Photocatalytic Degradation of Azo Dye Acid Yellow 23 in Water Using NiFe₂O₄ Nanoparticles Supported on Clinoptilolite as a Catalyst in a Circulating Fludized Bed Reactor

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ABSTRACT

In this investigation photocatalytic degradation of the azo dye Acid Yellow 23 (AY23) in water studied. NiFe₂O₄ nanoparticles was supported on Clinoptilolite (NiFe₂O₄/CP) using a precipitation method. NiFe₂O₄/CP catalysts have been characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and BET surface area analysis. Optimum conditions were determined for the removal of Acid Yellow 23 (AY23) dye in water using a factor at the time the experimental design method in a circulating fludized bed reactor under UV irradiation. The results showed that pH= 5, photocatalyst amount = 40 (mg/l), H₂O₂ concentration = 30 ppm and temperature = 20 ^{0}C was optimum conditions for this reaction. A first order reaction with k= 0.0214 min^{-1} was observed for the photocatalytic degradation reaction. The results showed that UV/NiFe₂O₄/CP process was more effective in degradation of Acid Yellow 23 dye.
KEYWORDS: Acid Yellow 23, Photodegradation, UV/NiFe₂O₄/CP, Circulating fludized bed reactor.

1. INTRODUCTION

Due to shortage of water resources and environmental problems and because of pollution of these sources is necessary and vital to prevent contamination of this valuable resource. Wastewater treatment plants in various industries are the best and most practical method and it is considered effective in this area.

According to available statistics, about fifteen percent of all global production of colors is used in textile (Zollinger 1991). Specified amounts of dye are lost in the process of manufacturing and utilization and often cause environmental pollution problems.

From the viewpoint of green chemistry, the photocatalytic decomposition of organic compounds in wastewater has attracted a great deal of attention (Ollis 1993; Fox et al., 1994; Greem and Rudham 1993; Mattews 1990).

In this method organic compounds can be completely decomposed to H₂O and CO₂ by photocatalysis and no secondary pollutants are generated. The aim of the present study is to evaluate photocatalytic degradation of Acid Yellow 23 (AY23) by using photocatalyst. The degradation of this dye has been previously studied by the use of UV/H₂O₂ (Arjomandirad et al., 2012). Zeolite seems to be a promising support for nickel ferrite (NiFe₂O₄) photocatalyst because of its regular pores and channel sizes, and good adsorption ability. NiFe₂O₄ supported on CP integrates the photocatalytic activity of NiFe₂O₄ with the adsorption properties of CP together, which induce a synergistic effect, resulting in the enhancement of photocatalytic efficiency. NiFe₂O₄ possess magnetic properties which increase photocatalytic activities. These compounds are two-partial oxides of transition elements which are a compound of NiO and Fe₂O₃. They are also from the large group spinel; are paramagnetic; include single electrons, and are used as catalyst (Sivakumar et al., 2011). The wastewaters generated by the textile industry contain considerable amounts of azo dyes. The discharge of these coloured wastewaters in the ecosystem has been problematic due to their toxicity and resistance to biodegradability. Among different techniques for the removal of coloured compounds, the traditional ones, such as adsorption, extraction, ultra-filtration, coagulation–flocculation, ozonation, H₂O₂ oxidation, photo-oxidation, and combination of several techniques have been applied (Gong et al., 2005; Madaeni and Mansourpanah 2004; Guibal and Roussy 2007; Nikazar et al., 2007).

The overall process of advanced oxidation processes (AOPs) refers to reactions decomposition and oxidation, which during the free radicals generated by irradiation UV, lead oxidation of matter organic and

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the most important free radicals created in this process in aqueous environment, is the hydroxyl radical. This radical intermediary element, in the next stage by solution molecular oxygen trapped then are making progress with the creation of radical's peroxides and proxies and complete the decomposition process. In finally organic pollutants are dissociated to simple substance such as water, carbon dioxide, nitrogen gas, and mineral acids (Comparellia et al., 2005). The scientific contribution of this paper are: 1) the process offers great potential as an industrial technology to detoxify wastewaters; 2) Wastewater treatment sectors and textile industry will benefit from the results.

A lot of experiments have focused on the use of photocatalytic oxidation techniques for wastewater treatment. The mechanism involving photocatalytic oxidation processes has been extensively discussed in the literature (Turchi and Ollis 1988; Sabate et al., 1991; Nikazar et al., 2008; Matthews and McEvoy 1992).

In the present study $NiFe_2O_4$ has been stabilized on Clinoptilolite. The precipitation method has been used to perform the experiment. $NiFe_2O_4/CP$ was selected to degrade Acid Yellow 23 dye and the photodegradation efficiency of $UV/H_2O_2/semiconductor$ system. Therefore, the effect of operational parameters such as initial pH of the solution, photocatalyst amount, H_2O_2 concentration and temperature was examined in the process.

2. MATERIALS AND METHOD

2.1. Materials

The raw materials were Iranian Clinoptilolite (CP) (Afrand Tuska Company, Iran) extracted from deposits in the region of Semnan.

The azo dye, Acid Yellow 23 (AY23) (C.I.=19140) was obtained from Merck Company and was used without further purification. The structure and characteristics of Acid Yellow 23 is shown in Table 1.

Other chemicals used in the project were purchased from the Merck Company (Germany).

