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UV/H_2O_2/iron loaded rice husk ash based advanced oxidation process for the removal of safranin from wastewater

Amir Ikhlaq[a,*], Mohsin Kazmi[b], Farhan Javed[c], Hira Fatima[d,*], Asia Akram[e], Samina Asif[a]

[a]*Institute of Environmental Engineering and Research, University of Engineering and Technology, GT Road, 54890, Lahore, Punjab, Pakistan, emails: aamirikhlaq@uet.edu.pk (A. Ikhlaq), saminaasif_11@yahoo.com (S. Asif)*
[b]*Department of Chemical Engineering, University of Engineering and Technology Lahore, KSK Campus, Pakistan, email: engr.smalikazmi@gmail.com*
[c]*Department of Chemical Engineering, University of Engineering and Technology Lahore, FSD Campus, Pakistan, email: farhan.javed@uet.edu.pk*
[d]*Curtin University Perth Bentley Campus, Australia, email: hira.fatima@postgrad.curtin.edu.au*
[e]*Imperial College of Technology, Board Wala Chok, Lahore, Pakistan, email: aish_886@hotmail.com*

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ABSTRACT

This study aims to investigate the removal efficiency of UV/H_2O_2/iron loaded rice husk ash (Fe-RHA) based advanced oxidation process for the removal of safranin in wastewater. The effects of several reaction parameters such as initial H_2O_2 concentration, initial pH and catalyst dose were studied. Moreover, Fenton-like process (Fe-RHA/H_2O_2), adsorption (Fe-RHA alone), UV alone and synergic process (UV/H_2O_2/Fe-RHA) were compared. Finally, the reuse performance of catalyst and removal of chemical oxygen demand (COD) was studied. The results show that synergic process (UV/H_2O_2/Fe-RHA) was found to be more efficient as compared with other processes. Furthermore, the decolorization of safranin was found to be the highest near acidic pH (pH = 3). The synergic process was also found to be effective near wastewater pH, achieving decolorization efficiency up to 46% at initial pH = 6. The results further reveal that significant amount (61% in 120 min) of COD was removed using UV/H_2O_2/Fe-RHA process. It is, therefore, concluded that the UV/H_2O_2/Fe-RHA synergic process is highly effective for the removal of dyes in wastewater.

Keywords: UV-enhanced Fenton-like process; Safranin; Iron loaded rice husk ash; Decolorization

1. Introduction

Advanced oxidation processes (AOPs) involve strong oxidant species such as hydroxyl radicals for the destruction of recalcitrant organic pollutants in wastewater [1]. Due to their ability to degrade even biologically resistant materials, the AOPs have been implied in combination with biological processes for the effective treatment of wastewater that results in complete mineralization into water, carbon dioxide and inorganic ions [2–5]. The various AOPs have been used for the removal of organic pollutants such as ozonation [5,6], catalytic ozonation [7], Fenton processes [8,9] and electrochemical advanced oxidation processes, etc. [10]. In the past two decades, homogeneous Fenton processes were extensively studied for the removal of hazardous pollutants. However, these processes have a limited operational pH range for effective oxidation [11]. Therefore, due to the broader operational pH range and lack of sludge formation, heterogeneous Fenton-like processes were considered to be most suitable for practical applications [12–15]. In the last few years due to economic considerations, agricultural waste materials have been implied as a support in Fenton-like oxidation processes [14–16].

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* Corresponding authors.

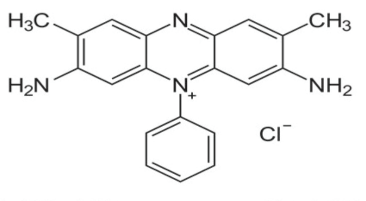
Pigments and dyes are extensively used in the textile and leather dyeing, pharmaceutical, laboratories, paper, printing and cosmetic industries. The presence of dyes in wastewater is most undesirable, due to their high visibility and toxicity to the aquatic environment. They absorb and reflect sunlight entering the water and hence they can hinder photosynthesis and interfere with the growth of bacteria in aquatic plants [16]. Therefore, removal of dyes from wastewater before they are discharged to the environment is important, due to increasingly stringent restrictions on the effect of the industrial effluents to the environment [16,17]. Safranin is difficult to biodegrade due to its structural stability [18]; therefore, in this present study, safranin (cationic dye) was selected as target pollutant.

