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Application of heterogeneous iron loaded zeolite A catalyst in photo-Fenton process for the removal of safranin in wastewater

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ABSTRACT

The current work evaluates the capability of iron loaded zeolite A (Fe-Z4A) for the first time as a heterogeneous catalyst in the (Fe-Z4A/H_2O_2/UV) photo Fenton process, Fenton process (Fe-Z4A/H_2O_2) and photo-catalytic process (Fe-Z4A/UV) for the treatment of textile dye safranin. The photo Fenton process (Fe-Z4A/H_2O_2/UV) was found to be the most efficient among the studied processes with the highest decolorization. The influence of experimental parameters such as pH, Fe-Z4A dose, H_2O_2 concentration, safranin concentration and tert-butyl alcohol (TBA) on the decolorization efficiency was studied. The catalytic performance of Z4A for the dye degradation was highly improved in the photo Fenton process (Fe-Z4A/H_2O_2/UV) that showed a remarkable synergetic effect with the second order kinetics. The synergic process achieved 88.34% decolorization at 0.1 g Fe-Z4A dose, 8 mM/L H_2O_2 concentration, 20 ppm safranin concentration after 120 min near wastewater pH 6. In conclusion, the photo Fenton process (Fe-Z4A/H_2O_2/UV) can be applied as an efficient and promising technique to treat the textile wastewater in real applications.

Keywords: Fenton process; Zeolite A; Photo-Fenton process; Safranin

1. Introduction

Dyes are the organic recalcitrant compounds found in the wastewater discharged from various industries like textile, chemical, pharmaceutical, pulp and paper, leather and cosmetics [1–6]. The textile industries are continuously releasing huge amount of heavily loaded wastewater into water resources annually which is composed of large amounts of dyes, suspended solids, salts, high COD, hydrocarbons, heavy metals and fluctuating pH [7]. Literature reveals that most of the dyes have been identified as toxic and carcinogenic, so the presence of these dyes in wastewater is hazardous for humans and aquatic environment as these are highly visible pollutant that blocks the sunlight penetration into the water and hinder bacterial growth and photosynthesis in aquatic plants and algae [4,8–12]. Treatment of dye containing wastewater is difficult task due to the recalcitrant organic structure of dyes that not only resist aerobic digestion but also stable to oxidizing agents, heat, and light [13]. The conventional processes (chemical, physical and biological) for removal of dyes from wastewater

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are less efficient due to complex structure, high operational cost, high energy requirement and large sludge produced [3,4,14–17]. Thus, it has forced researchers to innovate cost-effective and efficient methods for treatment of dyes from industrial wastewater.

Advanced oxidation processes are effective processes for the treatment of recalcitrant compounds from industrial wastewater [8,18–20]. The purpose of any advanced oxidation processes (AOPs) is to produce hydroxyl radicals (°OH) in solution as strong oxidant (E^0 = 2.80 V) to destroy contaminants that are difficult to oxidize by conventional oxidants [15,16,21–23]. Hydroxyl radicals destroy pollutants via hydroxylation or by dehydrogenation [8].The various AOPs (ozonation, catalytic ozonation, Fenton like processes, Photo Fenton like processes etc.) have been implied for the treatment of dyes in wastewater [15,19,24]. Although the Fenton and Fenton-like process are economical and do not produced toxic by-products as compared to some other AOPs, however most of the Fenton-like processes reported in literature have been found to be effective at acidic pH values [15,19,24]. Among these AOPs, Photo Fenton process proved highly effective even near wastewater pH, for dyes and organic pollutants removal [25–29]. The mechanism involved in the photo Fenton process is governed by the reactions [15,18,22,26,28,30,31].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot} \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\cdot} + H^+ \tag{2}$$

$$Fe^{3+} + H_2O \rightarrow Fe^{2+} + OH^{\cdot} + H^+ \tag{3}$$

$$H_2O_2 \rightarrow 2OH^{\cdot} \tag{4}$$

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HOO^{\cdot} \tag{5}$$

$$OH^{\cdot} + Dye \rightarrow Intermediates \rightarrow CO_2 + H_2O \tag{6}$$

The heterogeneous Fenton system was evolved to overcome the drawbacks of conventional Fenton system such as high efficiency in only acidic pH (2–3), iron sludge formation and decrease in efficiency due to quenching when excess of H_2O_2 and Fe^{2+} was used [15,21,22,24,30,32–34]. The various advantages of heterogeneous Fenton system as compared to conventional Fenton system include high catalyst stability, broader working pH range and catalyst reusability [15,22,24]. The heterogeneous Fenton processes have been effectively applied for the removal of textile dyes in the aqueous solution using numerous catalysts such as magnetite [35], Fe_2O_3 [36] mesoporous Fe_2O_3–SiO_2 [37] and zeolites [38]. Among these catalysts zeolites containing Fe^{+2} showed good results for the catalytic oxidation of organic contaminants and also minimal iron leaching [38]. The UV assisted Fenton process may be highly efficient as the energy supplied by a UV source not only causes the splitting of hydrogen peroxide into oxidant °OH radicals that increases reactivity but also inhibits the conversion of ferric ions to ferrous thereby increasing the pollutant degradation efficiency and kinetics [24,30,39]. Zeolites are characterized as porous three dimensional framework materials of aluminosilicates with unique properties like large specific surface area, uniform structure and pore size, electric charges and act as electron donors and acceptors for target species [1,2]. These can retain positive ions in their pores like Na^+, Ca^{2+}, K^+, Mg^{2+} and has been vastly applied for the treatment of dyes [3,40]. The various features of the photo Fenton process have been described by the researchers [41,42] such as fast pollutant degradation by °OH radicals produced by decomposition under UV irradiation, fast UV assisted generation of Fe^{2+} and lesser Fe sludge formation [41–44].