2.2. Preparation of $NiFe_2O_4$ Immobilized on Clinoptilolite

Other researchers have already described the preparation method of $NiFe_2O_4$ nano- particles (Xu et al., 2007). With this method, for preparing of $NiFe_2O_4$ nanoparticles were initially prepared using 2.5M $Fe(NO_3)_3$ and 1.25M $Ni(NO_3)_2$ solutions. Then they were mixed with 60 ml of each solution and 6M NaOH solution was added slowly into the mixture solution until pH 10 was obtained. At this stage dropwise $FeCl_2$ solution (1M) was added into the mixture until the mole ratio of Fe^{2+}/Fe^{3+} 0.02 was obtained. By the dropwise addition of NaOH solution (6M), the pH value of the resulting mixture was adjusted to ca. 10.0. This mixture was refluxed for 2 h. For several times solid phases were washed with de-ionized water and were separated using the centrifuge method. In this method, $NiFe_2O_4$ nanoparticles, was mixed with CP using ethanol (1:2:1w/w %) as a solvent using agate pestle and mortar. This material was dried at 110 ^{0}C in an oven for 2 h and calcined in air at 400 ^{0}C for 4 h. The precipitation was sieved using 100 mesh standard sieve.

2.3. Apparatus

Figure 1 shows the schematic diagram of Circulating Fludized Bed Reactor (C.F.B.R) which was used for photocatalytic decomposition of Acid Yellow 23. In this equipment, the total volume of photoreactor was 3 liters with three mercury lamp Philips 15W (UV-C) was used in photoreactor. UV/VIS Spectrophotometer, Jenway (6505) was employed for measuring absorbance using glass cells of path length 1 Cm. XRD analysis of the samples was done using a X-ray diffractometer Philips-XPert MPD, tube: Co kα , wavelength: λ=1.78897Å , Voltage: 40 kV, Current: 30 mA. The morphologies and specific surface areas of the photocatalyst were taken using a Philips XL30 scanning electron microscope (SEM) and a Micrometric-100E Brunauer Emmett Teller (BET).

2.4. Procedures

For the photodegradation of AY23, a solution containing known concentration of dye and photocatalyst were prepared. The suspension pH values were adjusted at the desired level using dilute NaOH and H_2SO_4 (the pH values were measured with Horiba M12 pH meter) and then were allowed to equilibrate for 30 min in darkness. Then the prepared suspension was transferred to a 3.5 liter Pyrex tank. The photodegradation reaction took place under the radiation of Mercury lamp in 3 photoreactors is shown in the, schematic diagram Figure 1. The concentration of the samples was determined (at 5 min intervals and centrifuged to discard any sediment) using a spectrophotometer (UV-vis spectrophotometer, Jenway (6505) at λmax = 432 nm. The degree of photodegradation (X) as a function of time is given by:

$$X = \frac{C_\circ - C}{C_\circ} \qquad (1)$$

where $C_\circ$ and C are the concentration of dye at t = 0 and t, respectively.

3. RESULTS AND DISCUSSION

3.1. The Characterization of Photocatalyst

Figure 2 shows the SEM images of (a) CP, (b) $NiFe_2O_4$ nanoparticles and (c) $NiFe_2O_4$/CP. It seems that the $NiFe_2O_4$ nanoparticles take place on the surface of Clinoptilolite. All levels of Clinoptilolite surface were not covered with $NiFe_2O_4$, thus pollutants could be absorbed by the surface of the Clinoptilolite. The BET surface areas of CP, $NiFe_2O_4$ and $NiFe_2O_4$/CP calculated by BET equation were 480, 134, 392 m^2g^{-1}, respectively.

To reveal the interaction between the $NiFe_2O_4$ and the CP, the crystal structures of the raw CP and the $NiFe_2O_4$/CP calcined at 400 ^{0}C after 4 h were measured is shown in Figure 3. The XRD patterns of samples are illustrated in the Figure 3. XRD patterns of the as-prepared samples (2θ ranges from 10° to 90°). Clearly the XRD patterns of $NiFe_2O_4$/CP consist of the raw CP which can be calcined at 400 ^{0}C for 4 h. It is implied that the frame structure of zeolite after $NiFe_2O_4$ loading will not be destructed and less amount of $NiFe_2O_4$ has loaded on CP. The comparison of XRD patterns of $NiFe_2O_4$ before and after being calcined at 400 ^{0}C indicated that the crystalline phase of the prepared $NiFe_2O_4$ (supported on Clinoptilolite) and Clinoptilolite were stable during the heat treatment process. The crystallite size of $NiFe_2O_4$/CP was calculated using the Debye-Scherer formula:
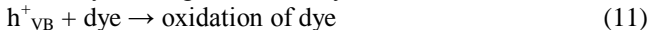
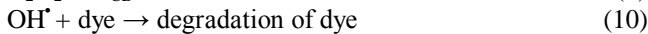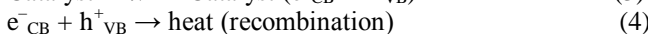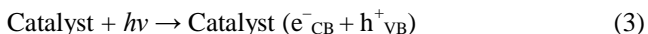D= 0.9 λ / β cosθ   (2)

where D is the average crystallite size, λ is the wavelength of Co kα , β is the full width at half maximum (FWHM) of the diffraction peaks, and θ is the Bragg's angle. The average crystallite size of $NiFe_2O_4$ supported on CP was estimated to be about 64 nm.

3.2. UV- Vis Spectra

Figure 4 shows typical time dependent UV-vis spectrum of AY23, respectively during photo irradiation with $NiFe_2O_4$/CP catalyst. The spectrum of AY23 in the visible region exhibits a main band with a maximum at 432 nm. Based on these results, it was shown that the ultraviolet radiation are broken the structure of dye molecules and reduced absorption intensity. Complete discoloration of dye was observed after 45 min under optimum conditions.

