solution by using a strong magnet and then were washed many times with distilled water .The precipitated magnetite is black in color .The powder was then dried in hot air oven at 373 K for 2 h. To evaluate the supporting treatment, nFeO-ZnO powder were leached twice with deionized distilled water and then dried. During treatment the tangible weight difference was not observed which indicated well-support. The method is simple and simultaneous synthesis-immobilization of magnetic nanosized Fe_3O_4 on ZnO leads to preparation of a more effective and easily separable nanophotocatalyst. The magnetic photocatalyst revealed the magnetic properties in water suspension when external magnetic field was applied (Fig. 1). For reusability evaluation of prepared photocatalyst, it was reused without any more pretreatment.

2.3. Photocatalytic degradation experiment

For the photodegradation of AO7, a solution containing the known concentrations of dye was prepared and then 1 L of the prepared solution was transferred into the designed photoreactor (Fig. 2) which consisted of jacketed cylindrical vessel with conical bottom Pyrex (D = 5 cm and length = 20 cm) and agitated with a mechanical stirrer during the experiment. To explore the effect of temperature on degradation, the solution temperature was adjusted with a heating-cooling system. Then the lamp was switched on to initiate the reaction. The concentration of the dye solution was determined with total organic carbon (TOC) analyzer (Shimadzu TOC-VCSH, North America). The degree of degradation of AO7 (removal efficiency) was calculated at different time intervals using the equation given below:

$$X\% = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

In which $X\%$ is the percentage of degradation, C_0 is the initial concentration of AO7, and C_t is the concentration of AO7 at time t.

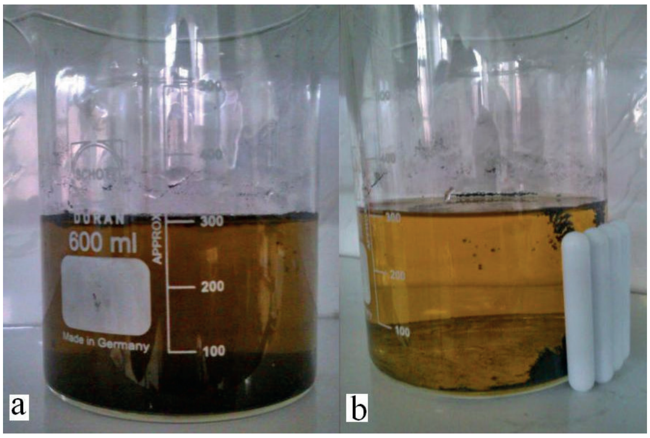

Fig. 1. Separation of magnetic photocatalyst with a magnet from suspension of nFeO-ZnO in acid orange 7 solution, before (a), after (b).

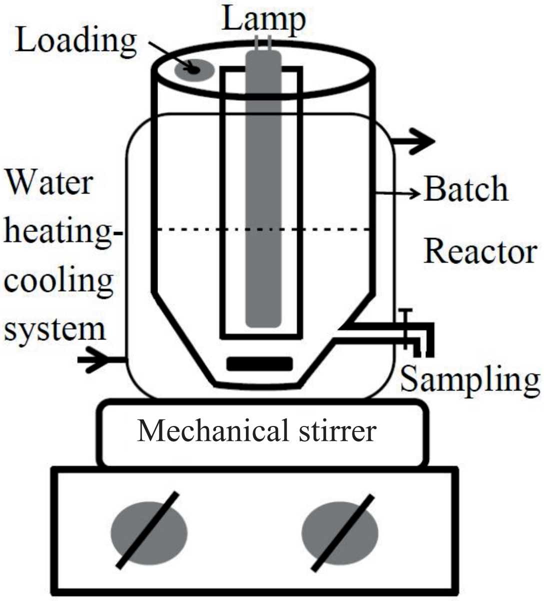

Fig. 2. The schematic diagram of experimental apparatus for degradation of AO7.