Various physical and chemical methods were implied to remove dyes such as ion exchange, reverse osmosis, chemical oxidation, electro-dialysis, adsorption using activated carbon and activated charcoal, etc. [14,16–20]. It has been found that most of the above-mentioned processes are costly and require higher energy to perform [17,18]. For these reasons, the interest in the exploration of some unconventional methods and materials for removal of colored compounds has been arisen recently, which are cheaper and consume relatively less energy. Therefore, low-cost agricultural waste materials have been used as a support in Fenton-like oxidation processes [14–16]. Among them, rice husk ash (RHA) was implied, due to its annual worldwide production and economic aspects [14,15]. However, previous findings indicate that iron loaded RHA show operation only in a limited pH range and was found to be effective only in an acidic pH range (pH ≤ 4) [14,15], which limits the scope of iron loaded Fenton-like catalyst for practical applications. Therefore, in current investigation a synergic process using UV/H_2O_2/Fe-RHA was studied for the decolorization and degradation of safranin from aqueous solutions. Previous studies indicate that synergic process (UV/H_2O_2/catalyst) could substantially increase the operating pH range [21]. To the author's knowledge, removal of dyes using combined synergic UV/H_2O_2/Fe-RHA process (implying Fe-RHA) was not studied previously. This study may further help to improve the removal efficiency of RHA based Fenton-like process and may help to increase the operational pH range of such processes.

2. Experimental section

2.1. Materials and reagents

Safranin (Fig. 1) was purchased from May & Baker, UK. 35% hydrogen peroxide solution was purchased from Merck, Germany. All the chemicals were used without further purification. Stock solution of safranin (100 mg/L) was prepared by dissolving powered safranin in distilled water. Safranin solutions of different concentrations were prepared by diluting the stock solution with ultrapure deionized water. The pH of prepared solutions was adjusted by using 1N HCl and 1N NaOH solutions. The rice husk was purchased from the local market, washed with deionized water, dried and burnt in a furnace at a temperature of 600°C to obtain its ash.



Type: Basic Cationic Dye
λ_{max}: 512nm

Chemical Formula: $C_{20}H_{19}N_4Cl$
Molecular weight: 350.85 g/mol

Fig. 1. Properties and structure of safranin.

2.2. Catalyst preparation

To prepare Fe-RHA catalyst, husk was obtained from a local market and after washing and drying, it was kept in a furnace at 600°C for 6 h. The powdered material (Rice husk ash) obtained was added in nitric acid solution (0.1 M) for 24 h. RHA was filtered. To obtained constant pH it was washed thoroughly with distilled water [15]. Afterwards, it was placed overnight in an oven at 110°C. Finally, Fe-RHA was prepared by impregnating iron (III) oxide on the RHA [22,23]. In this method, 6.0 g of $Fe(NO_3)_3.9H_2O$ (Merck) was dissolved in a beaker having 20 mL deionized water, in it 10 g of RHA was added. It was heated at 100°C until the water evaporated (agitation speed was kept at 120 rpm), Finally, the prepared iron loaded catalyst was dried in an oven (at 100°C) overnight and was calcined at 600°C for 6 h.

2.3. Catalyst characterization

The surface morphology of RHA and Fe-RHA was studied by using scanning electron microscope (SEM), Model, JSM-6480 LV JSM-6010LA, JEOL, Tokyo, Japan. The point of zero charge of the catalyst was found by mass transfer method [24]. The pore size and surface area were determined by Brunauer–Emmett–Teller (BET) method (ASAP 2020, Micrometrics, Georgia, USA).