3.3. The Effect of UV Irradiation and Photocatalyst Particles

The effects of UV irradiation, $NiFe_2O_4$ and CP on photodegradation of AY23 are shown in Figure 5. This figure indicates that in the presence of mixed photocatalyst ($NiFe_2O_4$/CP) and UV irradiation, 98.9% of dye was degraded at the irradiation time of 45 min while it was 78.4% for $NiFe_2O_4$ (without clinoptilolit) and UV irradiation. This was contrasted with 9.6% degradation for the same experiment performed in the absence of $NiFe_2O_4$, and a negligible 36.7% when the UV lamp had been switched on and the reaction was allowed to occur in the presence of CP (without $NiFe_2O_4$). These experiments demonstrated that both UV light and a photocatalyst, such as mixed photocatalyst ($NiFe_2O_4$/CP), are needed for the effective degradation of AY23. Photocatalyst mechanism was used for the study since the ultraviolet radiation to the semiconducting oxides; electrons can be transferred from the valance to conduction bonds. During this transition, some holes are created in the valance bond and additional electrons are also created in the conduction bond. Dissolved oxygen molecules in water take extra electrons from the conduction bond and after some reaction, radical hydroxide will be released. On the other hand, after reaction with several holes the water molecules and the hydroxide ions are created in the valance bond, thus hydroxide radicals are created. Finally, hydroxide radicals with organic pollutants react and cause the breakdowns and failures, thus convert them into minerals. Semiconductors, such as TiO_2 (Sabate et al., 1991) degradation of dye according to the following reactions is suggested:

Catalyst + hv → Catalyst (e^-_{CB} + h^+_{VB})   (3)
e^-_{CB} + h^+_{VB} → heat (recombination)   (4)
e^-_{CB} + O_2 → $O_2^{\bullet-}$ (5)
h^+_{VB} + H_2O → H^+ + $OH^{\bullet}$ (6)
$O_2^{\bullet-}$ + H^+ → $HO_2^{\bullet}$ (7)
2 $HO_2^{\bullet}$ → H_2O_2 + O_2 (8)
H_2O_2 + e^-_{CB} → $OH^{\bullet}$ + OH^- (9)
$OH^{\bullet}$ + dye → degradation of dye   (10)
h^+_{VB} + dye → oxidation of dye   (11)
e^-_{CB} + dye → reduction of dye   (12)
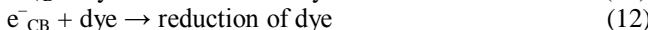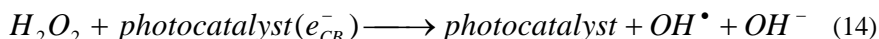
The mechanism is given in Figure 6 .

3.4. The Effect of Catalyst Concentration

At this stage, the effect of different amounts of catalyst between 20 - 50 mg/l of dye solution was tested. The results in Figure 7 shown that increasing the catalyst concentration to 40 mg/l reaction rate increased and with increasing amount of catalyst concentration, reaction rate decreased. Because of reduced activity of photocatalytic in concentrations more than 40 mg/l, which increases the amount of catalyst phenomenon distribution of light to contact light rays with the catalyst particles in the solution occurred, and lost the number of photons of light energy and thus is reduced the amount photocatalytic reactions (Goncalves et al., 1999).

According to the results the optimal amount 40 mg/l was selected.

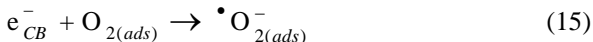## 3.5. The Effect of H_2O_2 Concentration

As it can be seen in Figure 8, the decolorization rate increased when H_2O_2 concentration changed from 12 - 30 ppm. In H_2O_2 solution, the formation rate of hydroxyl radical was increased in two ways. First, symmetrical breaking of hydrogen peroxide molecule by illumination would also produce hydroxyl radicals. Second, the reduction of H_2O_2 in the conduction band would produce hydroxyl radicals (So et al., 2002; Lee et al., 2003). So the optimal amount of H_2O_2 concentration was 30 ppm.

$$H_2O_2 + h\upsilon \longrightarrow 2OH^\bullet \tag{13}$$

$$H_2O_2 + photocatalyst(e_{CB}^-) \longrightarrow photocatalyst + OH^\bullet + OH^- \tag{14}$$

3.6. The Effect of pH

pH is one of the main factors influencing the rate of degradation of some organic compounds in the photocatalytic process (Hofstandler et al., 1994; Anpo et al., 1986). It is also an important operational variable in actual wastewater treatment. Figure 9 shown the photodegradation of AY23 at different pH from 3 - 9, which clearly shown that the best results were obtained in acidic solution, (pH =5, X =96%). The charge of $NiFe_2O_4$, its surface is presumably positively charged in acidic solution and negatively charged in alkaline solution. For the above reasons, dyes that have a sulfuric group in its structure, which is negatively charged, the acidic solution favors adsorption of dye onto the photocatalyst surface, thus the photodegradation efficiency increases. There is also the photocatalytic degradation of AY23 in acidic solutions, which is probably due to the formation of $^\bullet$OH as it can be inferred from the reactions (15)–(18) (Saien et al., 2009).

$$e_{CB}^- + O_{2(ads)} \rightarrow {}^\bullet O_{2(ads)}^- \tag{15}$$

$${}^\bullet O_{2(ads)}^- + H^+ \rightarrow HO_2^\bullet \tag{16}$$

$$2HO_2^\bullet \rightarrow O_2 + H_2O_2 \tag{17}$$

$$H_2O_2 + {}^\bullet O_{2(ads)}^- \rightarrow {}^\bullet OH + OH^- + O_2 \tag{18}$$
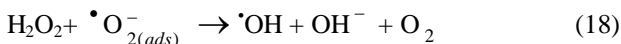
3.7. The Effect of Temperature

Effect of temperature on the degradation process was tested in the range of 15- 30 °C are shown in Figure 10. The positive influence of the temperature can be observed. Increasing temperature of 15-30°C indicated that the percent conversion of dye decreases with increasing temperature. It is necessary to cause the temperature of 30°C was not selected was that at temperatures higher may vaporization of the dye solution increases and caused change the concentration of pollutant. However, an increase in temperature helps the degradation reaction to compete more effectively with valance band hole (h_{VB}^+) and conduction band electron (e_{CB}^-) recombination. On the other hand, the increase in temperature decreases the solubility of oxygen in water which is not desirable for photocatalytic processes. Therefore, the temperature of 20 °C can be applied as a mild temperature with significant conversion of substrate.