The current study deals for the removal of textile dye safranin using iron loaded zeolite 4A (Fe-Z4A) as a heterogeneous catalyst in the (Fe-Z4A/UV) process, Fenton process (Fe-Z4A/H_2O_2) and photo Fenton process (Fe-Z4A/H_2O_2/UV). This work is the continuation of author's previous study to investigate the potential of zeolite 4A as heterogeneous catalyst in various advanced oxidation processes. Our previous study concern with the application of zeolite 4 A in catalytic ozonation process for the removal of pollutants in wastewater [45]. To the author's knowledge this is the first report to study the application of zeolite 4A as catalyst in (Fe-Z4A/UV) process. This process may help to operate effectively near wastewater pH, which was lacking in many previously reported Fenton-like catalysts. Therefore, current investigation may help to develop novel and practically applicable processes for the removal of dyes in wastewater. In the current investigation Safranin was selected as target pollutant, it's a cationic dye which may be difficult to biodegrade due to structural stability. Moreover, the influence of experimental parameters such as pH, Z4A dose, H_2O_2 concentration, safranin concentration and effect of hydroxyl radical scavenger, t-butanol(TBA) on the decolorization efficiency of safranin was studied. The kinetics of dye degradation was studied by applying first order and second order kinetic models. The study may further help to improve the removal efficiency of UV/H_2O_2/Fe process and may help to increase the operational pH range of such processes.

2. Materials and methods

2.1. Chemicals and reagents

Analytical grade Ferrous Sulfate ($FeSO_4 \cdot 7H_2O$) was procured from Sigma Aldrich. Safranin was obtained from May & Baker U.K. and H_2O_2 solution (35%) was procured from Merck, Germany, used as the source of hydroxyl radicals. All the chemicals were used as received. A stock solution of safranin (1000 mg/L) was prepared by mixing powered safranin in ultrapure deionized water. Safranin solutions of various concentrations were prepared by the stock solution dilution using the ultrapure deionized water. The pH of prepared solutions was set by using aliquots of 1 N HCl and 1 N NaOH solutions.

2.2. Catalyst preparation and characterization

Zeolite (Z4A) as provided by Sigma Aldrich was washed by ultrapure deionized water and then dried overnight in Oven at 105°C. After performing this step Z4A was immersed in 0.1 Nitric acid overnight. It was again washed after filtration and dried in Oven at 105°C. In order to impregnate Fe^{+2} on Z4A, incipient impregnation method was used [46,47]. In this method, 6.0 g of $FeSO_4{\cdot}7H_2O$ (Merck) was dissolved in 20 ml of ultrapure deionized water and then 10 gm of Z4A was added in this solution. The solution was heated and stirred 100°C and 120 rpm respectively. In final step,drying of Fe impregnated catalyst was done in oven at 100°C overnight.

The catalyst surface area and pore size (Z4A and Fe-Z4A) was determined by nitrogen isotherms at 77 K using the BET method (Micrometrics ASAP 2020). The active functional groups at the surface of catalyst were studied by FTIR (Perkin Elmer Spectrum 400 Analyzer). The surface morphology and the elemental composition study of base material (Z4A) and catalyst(Fe-Z4A) was done by the scanning electron microscope associated energy dispersive X-ray spectrometer (JSM 6010LA). The mass transfer method [48] was used to evaluate the point of zero charge of both base material and catalyst.

2.3. Analytical procedures

Safranin color measurements were recorded in 300–700 nm wavelength range using UV-Vis spectrophotometer (PerkinElmer Lambda 35). The wavelength of maximum absorbance (λ_{max}) was found to be 520 nm. The calibration curves were prepared at λ_{max} before experimentation. The treated samples were analysed at λ_{max} for the residual dye concentrations. The method has been validated by both inter-day and intra-day validations. Each experiment was performed three times to ensure accuracy and the RSD value was found to be less than 5%.

The dye removal efficiency was calculated by using following formula:

$$Decolorization\ efficiency[\%] = \frac{C_o - C}{C_o} \times 100$$

where C_o = concentration at time 0; C = concentration at time t.

The chemical oxygen demand was determined by open reflux titrimetric method and was calculated by the following equation.

$$COD\ removal\ efficiency[\%] = \frac{COD_o - COD_t}{COD_o} \times 100$$

where COD_o = chemical oxygen demand at time 0; COD_t = chemical oxygen demand at time t.

2.4. Experimental procedure

The batch photodegradation experiments were conducted using the 250 mL Erlenmeyer flask in enclosed wooden chamber. A stock solution of 100 ppm dye concentration was prepared in the ultrapure deionized water and working solution were made by dilutions. The pH adjustments were done using 1 N HCl or 1 N NaOH. 35% H_2O_2 solution was used to prepare H_2O_2 solutions of different molar concentration from 2 mM to 16 mM. Ultraviolet light was supplied by UV lamp (20 W, Wavelength 368 nm, Sylvania, Germany). For each run, 100 ml of dye solution was taken in the flask and desired catalyst dose and H_2O_2 were added. The samples were obtained after fixed intervals of time and were analysed on PerkinElmer Lambda 35 double beam UV-VIS spectrophotometer.