2.4. Safranin removal experiments

The removal studies of safranin were conducted in 250 mL flask (Fig. 2). 100 mL of safranin solution (15 ppm) was taken in the flask (35% H_2O_2 solution was used to prepare H_2O_2 solutions of different molar concentration from 2 to 16 mM) and weighted amount of catalyst was added in it. The pH of the solutions was adjusted with 1 N HCl and 1 N NaOH solutions. The flask was placed in a container equipped with UV lamp. The lamp emitting UV-A rays

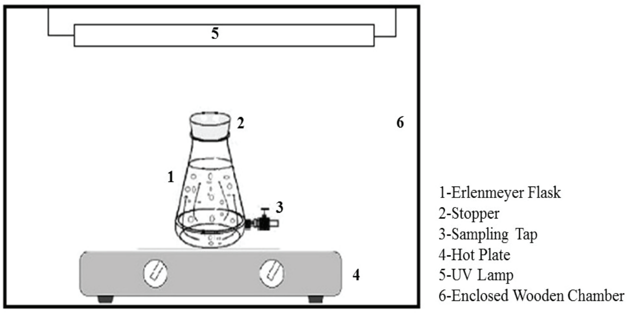


Fig. 2. Experimental setup for the removal of safranin.

(20 W) with a maximum wavelength of 368 nm (Sylvania, Germany) was used in this study (Fig. 2). The samples were obtained after fixed intervals of time, and were analyzed on PerkinElmer Lambda 35 double beam UV-VIS spectrophotometer.

The dye removal efficiency was calculated by using the following formula:

$$\text{Decolorization efficiency [\%]} = \frac{A_o - A_t}{A_o} \times 100 \qquad (1)$$

where A_o = absorbance at time 0; A_t = absorbance at time *t*.

The chemical oxygen demand (COD) removal studies were performed in the same apparatus as discussed above, by taking 100 mL of safranin solution in a flask. The COD before and after treatment was found out by open reflux titration method [25]. The COD removal efficiency was quantified by using the following relation:

$$\text{COD removal efficiency [\%]} = \frac{\text{COD}_o - \text{COD}_t}{\text{COD}_o} \times 100 \qquad (2)$$

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

2.5. Analytical procedures

2.5.1. Safranin concentration

Safranin concentrations in the aqueous solutions were determined by UV–Vis spectrophotometer (Lambda 35, PerkinElmer, Massachusetts, USA). The maximum absorption value (λ_{max}) was found to be 512 nm. The calibration curves were prepared before experimentation. The method has been validated by both inter-day and intraday validations. Each experiment was performed three times to ensure accuracy and the RSD value was found to be less than 5%.

2.5.2. Iron analysis

To determine concentrations of leached out iron during the various processes, atomic absorption spectroscopy (AAnalyst800, PerkinElmer, Massachusetts, USA) was used.