3. Results and discussion

3.1. Characterization of nFeO-ZnO

The results from X-ray Diffraction (XRD) analysis are shown in Fig. 2. The average crystallite size (D in nm) of iron oxide nanoparticles (mainly Fe_2O_3) was determined using XRD (Bruker) pattern of the redox nanocomposite according to the Scherrer equation [6]:

$$D = k\frac{\lambda}{\beta.\text{Cos}\,\theta} \tag{2}$$

where k is a constant which is 0.89, λ is the XRD wavelength which is 0.154 nm, β is the full width at half maximum (0.0036 Radian) and θ is the half diffraction angle which is 18.

This Fig. 3 shows clearly the same pattern for the prepared nFeO-ZnO when compared to the standard Fe_3O_4–ZnO powder and the results of the calculation show that the average particle size is about 35 nm.

Fig. 4 shows the SEM image of prepared photocatalyst. The morphology of the prepared nFeO-ZnO was determined using a Leo 440i scanning electron microscope (SEM) followed by Au coated by the sputtering method using a coater sputter SC 761. SEM analysis demonstrated that the nanoparticles of all prepared iron oxides have particle sizes below 100 nm.

3.2. Comparative study

It has been established that the photocatalytic degradation of organic matter in solution is initiated by photoexcitation of the semiconductor, followed by the formation of an electron–hole pair on the surface of catalyst. The high oxidative potential of the hole (h_{VB}^+) in the catalyst permits the direct oxidation of organic matter (dye) to reactive intermediates. A more reactive hydroxyl radicals can also be formed either by the decomposition of water or by the reaction of the hole with •OH. The hydroxyl radical is an extremely strong, non-selective oxidant that leads to degradation of organic chemicals [5].

For the evaluation of the photocatalytic activity of the prepared photocatalyst, an experiment in basic condition (initial concentration of AO7 = 50 mg.l^{-1}, pH = 7, the weight of nFeO-ZnO = 5 g, T = 298.15 K, the volume of solution = 1 L, and reaction time = 90 min) was designed in order to measure the degree of degradation or adsorption of AO7 on magnetic photocatalyst in dark condition. These experiments demonstrated that both the UV or visible light and the photocatalyst were needed for the effective destruction of AO7 (Fig. 5) and TOC results showed that the degradation process has occurred in the presence of UV and visible light almost the same. The mineralization was completed in 120 min under basic conditions. The reusability of photocatalyst was also studied. Fig. 5 showed that the difference between the catalyst and reused catalyst is not significant. The major advantage of prepared nFeO-ZnO in comparison with ZnO is its adsorption over a larger fraction of UV-Vis. spectrum and easily separation of its fine powder. Also, nFeO-ZnO has more efficiency compared to CuO-ZnO immobilized on expanded perlite (nCuO-ZnO-P) [6] in a previous work.