3. Results and discussion

3.1. Catalyst (Fe-Z4A) characteristics

The properties of the catalyst Z4A and Fe-Z4A employed in the current study are shown in Table 1. Z4A is sodium zeolite with composition $2Na_2O\text{-}Al_2O_3\text{-}1{\cdot}75SiO_2\text{-}6H_2O$. The determined surface area of Z4A was 91.35 m^2/g while that of Fe-Z4A was 86.71 m^2/g and average pore size was about 4°A. A slight reduction in the Fe-Z4A surface area as compared to the Z4A may be due to the capping of pores by the loaded Fe ions [49]. FTIR results of Z4A catalyst before and after Fe loading, are shown in Fig. 1. The sharp peaks observed at 971.44 cm^{-1} and 974.69 cm^{-1} are the characteristics of Al-OH and Si-O stretching vibrations [50,51]. The

Table 1
Z4A [45] and Fe-Z4A properties

Material	Surface area	Pore size	Point of zero charge (pH_{pzc})
Z4A	91.35 m^2/g	4 °A	6.4 + 0.3
Fe-Z4A	86.71 m^2/g	4 °A	5.9 + 0.3

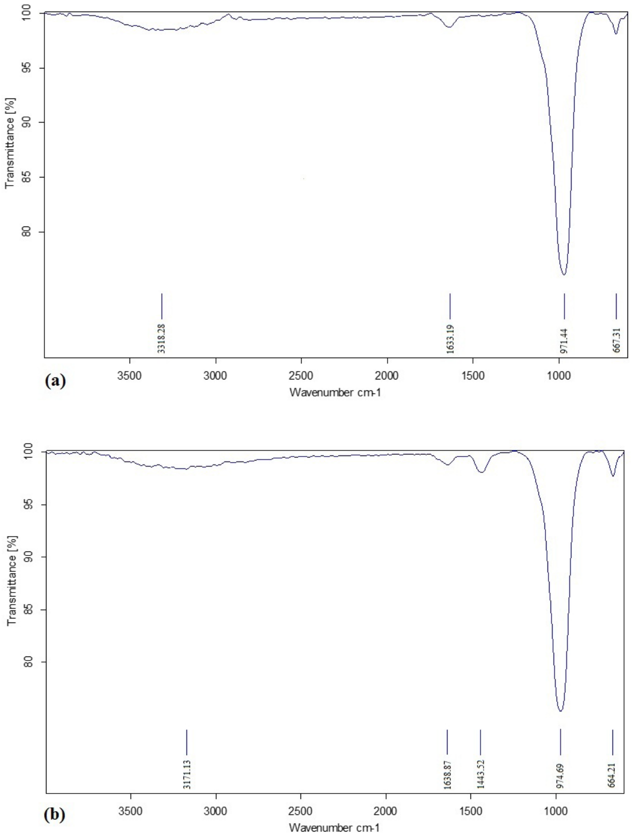


Fig. 1. FTIR of (a) Z4A(b) Fe-Z4A.

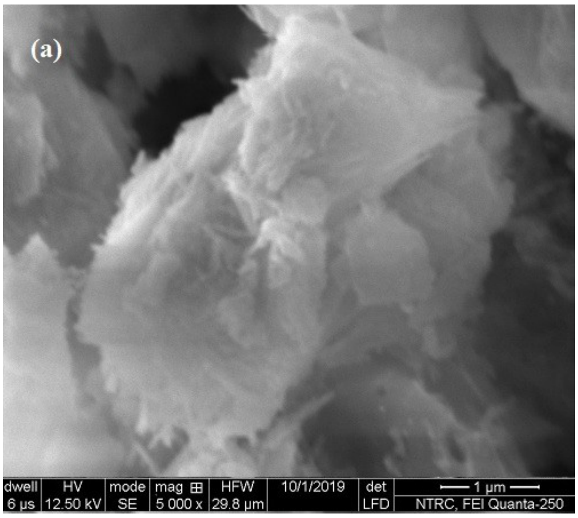
peaks at 667.31 cm^{-1}, 1633.19 cm^{-1}, and 3318.28 cm^{-1} correspond to the Si-O-Si and O-H stretching vibrations [50,51]. A drift in the peaks and a new peak was observed at 1443.52 cm^{-1} which correspond to Fe-OH stretch [50,51]. The SEM images of Fe-Z4A catalyst before and after treatment are shown in Fig. 2 which represents a porous surface texture and no significant change in the texture was observed after the treatment. The EDX spectrum of catalyst before and after iron loading are shown in Fig. 3 and elemental composition is given in Table 2. The EDX analysis showed a 10.26% mass loading of the iron on Fe-Z4A surface. The point of zero charge of Z4A was 5.9 + 0.3 and increased to 6.4 + 0.3 in the case of Fe-Z4A due to the iron loading [49].

3.2. Comparison of processes

The safranin percentage removal with the reaction time as a function of three processes such as photo-catalytic process [Fe-Z4A/UV], Fenton process [Fe-Z4A/H_2O_2], Photo Fenton process (Fe-Z4A/H_2O_2/UV) to evaluate the synergistic effect of Z4A catalyst was performed (Fig. 4). The Photo Fenton process of Fe-Z4A/H_2O_2/UV at a fixed catalyst dose of 0.1 g and H_2O_2 concentration of 8 mM, showed the highest dye removal of 88.34% at pH 6 after 120 min. While the safranin percentage removal achieved in Fenton process (Fe-Z4A/H_2O_2) and photo-catalytic process (Fe-Z4A/UV) when no H_2O_2 was added, were only 47% and 8.73% respectively, which confirms that the catalytic performance of the Fe-Z4A catalyst may be greatly enhanced in H_2O_2 presence. The results revealed the suitability of Photo Fenton process (Fe-Z4A/H_2O_2/UV) for safranin removal as a significant enhancement in dye percentage removal was achieved that may be due to individual mechanisms of active sites provided by the catalyst, H_2O_2 decomposition by Fe^{2+} on solid catalyst surface to generate the ^{o}OH radicals and UV degradation of the dye [30,52].