3.8. Kinetics of Photocatalytic Degradation of AY23

Photocatalytic decomposition reaction kinetics of AY23 completely corresponds to the kinetic of pseudo-first-order model reaction (Saquib and Muneer 2003). In the kinetic equation of pseudo-first-order, the relationship between concentration(C) and time (t) is as follows:
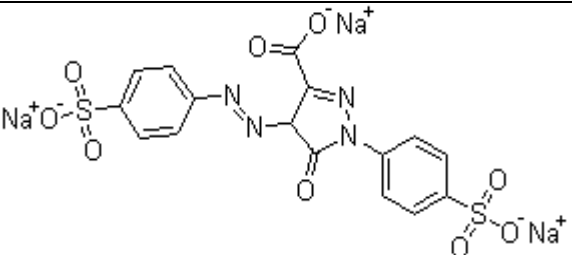
$$\frac{-dC}{dt} = k_{app}C \tag{19}$$

The integral equation is as follows:

$$\ln(\frac{C_0}{C}) = k_{app}t \qquad\qquad (20)$$

in which k_{app} is the apparent pseudo-first-order rate constant (that is affected by
dye concentration), and t, is the reaction time.

   A plot of ln (C_0/C) versus t, in optimal condition for photocatalytic degradation of AY23 is shown in
Figure 11. The linear plot suggests that the photodegradation reaction approximately follows the pseudo-
first-order kinetics with rate coefficient k= 0.0214 min^{-1}.

Table 1. Structure and characteristic of Acid Yellow 23 dye.

