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Photocatalytic efficiency of CuFe_2O_4 for photodegradation of acid red 206

ABSTRACT

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In this paper CuFe_2O_4 , nanocrystalline powders were prepared. Also, the supported Cu ferrite was obtained by impregnation of the supports with Cu and Fe nitrates solutions, for calcination temperature 450 °C. The samples were characterized by X-ray powder diffraction (XRD) and Fourier transform-infrared spectroscopy (FT-IR). In this investigation photocatalytic degradation of Acid red 206 in water was studied. The results show that the CuFe_2O_4 is an active photocatalyst. A first order reaction with $k = 0.123 \text{ min}^{-1}$ was observed. The effects of some parameters such as pH, amount of photocatalyst, initial concentration of dye were examined.

Keywords: Photodegradation; Photocatalysts; CuFe_2O_4 ; Acid Red 206; Adsorption.

INTRODUCTION

Environmental pollution is a serious day-to-day problem faced by the developing and the developed nations in the world. Air, water and solid waste (plastics) pollution due to the anthropogenic sources contribute a major share to the overall imbalance of the ecosystem.

Dyes are organic compounds consisting of two main groups of compounds, chromophores (responsible for color of the dye) and auxochromes (responsible for intensity of the color) [1]. Dyes are classified according to the chemical structure and type of application. Methods for nanoparticle deposition on supports contaminants such as pesticides are removed through homogeneous or heterogeneous chemistry. In the homogeneous process, the molecules of relevance are degraded by the nanoparticles dispersed in the solution phase. This methodology is attractive because it utilizes all the available surface area offered by nanoparticles. However, a major issue of concern is the possible presence of nanoparticles contaminating the purified water.

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The removal of colored and colorless organic pollutants from industrial wastewater is considered as an important application of adsorption processes using suitable adsorbent [2].

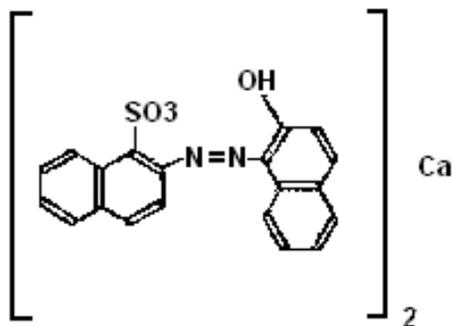
Spinel of the type $M^{2+}M_2^{3+}O_4$ attract the research interest because of their versatile practical applications [6]. In the case of $M^{3+} = Fe$, the resulting spinel ferrites having a general chemical composition of MFe_2O_4 ($M = Mn, Mg, Zn, Ni, Co, Cd, etc.$) are widely used as magnetic materials. Currently, a large number of metal oxides, mixed oxides and ferrites have shown sensitivity to certain gas species. Spinel compounds, with a general formula of AB_2O_4 , have also been proved as important oxides in gas sensors, and have been investigated for the detection of reducing gases. $NiFe_2O_4$, $CdFe_2O_4$ and $ZnFe_2O_4$ spinel ferrites have been extensively studied for various gas-sensing applications [3,4]. Copper ferrite ($CuFe_2O_4$) is one of the important ferrites [5]. The magnetic behavior of $CuFe_2O_4$ has been drawn much interest and has been a subject of intensive studies [6,7]. $CuFe_2O_4$ can be used in the form of a fine powder or crystals dispersed in wastewater treatment applications.

In this work, we reported the synthesis and characterization of $CuFe_2O_4$ nanoparticles. $CuFe_2O_4$ was used for degradation of aqueous Acid Red 206.

EXPERIMENTAL

Materials

All the compounds used were prepared from MERCK Company. Acid Red 206, was obtained from the Kimiagostar company (Iran) and used without further purification. The molecular structure of Acid Red 206 is shown in Scheme I.



Scheme I. Molecular structure of Acid Red 206

Apparatus

For the UV/photocatalyst process, irradiation was performed in a batch photoreactor of 2 liters in volume with four mercury lamps, Philips 8W (UV-C). A magnetic stirrer was used to ensure complete mixing in the tank (stirring speed = 250 rpm) and air was dispersed at a flow rate of 1 $lit. min^{-1}$ by using an air diffuser to supply oxygen for the enhancement of photo-oxidation UV/VIS Spectrophotometer, (Shimadzu 2101) was employed for absorbance measurements using silica cells of path length 1 cm. XRD analysis of the samples was done using a D-500 diffractometer (Siemens). FTIR spectra were recorded on a Nicolet-Magna 550 equipment, with CsI optics, applying the "pellets" KBr technique.