$$H_2O_2 + h\nu \rightarrow 2OH^{\cdot} \tag{7}$$

The Fe-Z4A catalyst activates the H_2O_2 in the presence of UV to release more ^{o}OH radicals that enhances the treatment efficiency [25]. The further studies on the parameters



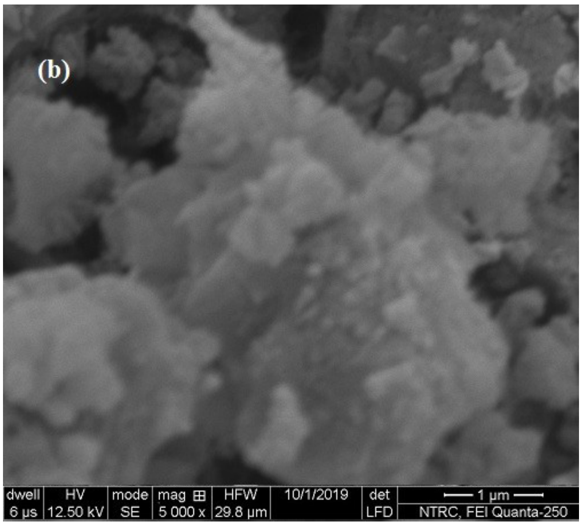


Fig. 2. SEM images of Fe-Z4A (a) before treatment (b) after treatment.

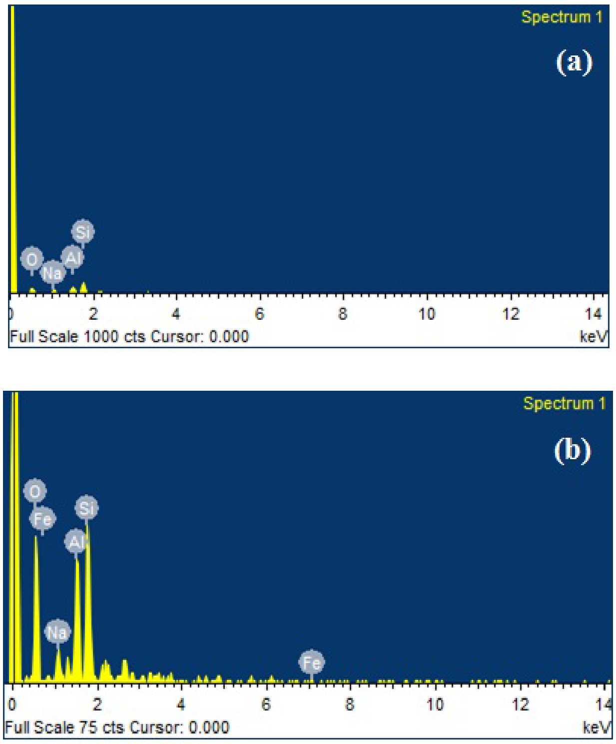


Fig. 3. EDX of (a) Z4A (b) Fe-Z4A.

Table 2
Elemental composition of Z4A and Fe-Z4A

Elemental composition (Weight %)	O	Na	Al	Si	Fe
Z4A	44.31	11.40	14.54	29.74	–
Fe-Z4A	49.17	5.91	14.21	21.42	10.26

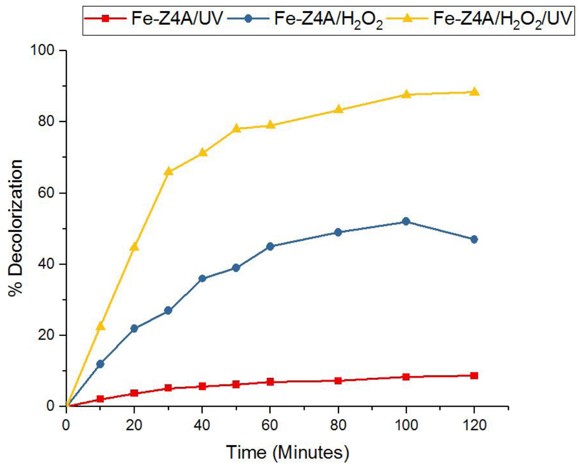


Fig. 4. Comparison of Safranin removal as a function of various studied processes (T = 30°C; pH = 6, H_2O_2 = 8 mM; V = 100 mL; $C_{o\,(\text{Safranin})}$ = 20 mg/L; Catalyst dose = 0.1 g).

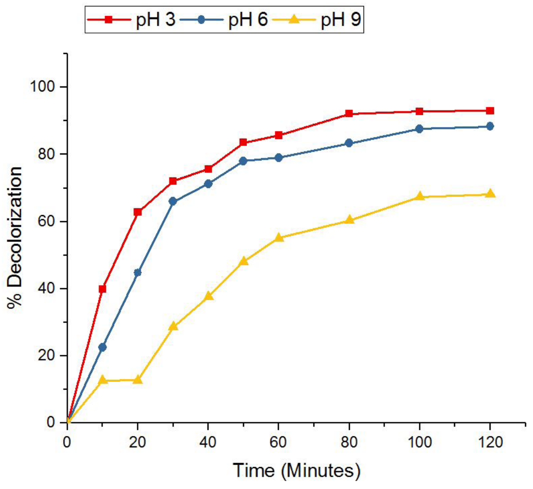


Fig. 6. Effect of initial pH on safranin removal in Fe-Z4A/H_2O_2/UV process ($C_{o\,(\text{safranin})}$ = 20 mg/L; V = 100 mL; T = 30°C; H_2O_2 = 8 mM; Catalyst dose = 0.1 g).