3. Results and discussion

3.1. Catalyst characterization

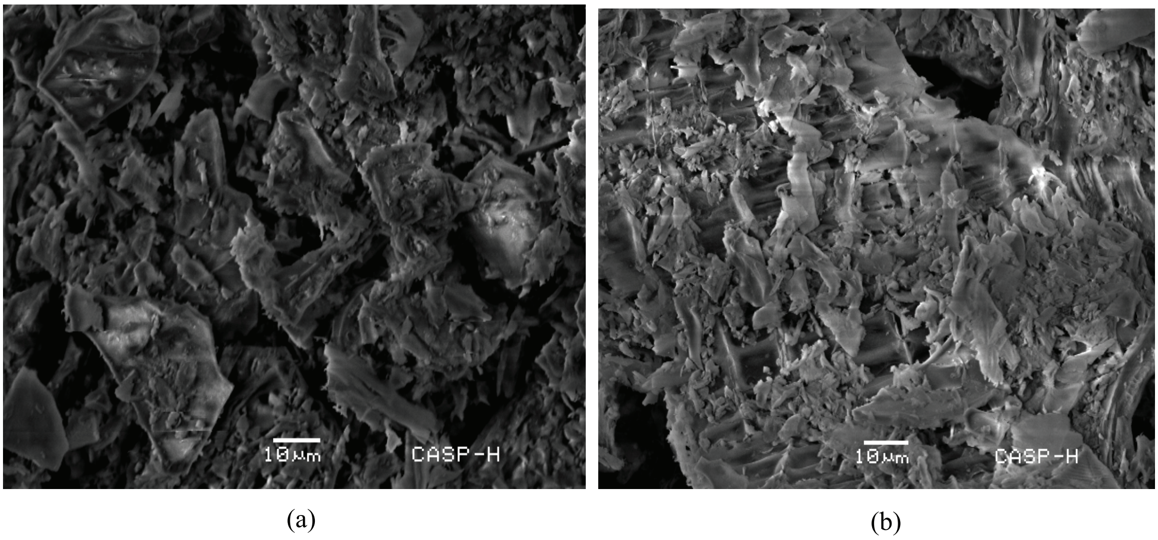
Catalyst (Fe-RHA) point of zero charge was found to be 3.3 ± 0.3. The SEM images clearly indicate that the surface morphology of both RHA and iron impregnated RHA (Figs. 3(a) and (b)) is retained, hence no marked change was found even after iron loading on RHA. The surface area of Fe-RHA catalyst was found to be 80.01 m^2/g and average pore size was 19.5 Å. The elemental composition with energy dispersive X-rays (Figs. 4(a) and (b)) confirmed the presence of minute quantity of iron on Fe-RHA.

Surface areas were found to be 80.1 and 90.3 m^2/g, and the average pore sizes were 19.5 and 18.1 Å for Fe-RHA and RHA, respectively (Table 1). The comparative study of BET surface areas for Fe-RHA and RHA shows that because of incorporation of Fe^{3+} a decrease in surface area was observed (Table 1). This reduction in surface area in the case of Fe-RHA, by iron loading may be due to the capping of the pores by loaded iron [26]. Similar trends were obtained in some previous findings [26]. The point of zero charge was slightly higher for Fe-RHA, this may be due to the loading of iron, it was pH_{pzc} = 3.3 ± 0.2 and 2.9 ± 0.1 for RHA and Fe-RHA, respectively (Table 1).

3.2. Removal of safranin

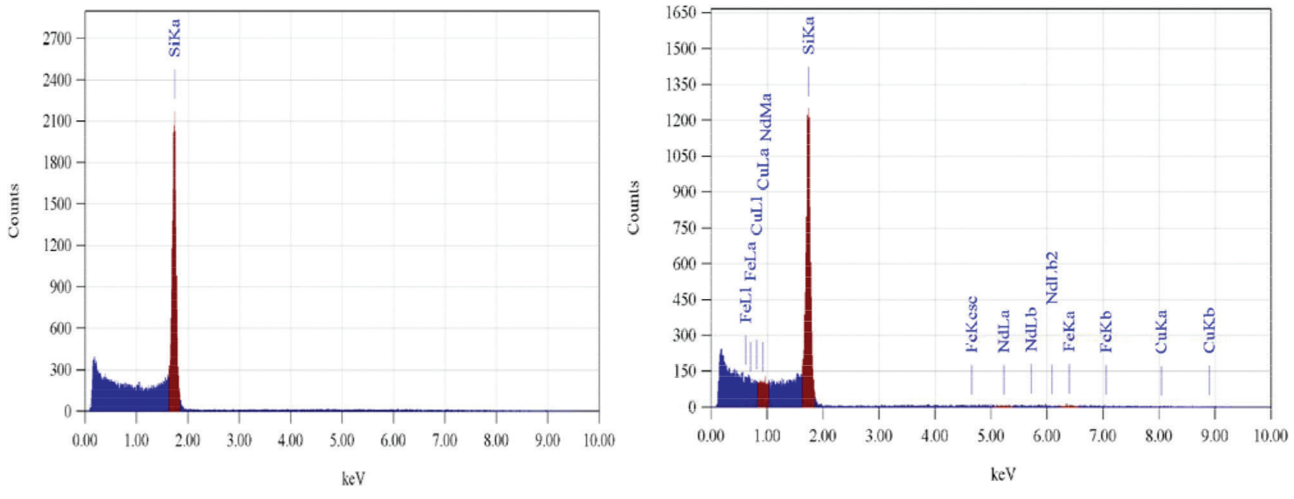
3.2.1. Comparison between catalytic and non-catalytic processes