Preparation of $CuFe_2O_4$ Catalysts

0.005 mol $Cu(NO_3)_2$ and 0.01 mol $Fe(NO_3)_3$ were dissolved together in 50 ml distilled deionized water to get a mixed solution. The mixed solution was subsequently added into 100 ml 0.3M citric acid solution and produced a transparent mixed sol. During this mixing procedure, the temperature was controlled at around 80 °C by using a water bath. Then the temperature was further kept at 80 °C until a transparent and viscous gel was obtained. The as-obtained gel was subsequently transferred into an oven and kept at 130 °C for 3 h. The as-prepared precursors were then annealed at 850 °C for 3 h with a heating rate of 10 °C/min.

Procedures

For the photodegradation of Acid Red 206, a solution containing a known concentration of dye and photocatalyst was prepared and was allowed to equilibrate for 30 min in the darkness. The suspension pH values were adjusted at the desired level using dilute NaOH and H_2SO_4 (the pH values were measured with a Horiba D-14 pH meter). The photo degradation reaction took place under the radiation of a mercury lamp while agitation was maintained to keep the suspension homogeneous. The concentration of the samples was determined using a spectrophotometer (UV/VIS Spectrophotometer, Shimadzu 160A) at $\lambda_{max} = 513$ nm. The samples were filtered before the UV-vis spectroscopy to remove the photocatalyst. The degree of photodegradation (X) as a function of time is given by:

$$X = \frac{C_0 - C}{C_0}$$

Where C_0 and C are the concentration of dye at $t = 0$ and t , respectively.

RESULTS AND DISCUSSION

Characterization of photocatalyst

The surface morphology of was studied by scanning electron microscopy and the SEM picture are presented in Figure 1.

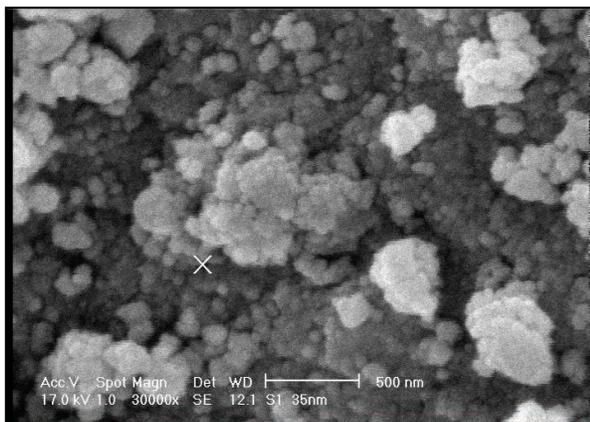


Fig.1. SEM image CuFe_2O_4

The absorptions associated to Fe/Cu complex with citrate, formed on the support surface and cavities, can be observed in the middle region of the spectrum. The frequencies around 1636 and 1442 cm^{-1} , assignable to the functional groups present in the Fe/2Cu complex, as well as a band due to the free ligand centered in $\sim 1727 \text{ cm}^{-1}$, are noticeable.

Figure 2 shows the XRD pattern of the photocatalyst.

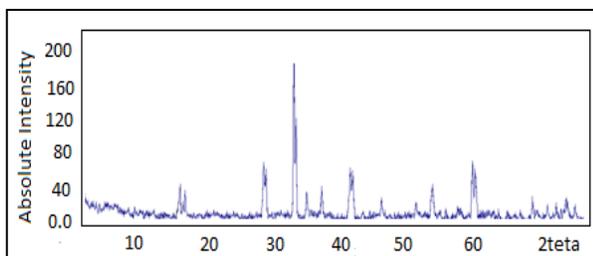


Fig.2. X-ray diffraction pattern of CuFe_2O_4

The absorbance of Acid Red 206 solutions during the photocatalytic process at initial and after 2 h irradiation time verses λ are shown in Figure 3. The decrease of absorption peaks of Acid Red 206 at $\lambda_{\text{max}} = 513 \text{ nm}$ in this Figure indicates a rapid degradation of the azo dye. Complete discoloration of dye was observed after 3 h under optimum conditions.

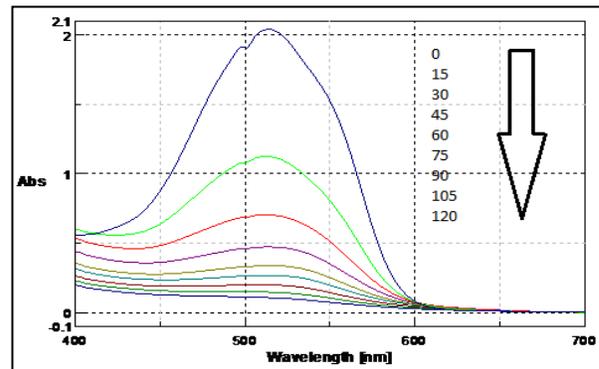
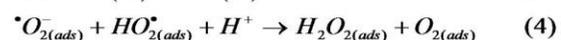


Fig.3. UV-Vis spectra of AR206 (90 ppm) in aqueous photocatalyst (CuFe_2O_4) dispersion with concentration of 60 ppm, irradiated with a mercury lamp light at $\text{pH} = 4$, $T = 298 \text{ K}$, at: $t = 0, 15, 30, 45, 60, 75, 90, 105, 120 \text{ min}$.