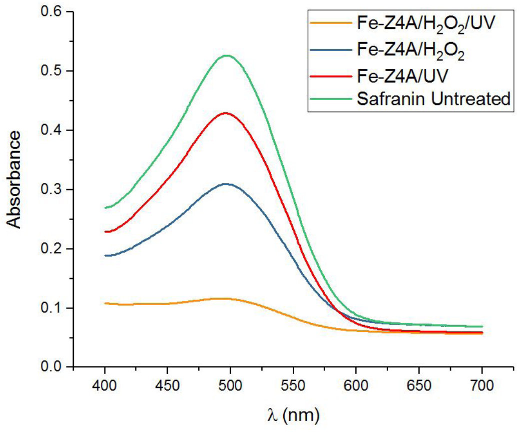


Fig. 5. Dye spectral changes as a function of oxidation processes (T = 30°C; pH = 6, H_2O_2 = 8 mM; V = 100 mL; $C_{o\,(\text{Safranin})}$ = 20 mg/L; Catalyst dose = 0.1 g, Time = 120 min).

was done using Photo Fenton process (Fe-Z4A/H_2O_2/UV). The dye spectral changes were studied as a function of various oxidation processes and the results are shown in Fig. 5. The largest spectral changes were observed in the Photo Fenton process (Fe-Z4A/H_2O_2/UV) which confirms the highest decolorization efficiency achieved in the said process.

3.3. Effect of pH

The catalytic activity of the heterogeneous catalyst Fe-Z4A was checked as a function of solution pH in terms of dye removal. The effect was studied at pH values of 3, 6 and 9 with 0.1 g catalyst dose (Fig. 6). The percentage removal of safranin decreased with a pH augmentation from acidic to alkaline conditions. Upto 92.99% safranin was removed at pH 3 after 120 min with 0.1 g catalyst dose and 8 mM H_2O_2 concentration. The percentage removal achieved at pH 6 and pH 9 was 88.34% and 68.13% respectively. The higher safranin removal at acidic pH may be ascribed on following basis, the oxidation potential of hydroxyl radicals decreases with arise in pH, at pH higher than 3, the sluggish formation of OH radicals takes place due to hydrolysis of Fe^{2+} and reduction in the oxidation rate decreases Fenton process efficiency [52,53]. At alkaline pH, H_2O_2 undergoes auto decomposition that decreases its concentration and hydroxyl radicals convert to less reactive conjugate base furthermore the iron leaching from the zeolite structure takes place that forms iron sludge thereby decreasing the catalytic activity [15,19,30,54]. However, it is important to mentioned here that high removal efficiency (88%) of studied dye was found to be near wastewater pH (pH = 6).

$$2H_2O_2 \rightarrow O_2 + 2H_2O \tag{8}$$

$$OH^{\cdot} + OH^{-} \rightarrow O^{\cdot -} + H_2O \tag{9}$$

The adsorption may have a positive or a negative effect in Fenton type processes. At the acidic pH, the adsorption of the safranin on Fe-Z4A surface may be minimal due to the electrostatic forces of repulsion, however the higher removal efficiency at acidic pH in the studied process may be explained as, in Fenton type processes, the interaction of H_2O_2 with the catalyst active sites (Fe) are important to produce ^{o}OH radicals [55]. It has been found that the increase in the pH, may result in the poisoning of active sites by hydroxide ions ($^{-}$OH) present inside the solution at higher pH values [55], therefore, the removal efficiency in such processes (Fenton-like, Photo-Fenton-like) may decreased with the increase in pH of water.

3.4. Effect of Z4A dose

The catalytic performance of Fe-Z4A in heterogeneous Fenton process for safranin removal was evaluated by increasing the dose from 0.05 g to 0.1 g and 0.2 g. A significant increase in safranin removal with the Fe-Z4A dosage was obtained (Fig. 7), that confirms the catalytic

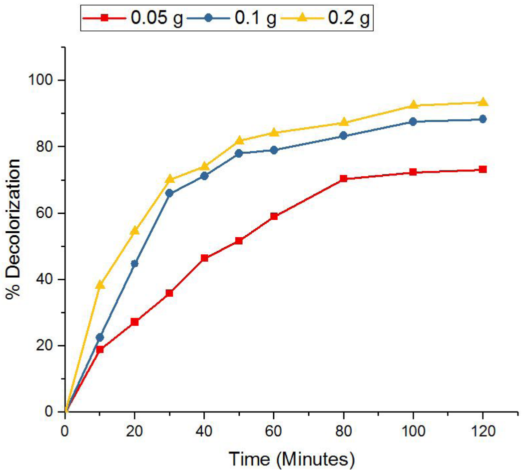


Fig. 7. Effect of Z4A dose on safranin removal in Fe-Z4A/H_2O_2/UV process ($C_{o\,(\text{safranin})}$ = 20 mg/L; T = 30°C; H_2O_2 = 8 mM; V = 100 mL; pH = 6).