Dye	Structure	λ max (nm)	Molecular weight (g mol^{-1})
Acid Yellow 23 (AY23)		432	534.37
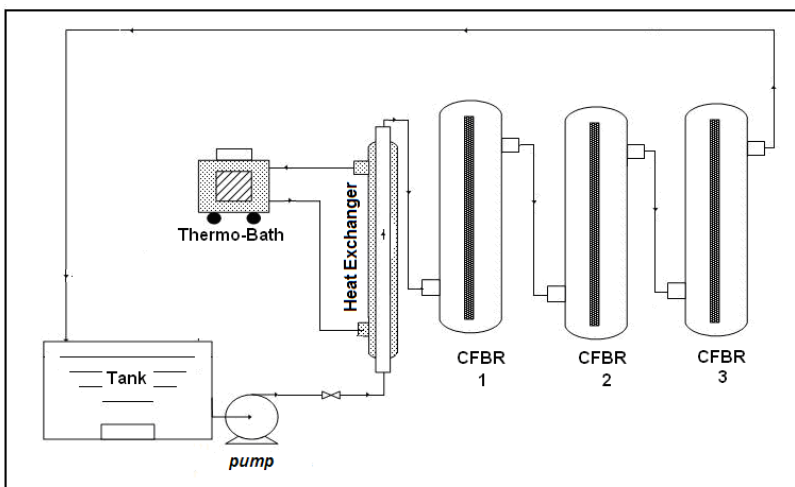
Figure 1. Schematic diagram of C.F.B.R.
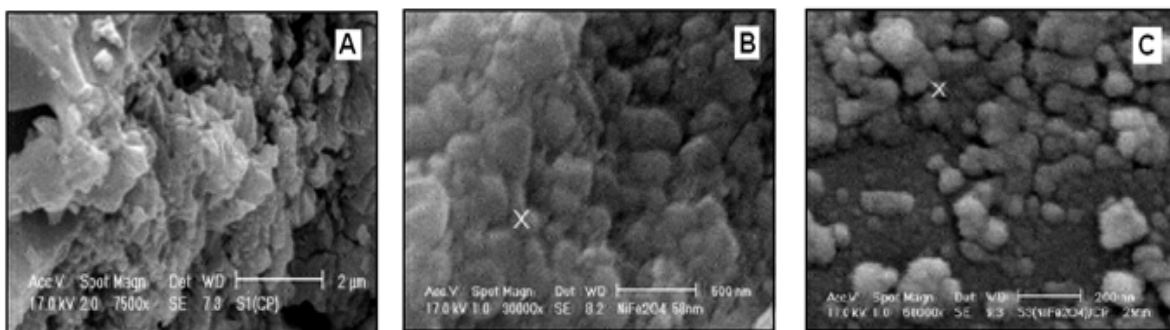
Figure 2. SEM images of (A) CP, (B) NiFe$_2$O$_4$ nano particles and (C) NiFe$_2$O$_4$/CP.
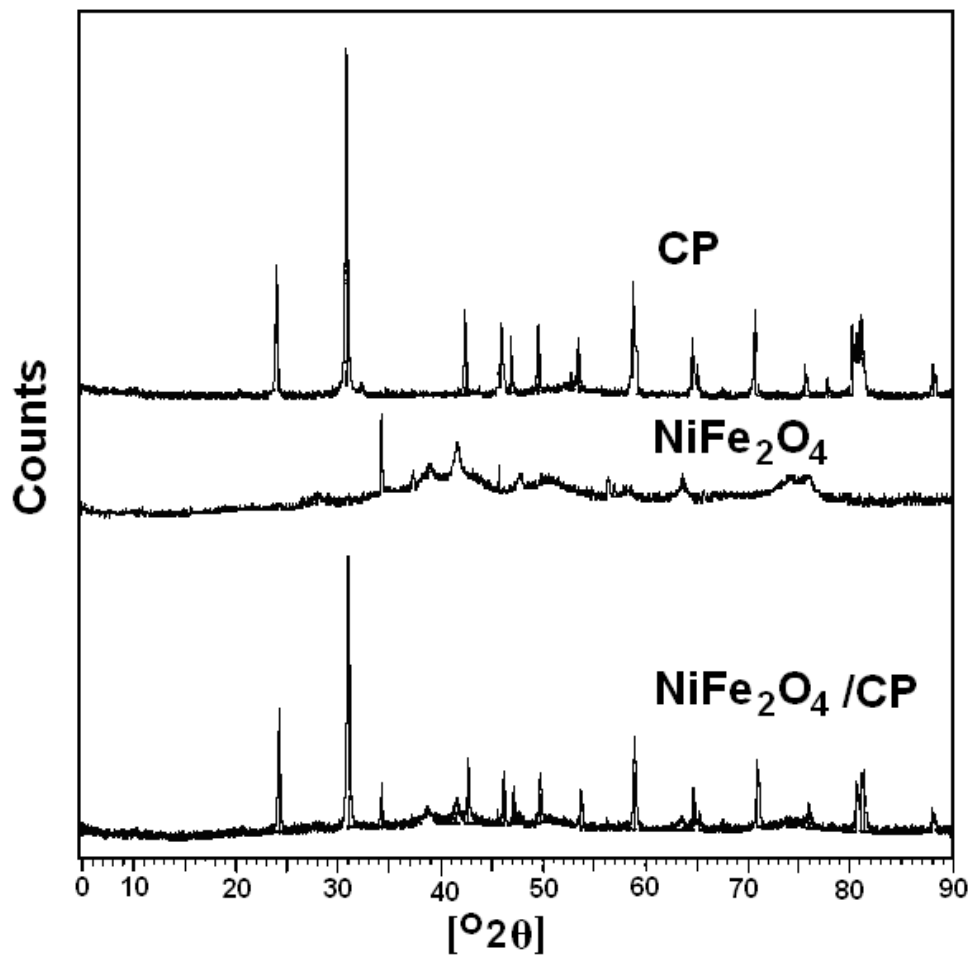
Figure 3. XRD pattern of raw CP after calcined in air at 400 ^{0}C for 4 h, pure NiFe$_2$O$_4$ and NiFe$_2$O$_4$/CP after calcined in air at 400 ^{0}C for 4 h.
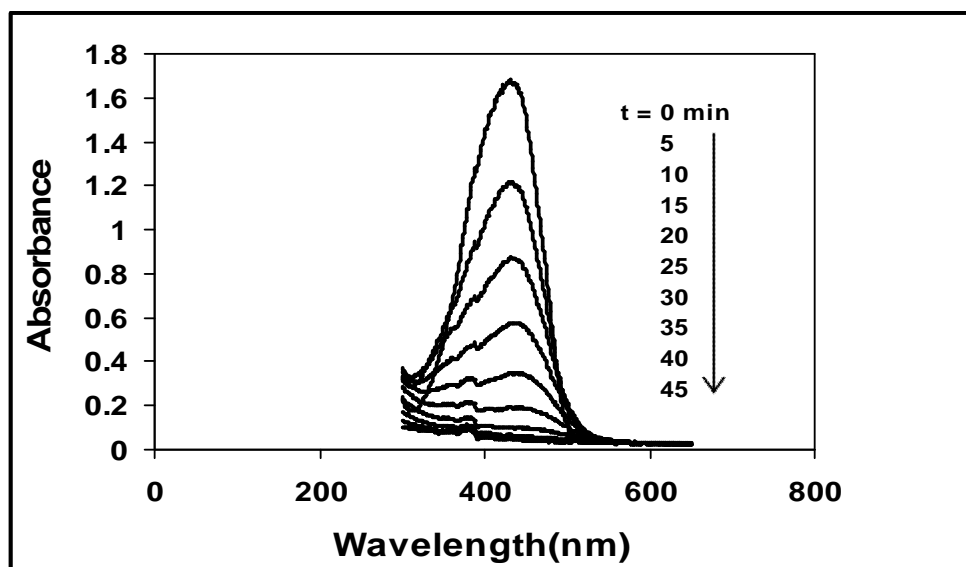