The safranin removal was studied by varying the pH in the range 3–10 and comparison of catalytic, non-catalytic and integrated processes was done (Fig. 5). Among the



(a) (b)

Fig. 3. SEM images of RHA and RHA/Fe^{+3}. (a) RHA and (b) RHA/Fe^{+3}.



a) b)

Fig. 4. EDX patterns of RHA and RHA/Fe^{+3}. (a) RHA and (b) RHA/Fe^{+3}

Table 1
Characteristics of rice husk ash (RHA) and iron loaded rice husk ash (Fe-RHA) catalyst

Material	Surface area	Average pore size	pH_{pzc}
Fe-RHA	80.1 m^2/g	19.5 Å	3.3 ± 0.2
RHA	90.3 m^2/g	18.1 Å	2.8 ± 0.1

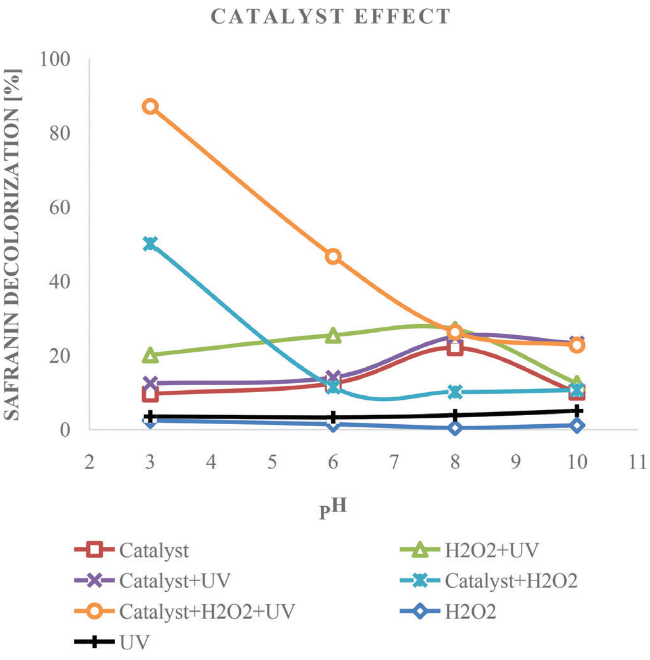


Fig. 5. Comparison of decolorization efficiency of safranin for different processes ($C_{o\,(SAF)}$ =15 mg/L; T = 30°C; initial pH = 3, 6, 8 and 10; t = 120 min; H_2O_2 = 8 mM; catalyst = 0.1 g; V = 100 mL).