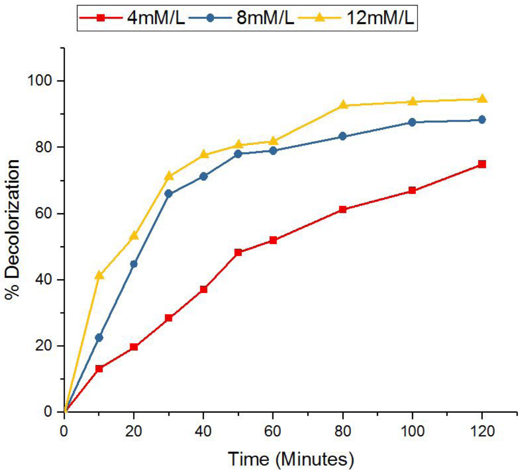


Fig. 8. Effect of H_2O_2 concentration on safranin removal in Fe-Z4A/H_2O_2/UV process ($C_{o\,(\text{safranin})}$ = 20 mg/L; pH = 6; T = 30°C; V = 100 mL; Catalyst dose = 0.1 g).

effect of Fe-Z4A in heterogeneous Fenton process. The percentage removal of safranin was enhanced from 35.9% to 70.2% after 30 min when the Fe-Z4A dose increased from 0.05 g to 0.2 g respectively. Highest percentage removal of 93.4% was observed at a 0.2 g Fe-Z4A dose after 120 min. The increase in percentage removal with the Fe-Z4A dose may be ascribed to increase in the catalytic performance by enhancement of the available active sites for the catalytic Fenton reaction [15,53]. The dye molecules are firstly trapped by adsorption in cage type structure of the pores in zeolite where the local concentration of dye increases, the photocatalytic effect of Fe-Z4A then degrades the adsorbed dye thereby further reaction sites become available that enhances the overall degradation performance [29].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \tag{10}$$

However, a very high dose of catalyst causes a decrease in the dye removal due to the fact that at a certain H_2O_2 concentration, higher catalyst dose leads to the scavenging of $OH^{\cdot}$ radicals [15]. Therefore, in current investigation catalyst dose was selected from 0.05–0.2 g.

$$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^{-} \tag{11}$$

3.5. Effect of H_2O_2 concentration

The safranin removal was studied by altering the initial concentration of H_2O_2 to 4 mM, 8 mM and 12 mM. The experimental results revealed that the initial H_2O_2 concentration had a significant role in the safranin removal as shown in Fig. 8. The safranin percentage removal was increased from 28.5% to 71.3% after 30 min when H_2O_2 concentration increased from 4 mM to 12 mM with a maximum removal of 94.6% (Fig. 8). The increase in safranin percentage removal with H_2O_2 concentration may be due to the high generation of fast attacking $^{\circ}OH$ radicals that accelerate the dye degradation [18,54,56].

$$Safranin\ Dye + OH^{\cdot} \xrightarrow{uv} Intermediates \xrightarrow{uv} CO_2 + H_2O \tag{12}$$

However, some reports suggested that high concentration of H_2O_2 lowers the dye degradation efficiency due to the generation of low reactivity hydroperoxyl radicals [25].

$$H_2O_2 + OH^{\cdot} \rightarrow O_2H^{\cdot} + H_2O \tag{13}$$

Similar trends were reported by some other findings [53,54,56]. Therefore, based on the experimental results, 8 mM was selected as optimum initial H_2O_2 concentration.

3.6. Effect of safranin concentration

The safranin removal as a function of initial dye concentration in UV enhanced heterogeneous Fenton process was studied. The dye removal was enhanced with the rise in the initial safranin concentration (Fig. 9). The percentage decolorization of 71.92%, 88.34% and 93.62% was obtained at initial dye concentration of 10 ppm, 20 ppm and 40 ppm. The results may be explained as at too low dye concentrations, the excess H_2O_2 causes the scavenging of hydroxyl radicals generating less reactive $O^2H^{\cdot}$ radicals and H_2O [52].

3.7. Effect of TBA

The TBA was added to the heterogeneous Fenton system as a hydroxyl radical scavenger to study the catalytic activity. A significant decrease in the safranin removal percentage was observed after the addition of TBA. The results (Fig. 10) reveals that the safranin percentage decolorization was decreased from 88.34% to 38.81% when only 10 ppm TBA was added to the solution. The decolorization were 33.94% and 29.92% at TBA concentration of 50 ppm and 100 ppm. The decrease in percentage decolorization with the TBA concentration verifies role of $^{\circ}OH$ radicals in safranin degradation [15,56]. The photo Fenton processes operate with the continuous generation of the $^{\circ}OH$ radicals as shown in the reactions [Eqs. (1)–(7)]. The degradation of the dyes may take

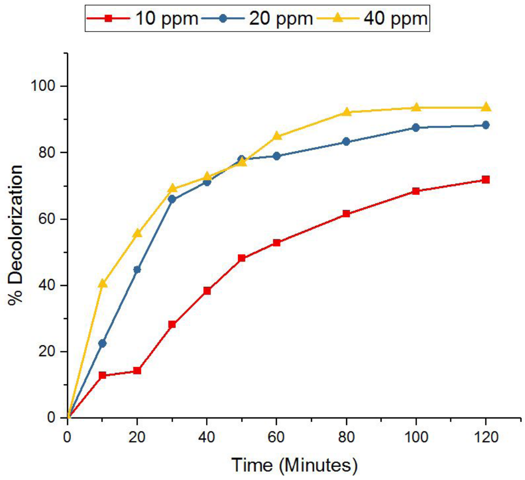


Fig. 9. Effect of dye concentration on removal in Fe-Z4A/H_2O_2/UV process (Catalyst dose = 0.1 g; V = 100 mL; H_2O_2 = 8 mM; T = 30°C; pH = 6; $C_{o\,(safranin)}$ = 20 mg/L).