Figure 4. UV- vis spectra of AY23.(concentration of dye= 45 ppm, concentration of photocatalyst= 40 mg/l, H$_2$O$_2$ concentration= 30 ppm, pH= 5, T=20 ^{0}C, irradiation times= 0- 45 min).
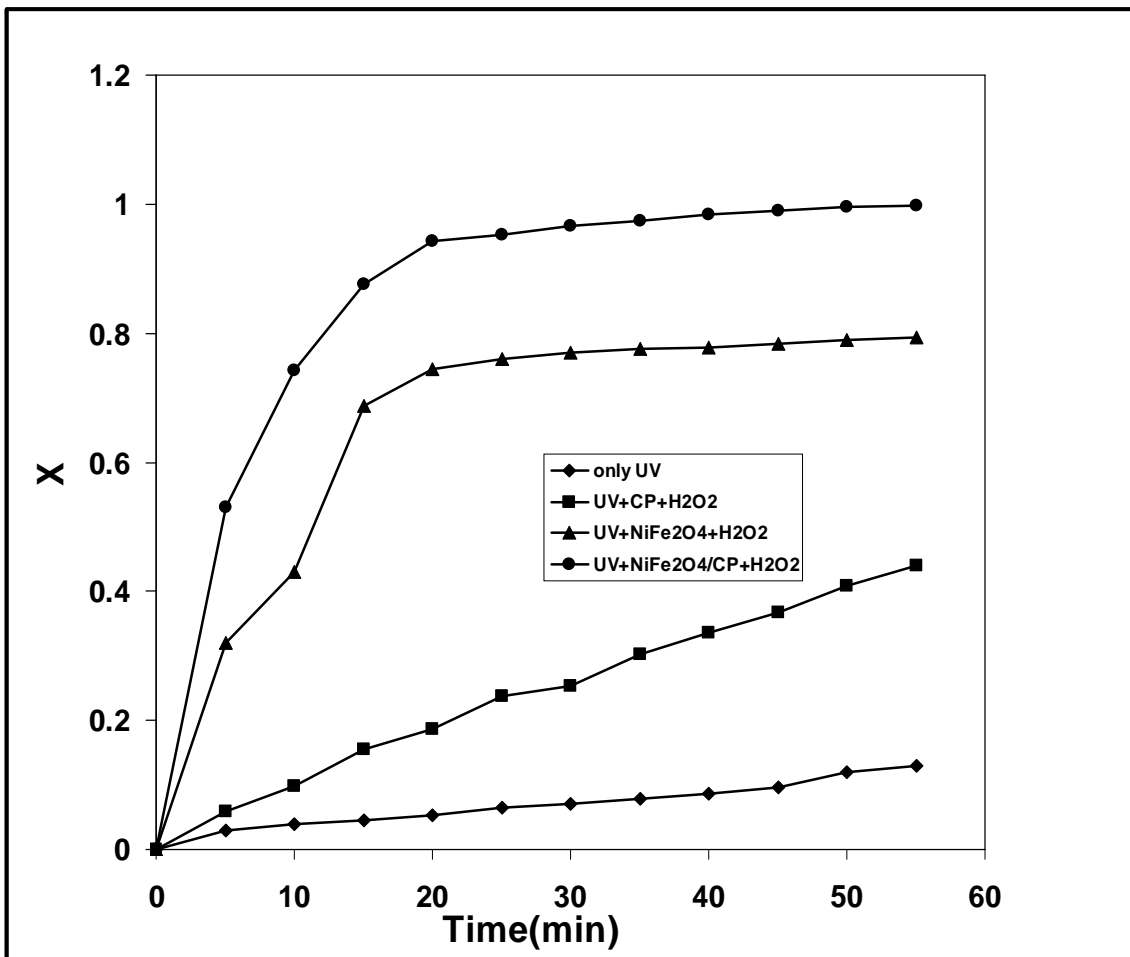
Figure 5. Effect of UV light and different photocatalysts on photocatalytic degradation of AY23.
(concentration of dye= 45 ppm, concentration of photocatalyst= 40 mg/l, H_2O_2 concentration= 30 ppm,
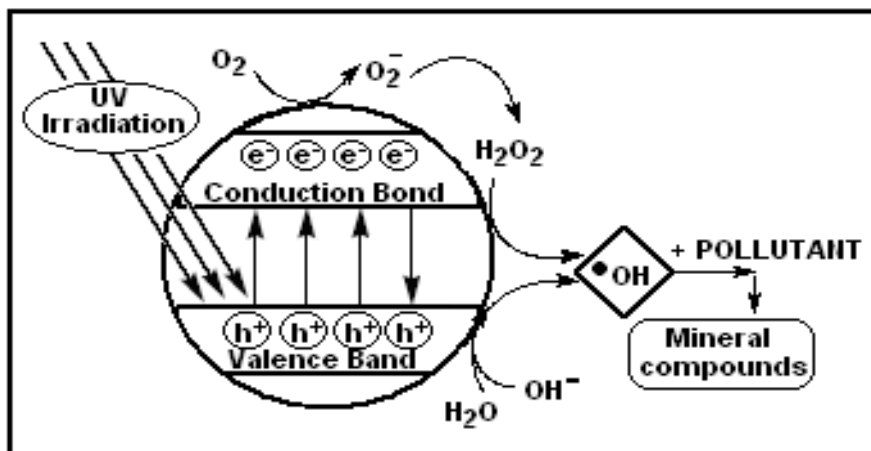pH= 5, T=20 ^{0}C).

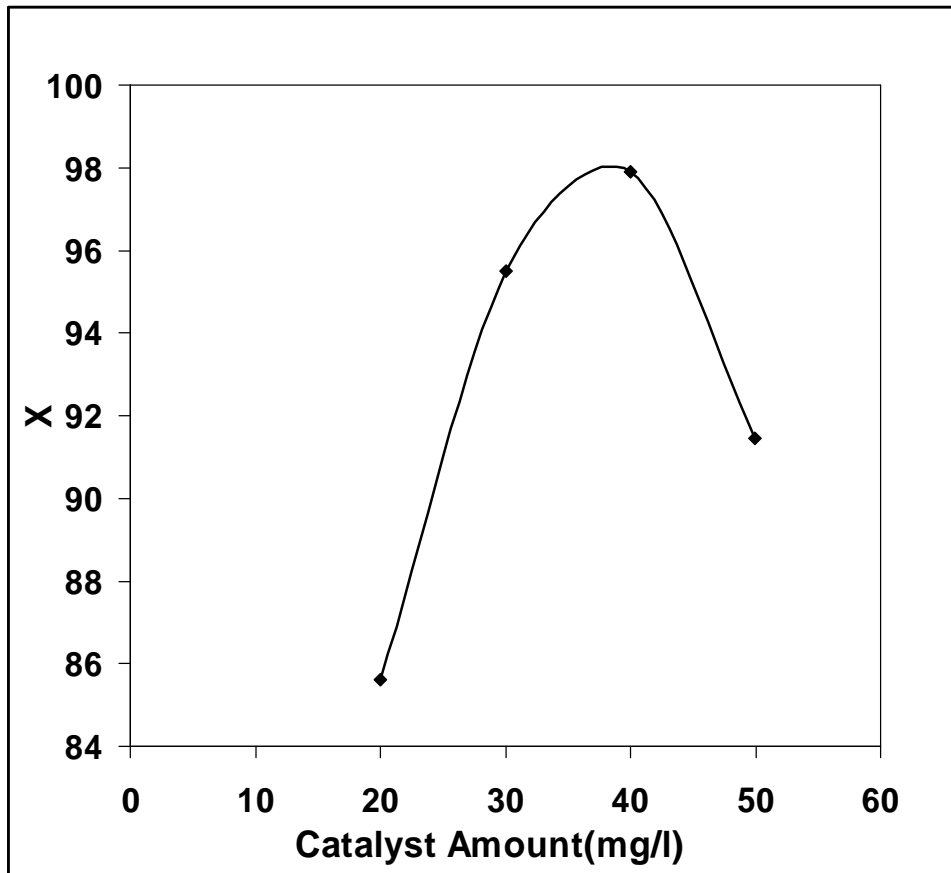Figure 6. General mechanism of the photocatalysis.