non-catalytic processes, UV, H_2O_2 and UV-H_2O_2 integrated process were studied. Negligible dye removal was achieved with UV and H_2O_2 while dye removal of 10%–27.1% was obtained at studied pH values in the case of UV-H_2O_2 integrated process (Fig. 5). This may be due to the dissociation of H_2O_2 leading to the production of hydroxyl radicals [27]. The catalytic processes studied for safranin removal were catalyst, catalyst-UV, catalyst-H_2O_2 and catalyst-UV-H_2O_2 integrated process (Fig. 5). The maximum dye removal of 87.1% was obtained by catalyst-UV-H_2O_2 integrated process at pH 3. This may be explained that UV enhances the radical formation inside the solution as well as higher amounts of hydroxyl radical production due to the interactions of H_2O_2 with Fe-RHA. Furthermore, the adsorption of dye may also play a significant role in the overall removal efficiency [21]. Moreover, the decrease in dye removal at alkaline pH can be explained as the less hydroxyl radicals may produce by hydrogen peroxide due to the high concentration of hydroxide ions that may poison the active sites of catalyst [15,21]. Therefore, results clearly suggest that the combined UV/H_2O_2/Fe-RHA process catalyzes the decolorization of safranin more effectively as compared with other processes (Fig. 5). Furthermore, synergic process was found to be effective near wastewater pH. For example, the removal efficiency of safranin was found to be 46.7% at pH 6 in the case of UV/H_2O_2/Fe-RHA process (Fig. 5). However, in previous findings Fe-RHA Fenton-like catalytic process (Fe-RHA/H_2O_2 only) was only effective at acidic pH (pH < 4) [15,28]. Therefore, by combining Fe-RHA/H_2O_2 with UV process, significantly higher removal of dyes may be achieved even near wastewater pH, which may be practically feasible.

The comparative study of various processes with varying time intervals (Fig. 6) shows that the synergic process has significantly higher removal as compared with other processes. The iron loading effect was clearly indicated while comparing adsorption alone and catalytic process (Fig. 6). The results further reveal that the removal efficiency was found to be significantly higher in first 40 min and then decreases (Fig. 6), this may be due to the formation of by-products in solution which might compete for the reactions with hydroxyl radicals and safranin.

It is hypothesized that in the case of synergic process (studied in current investigation) significantly higher production of hydroxyl radicals as compared with previous findings may lead to the high removal efficiencies even near wastewater

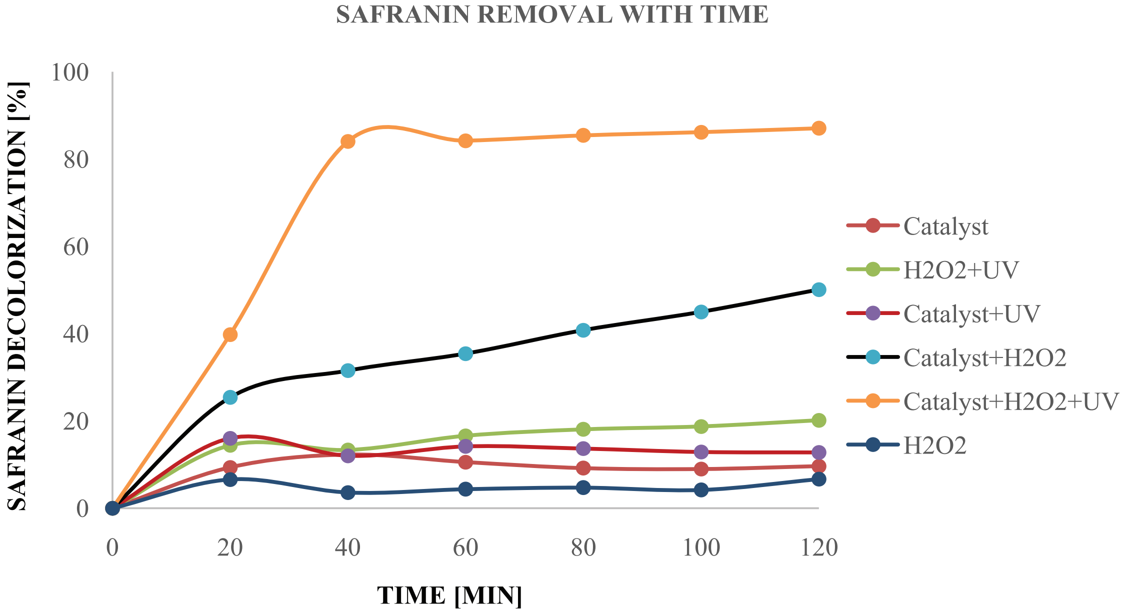


Fig. 6. Comparison of decolorization efficiency of safranin for different processes with time ($C_{o\,(SAF)}$ =15 mg/L; H_2O_2 = 8 mM; initial pH = 3; T = 30°C; t = 120 min; catalyst dose = 0.1 g; V = 100 mL).