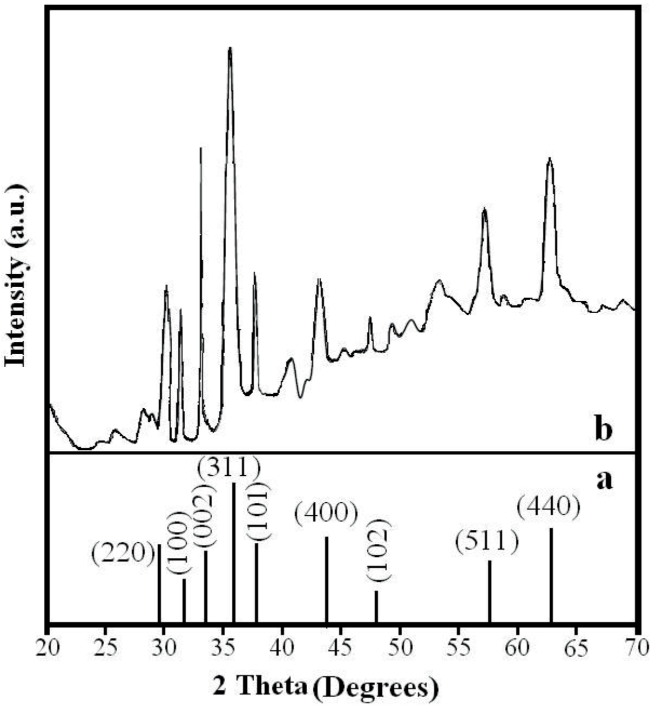

Fig. 3. XRD of standard Fe_3O_4–ZnO powder (a) and nano nFeO-ZnO (b): The diffraction peaks (220), (311), (400), (511) and (440) Fe_3O_4 and (100), (002), (101) and (102) for ZnO.

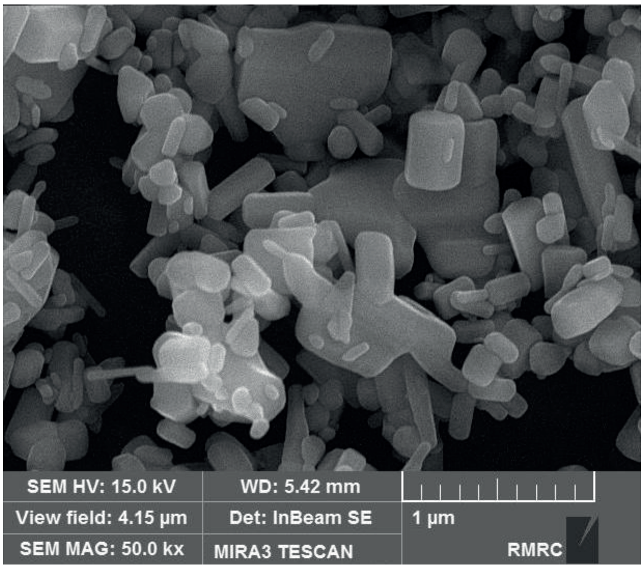

Fig. 4. SEM images of nFeO-ZnO.

3.3. Kinetics study

For kinetics study in different temperatures and to determine the activation energy (Ea), at first, the effect of temperature on degradation process was evaluated. Hence, the experiments were carried out with different temperatures varying from 278.15 to 318.15 K and other parameters were kept in basic conditions. The changes in dye concentration

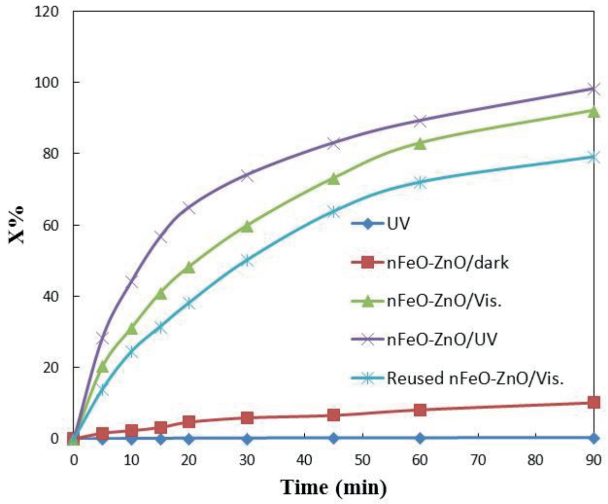

Fig. 5. Evaluation of the photocatalytic activity of the prepared magnetic photocatalyst.

with time during the degradation process at each temperature show the differences in the degradation efficiency of dye. These differences should originate from the effect of energy of reaction [6].