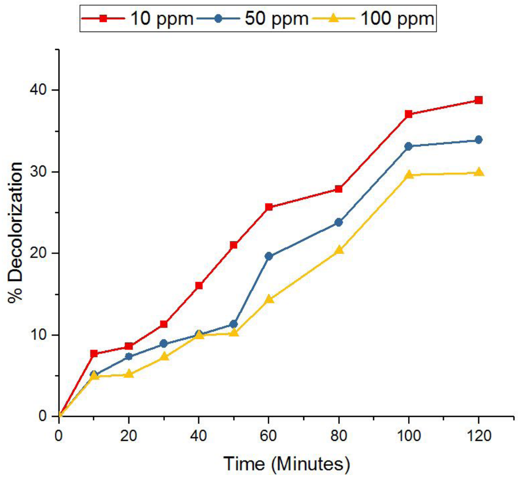


Fig. 10. Effect of TBA concentration on safranin removal in Fe-Z4A/H_2O_2/UV process ($C_{o\,(safranin)}$ = 20 mg/L; pH = 6; Catalyst dose = 0.1 g; H_2O_2 = 8 mM, T = 30°C; V = 100 mL).

place at both inside the solution and on the surface of the Fe-Z4A catalyst. However, the surface reactions may depend upon the adsorption of the dyes and pH of the solution [55]. At acidic pH, since the studied dye and the catalyst may be positively charged, the surface reactions between safranin and ^{o}OH radicals may be negligible, therefore, the at acidic pH the dominant mechanism involve the removal of safranin due to the reactions of both safranin and hydroxyl radicals inside the solution. However, with the increase in pH, both the surface reactions and the reactions inside the solution may lead to the degradation of studied pollutant [55].

3.8. Dye degradation

To investigate the degradation efficiency of safranin, COD removal was studied in the oxidation processes. The results shown in Fig. 11, revealed that the dye degradation efficiency was lower as compared to decolorization efficiency. The COD removal efficiencies of 3.1%, 33.5% and 58.1% were achieved in the photo-catalytic process (Fe-Z4A/UV), Fenton process (Fe-Z4A/H_2O_2) and photo Fenton Process (Fe-Z4A/H_2O_2/UV) respectively after 120 min. The photo Fenton Process (Fe-Z4A/H_2O_2/UV) was the most effective for safranin degradation.

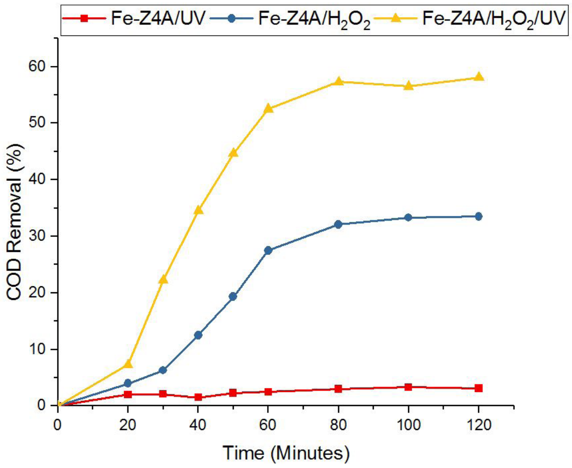


Fig. 11. COD removal efficiency as a function of oxidation processes (T = 30°C; pH = 6, H_2O_2 = 8 mM; V = 100 mL; $C_{o\,(Safranin)}$ = 20 mg/L; Catalyst dose = 0.1 g).

3.9. Catalyst reuse performance

The Fe-Z4A catalyst reuse performance for the safranin decolorization was studied and the results are shown in Fig. 12. A decrease in the catalyst performance for the safranin decolorization was observed after consecutive runs. The safranin percentage decolorization of 88% was achieved at first run and reduced to 54% and 38% at cyclic run 2 and 3 respectively. The iron leach out was determined in the catalyst reuse performance analysis and obtained results are shown in Fig. 13. The Fe leach out enhanced with the number of cycles with 0.025 mg/L in first cycle and 0.087 mg/L in third cycle. The reduction in the catalyst reuse performance after consecutive runs may be due to the iron leach out effect from the surface of catalyst [55] and the blockage of catalyst active sites by the by products formed during the pollutant degradation [55].

3.10. Kinetic studies

The first order and second order kinetic models were applied to dye degradation by Fe-Z4A assisted by UV and H_2O_2 (Fe-Z4A/H_2O_2/UV) [39].

The plots of kinetic models were presented in Figs. 14a, b. The selected kinetic model's parameters are given in Table 3. The results revealed that the kinetics of safranin degradation followed the second order kinetics, as the data was found fit to the second order model with high R^2 values as compared to the first order kinetics. The best fit was achieved with UV assisted Fenton process (Fe-Z4A/H_2O_2/UV) with R^2 value of 0.986 and K_2 of 3.4×10^{-3} ($g\cdot mg^{-1}\cdot min^{-1}$). While R^2 values and K_2 values in Fenton process [Fe-Z4A/

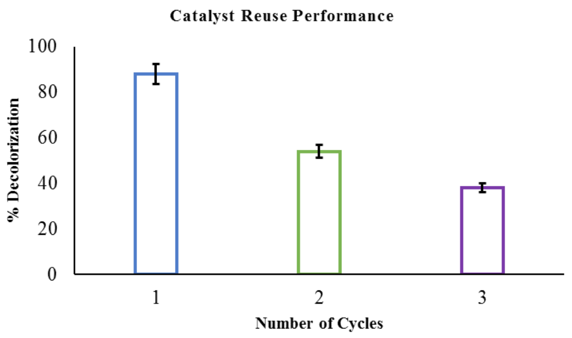


Fig. 12. Fe-Z4A catalyst reuse performance ($C_{o\ (SAF)}$ = 20 mg/L; T = 30°C; pH = 6, H_2O_2 = 8 mM; Catalyst Dose = 0.1 g; V = 100 mL).