Figure 7. Effect of photocatalyst amount on photocatalytic degradation of AY23.(concentration of dye= 45 ppm, H_2O_2 concentration= 30 ppm, pH= 5, T=20 ^{0}C).
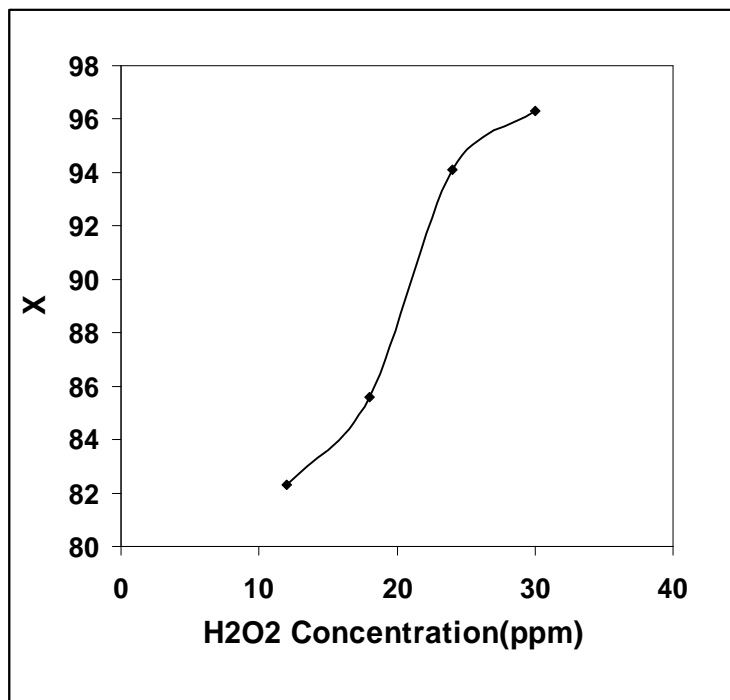

Figure 8. Effect of H_2O_2 concentration on photocatalytic degradation of AY23.(concentration of dye= 45 ppm, concentration of photocatalyst= 40 mg/l, pH= 5,T=20 ^{0}C).
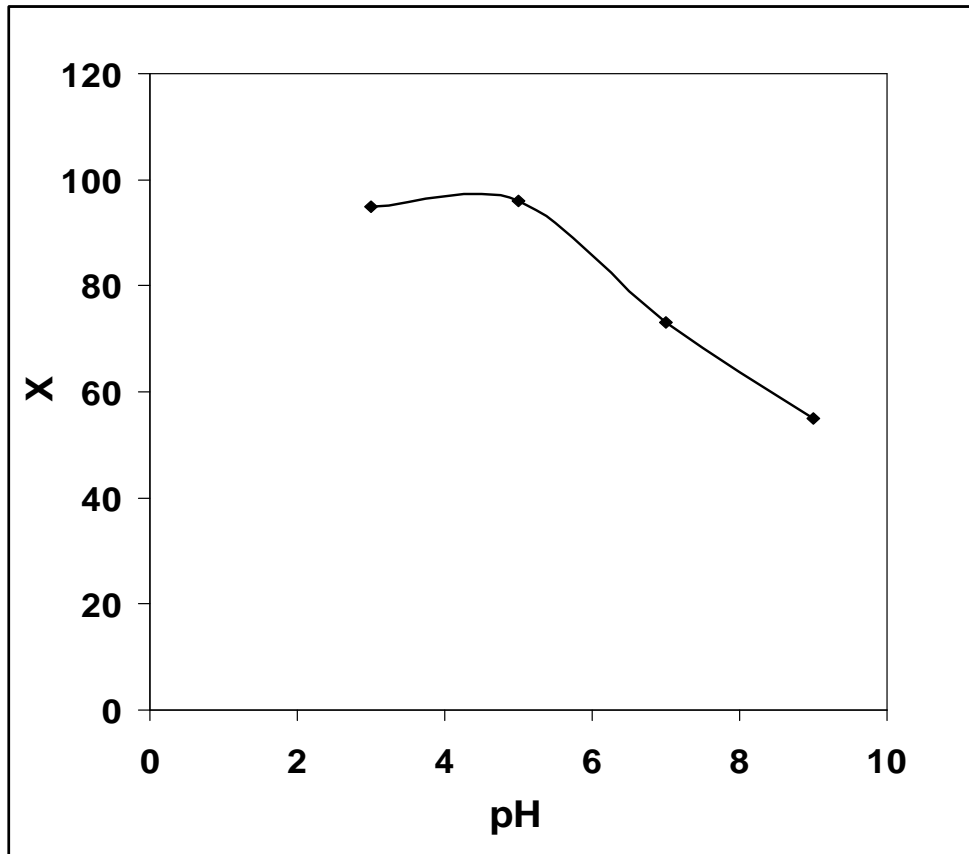
Figure 9. Effect of pH on photodegradation efficiency of AY23.(concentration of dye= 45 ppm, concentration of photocatalyst= 40 mg/l, H_2O_2 concentration= 30 ppm, , T=20 ^{0}C).
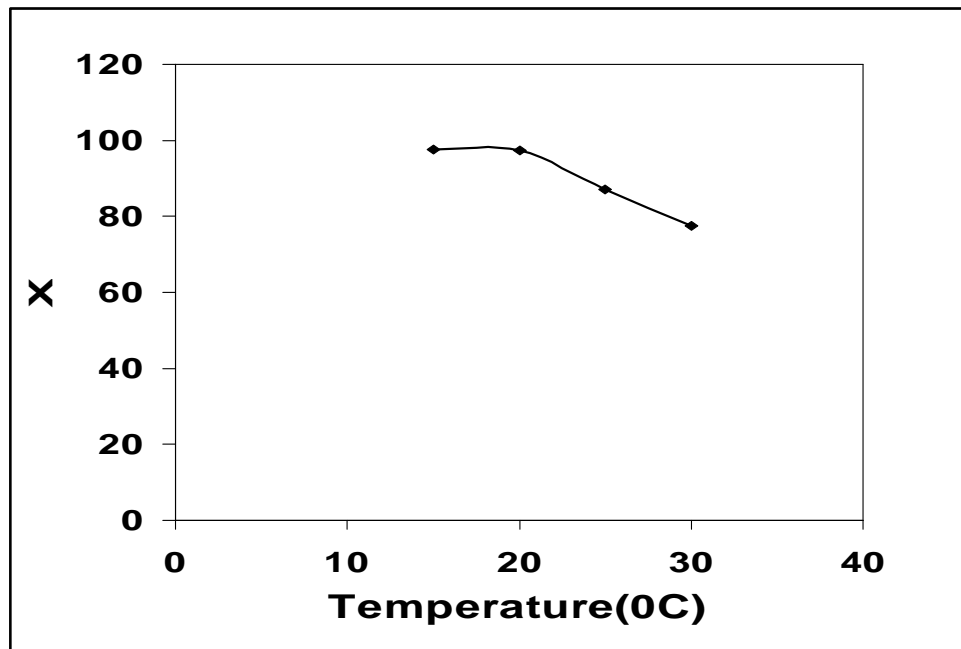