Effect of pH

pH is one of the main factors influencing the rate of degradation of some organic compounds in the photocatalytic process[8]. It is also an important operational variable in actual wastewater treatment. The photodegradation of AR206 at different pH from 4 to 10 were studied, and the best results obtained in acidic solution, ($\text{pH} = 4$)(Fig.4). The CuFe_2O_4 surface is presumably positively charged in acidic solution and negatively charged in alkaline solution [9]. For the above reasons, for dyes that have a sulfuric group in their structure, which is negatively charged, the acidic solution favors adsorption of dye on to the photocatalyst surface, thus the photodegradation efficiency increases. There is also the photocatalytic degradation of AR206 in acidic solutions, which is probably due to the formation of OH^\bullet as it can be inferred from the reactions (1-4)[10].



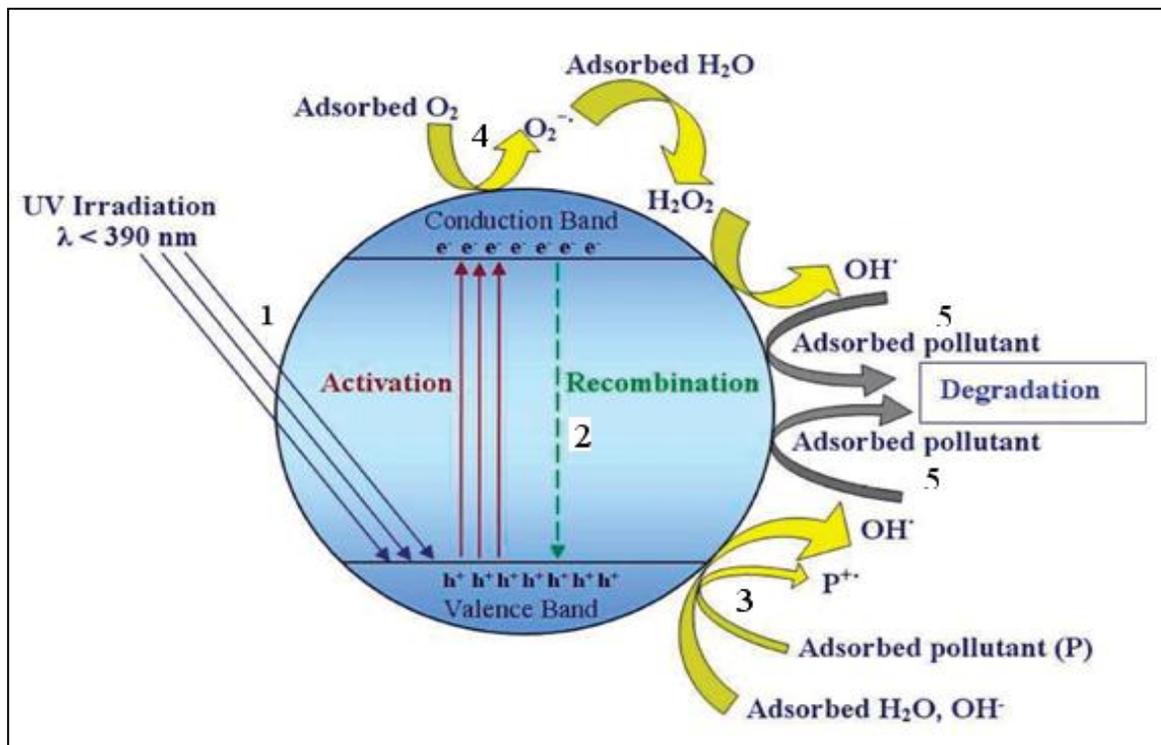


Fig. 4. General mechanism of the photocatalysis.

Kinetics of Photocatalytic Degradation of AR206

Several experimental results indicated that the degradation rates of photocatalytic oxidation of various dyes over illuminated CuFe₂O₄ fitted by the first-order kinetic model [11-17] shows the plot of $\ln ([\text{Dye}]_0/[\text{Dye}])$ versus irradiation time for AR206. The linear plot of $([\text{Dye}]_0/[\text{Dye}])$ versus irradiation time suggests that the photodegradation reaction approximately follows the pseudo-first order kinetics with rate coefficient $K = 0.123 \text{ min}^{-1}$.

CONCLUSIONS

- The photodegradation conversion of AR206 decreases with an increase in the initial concentration of AR206.
- pH is one of the main factors and the optimum pH was obtained about 4.
- Kinetics of photocatalytic degradation of AR206 is pseudo-first order with $K = 0.123 \text{ min}^{-1}$.

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