In literature, photodegradation processes exhibited pseudo first-order kinetics with respect to the concentration of the organic compound, by using the equation given below [6].

$$Y_R = \frac{-dC_R}{dt} = \frac{k_Y K C_R}{1 + KC_R} \tag{3}$$

where r_R is the rate of reaction (degradation of the solute R), C_R is the solute concentration, t is the time of the reaction, and k_r and K are the reaction and adsorption constants associated with the solute, respectively. When the concentration is low, the term KC_R is often negligible, and the apparent reaction rate will follow a pseudo-first-order model. Integration of the equation under this assumption with boundary conditions of $C_R = C_{R0}$ at $t = 0$ yields [6]:

$$-\ln\left(\frac{C_R}{C_{R0}}\right) = k_{\text{app}} t \tag{4}$$

where C_{R0} is the initial substrate concentration and k_{app} is the apparent first order reaction rate. The photocatalytic reactions in many cases show this behavior. The relative deviation modulus, P, was used for determination of linear trend of the line ($-\ln(C_R/C_{R0})$ vs. t). The fit accepted to be good when P is below 5 [6]. Fig. 6 shows the plots of $-\ln(C_R/C_{R0})$ vs. time. According to the value of P, the reaction follows a pseudo-first-order kinetics and the results show that reaction rate enhances as temperature increases from 278.15 to 318.15 K (Table 1).

Also, for calculation of activation energy, the Arrhenius equation was used as [6]:

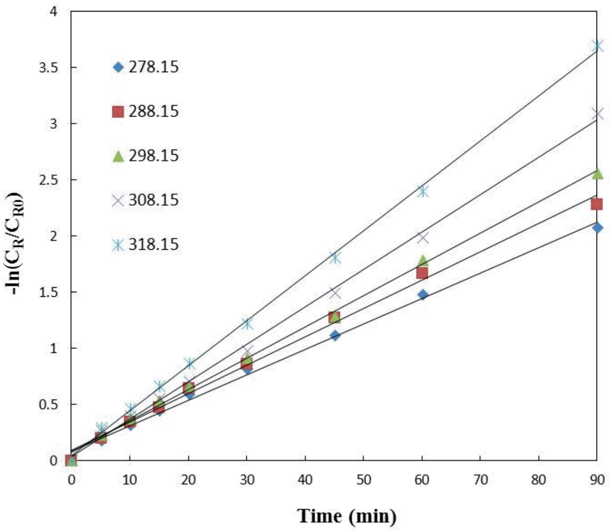

Fig. 6. The plots of $-\ln(C_R/C_{R0})$ vs. time.

Table 1
The apparent rate constant of reaction in different temperatures

T (K)	278.15	288.15	298.15	308.15	318.15
X%	87.38	89.78	92.26	95.44	97.52
R^2	0.995	0.995	0.998	0.998	0.999
P	4.08	3.88	2.94	4.65	2.13
k_{app} (min^{-1})	0.0227	0.0253	0.0278	0.0333	0.0401

$$-In\ k = -\ In\ A + \frac{E_a}{R}\left(\frac{1}{T}\right) \tag{5}$$

where k = rate constant in min^{-1}, T = temperature in K.

The low activation energy (E_a) value (3.89 KJ.mol^{-1}), calculated by Fig. 6 results (from the slope of line: $-\ln k$ vs. $1/T$), suggests that degradation of AO7 is limited by diffusion step and the apparent rate constant reflects the rate at which AO7 molecules migrate from bulk solution to the reaction zone (i.e., the solution–bubble interfacial regions where temperature and OH radical concentration are high) [22]. In related studies, photodegradation of dyes was also found to be controlled by diffusion [5,6].

4. Conclusion

The characterization methods of XRD and SEM confirm the synthesis of nanosized Fe_3O_4 immobilized on ZnO powder via a simple and low cost method. The results show that the average particle size is about 35 nm. The photocatalytic activity of the magnetic separable photocatalyst was tested for degradation of the AO7 as a pollutant in visible light. The TOC analysis showed a good photocatalytic activity for the photocatalysts in visible light. Photolysis and adsorption were found to be negligible in overall degradation process. The degradation degree (X%) of photodegradation process was 92.26% under basic conditions. Pseudo-first-order kinetics model was confirmed to satisfy these reactions in basis of *P*. The activation energy was 3.89 kJ/mol in temperature range of 278.15 to 318.15 K, suggesting a diffusion-controlled reaction.

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