Figure 10. Effect of temperature on photocatalytic degradation of AY23.(concentration of dye= 45 ppm, concentration of photocatalyst= 40 mg/l, H_2O_2 concentration= 30 ppm, pH= 5).
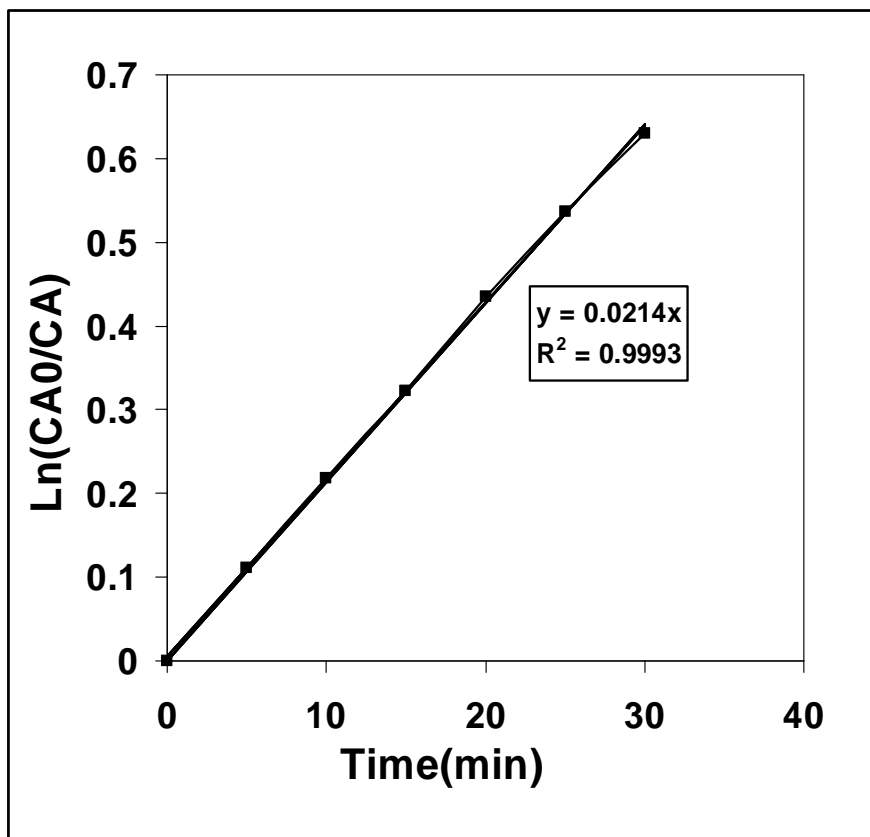
Figure 11. Kinetic plot of pseudo- first order photocatalytic degradation of AY23 in optimal condition.(concentration of dye= 45 ppm, concentration of photocatalyst= 40 mg/l, H_2O_2 concentration= 30 ppm, pH= 5, T=20 ^{0}C).

4. Conclusions

In this study, photocatalytic decolorization of the azo dye Acid Yellow 23, was investigated by the use of $NiFe_2O_4$/CP catalyst. Physical and chemical characterization of supported photocatalyst was determined by SEM, XRD and BET techniques. According to the literature, the results demonstrated that the produced $NiFe_2O_4$/CP have sufficient properties as a photocatalyst for degradation of dye. Various factors affecting the degradation process were analyzed and optimized. The optimal conditions (pH=5, photocatalyst amount = 40 (mg/l), H_2O_2 concentrations = 30 (ppm), temperature = 20 ^{0}C as analyzed and kinetics of photocatalytic decomposition reaction was determined. Pseudo-first-order model reaction corresponds to the experiment data of photocatalytic degradation of dye.

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