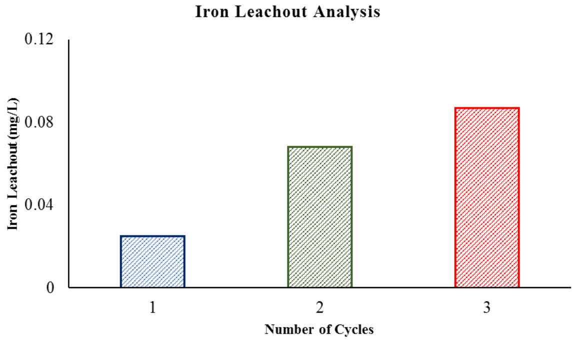


Fig. 13. Iron leach out analysis ($C_{o\ (SAF)}$ = 20 mg/L; T = 30°C; pH = 6, H_2O_2 = 8 mM; Catalyst Dose = 0.1 g; V = 100 mL).

H_2O_2] and [Fe-Z4A/UV] process was 0.826, 0.903 and 0.2, 0.02 respectively (Table 3). However, the higher values of rate constants were obtained in first order model. The results showed that the safranin degradation was accelerated by parallel mechanisms. Similar results were reported in some previous findings [39].

3.11. Dye removal mechanism

The mechanism of dye removal on Fe-Z4A catalyst in (Fe-Z4A/H_2O_2/UV) photo Fenton process is governed by the various factors such as pH of the solution, charge of the dye, charge on the catalyst surface, availability of H_2O_2 and intensity of UV irradiation [6,41]. It is hypothesized that the H_2O_2 present in the solution may interact with the active sites (Fe) of the catalyst resulting in the production of °OH radicals which attack the pollutant leading to the degradation of the safranin dye [6,41], as shown in the reactions [Eqs. (1)–(6), (10)–(13)]. Moreover, the adsorbed H_2O_2 at the catalyst surface will interact with the UV irradiation to generates the °OH radicals [Eq. (7)] that may accelerate the pollutant degradation [6,41].

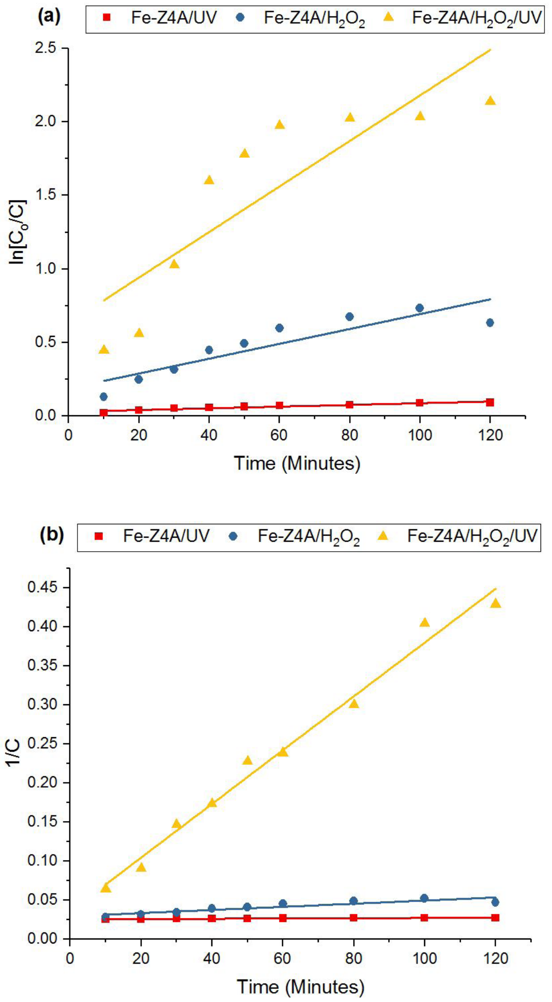


Fig. 14. Kinetic model plots of processes (a) first order (b) second order.

Table 3
Parameters of kinetic study

Process	First order model parameters		Second order model parameters	
	$K_1\times10^{-3}$ (min^{-1})	R^2	$K_2\times10^{-3}$ (g·mg^{-1}·min^{-1})	R^2
Fe-Z4A/UV	0.6	0.896	0.02	0.903
Fe-Z4A/H_2O_2	5	0.811	0.2	0.826
Fe-Z4A/H_2O_2/UV	16.4	0.895	3.4	0.986

4. Conclusions

1. The photo Fenton process (Fe-Z4A/H_2O_2/UV) was found to be the most efficient for the safranin degradation near wastewater (pH = 6) when compared to the Fenton process (Fe-Z4A/H_2O_2) and catalyst alone UV process (Fe-Z4A/UV).
2. The catalytic performance of Fe-Z4A was remarkable in the photo Fenton process (Fe-Z4A/H_2O_2/UV) in the presence of UV showing its suitability in dye degradation.
3. The pH highly influenced the safranin degradation and higher decolorization was achieved at acidic pH value.

4. The reduction in dye removal with the rise in TBA concentration reveal the important role of ^{o}OH radicals in safranin degradation in studied process.
5. The dye degradation kinetics followed second order kinetics.

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