pH. The production of hydroxyl radicals may be inside the solution due to direct UV and H_2O_2 interaction in addition to the production of radicals via interaction of H_2O_2 with active sites on catalyst (Fe-RHA) [29]. Moreover, the surface of catalyst plays an important role in catalytic processes, the adsorbed H_2O_2 on the surface of the catalyst (Fe-RHA) may further lead to the formation of hydroxyl radicals via interacting with UV rays on the surface of catalyst [29]. However, in the case of previous studies on Fe-RHA, it was used without UV irradiation [15,28]. Based on previous findings [29], following reactions may summarize the mechanism in the case of Fenton-process using Fe-RHA (where Fe^{+3} was the active site).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\cdot} + H^{+} \quad (3)$$

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + OH^{\cdot} + H^{+} \quad (4)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH^{\cdot} \quad (5)$$

$$H_2O_2 \rightarrow 2OH^{\cdot} \quad (6)$$

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HOO^{\cdot} \quad (7)$$

$$OH^{\cdot} + Dye \rightarrow Intermediates \rightarrow CO_2 + H_2O \quad (8)$$

No significant change in pH was observed ($pH_{initial}$ = 0.3) during the studied processes. In the current investigation, removal efficiencies of various processes in buffer solutions were not investigated due to the hydroxyl radical scavenging effect of buffers [30]. Since advanced oxidation processes involve the production of hydroxyl radicals, therefore radical scavengers may affect overall efficiency of catalyst to remove target pollutant [30].

3.2.2. Effect of initial concentration of hydrogen peroxide

The decolorization efficiency was studied (for, Fe-RHA/H_2O_2/UV process) at different initial concentrations of hydrogen peroxide to obtain the optimum initial concentration of hydrogen peroxide due to its high cost and environmental concerns. The safranin removal of 49.45%, 74.33%, 87.94% and 90.02% was achieved in 120 min, at initial concentration of hydrogen peroxide of 2, 4, 8 and 16 mM, respectively (Fig. 6). The results show that the decolorization efficiency increases with the increase in the initial concentration of hydrogen peroxide. The hydrogen peroxide is the source of formation of hydroxyl radicals that enhance the rate of decolorization [14,21]. From the results, 8 mM was selected as optimum value of H_2O_2. This concentration was selected by keeping in view its scavenging effect, cost, ecological effects and decolorization efficiency [14,15].

3.2.3. Effect of catalyst dose

The dye removal was studied at a catalyst dose of 0.05, 0.1 and 0.3 g. The dye removal increased with the catalyst dose (Fig. 7). For example, in 120 min, the percentage removal obtained was 61.76%, 87.94% and 88.97% for the catalyst dose of 0.05, 0.1 and 0.3 g, respectively. The increase in the decolorization efficiency with the catalyst dose may be explained by the increase in the availability of fresh active sites (that interacts with H_2O_2 leading to the production of hydroxyl radicals) and adsorption sites with increase in catalyst dose at a fixed dye concentration [15,21]. 0.1 g was selected as optimum catalyst dose. The results also indicate that catalyst (Fe-RHA) plays an important role in synergic UV/H_2O_2/Fe-RHA process (Fig. 7).

3.2.4. Effect of the initial concentrations of safranin

The safranin removal efficiency was studied by varying initial concentrations in the range of 15–50 mg/L with a fixed amount of hydrogen peroxide (8 mM) and catalyst (0.1 g) at pH 3. The experimental results (Fig. 8) revealed that the safranin removal increased with the increase in initial dye concentration from 15 mg/L (11.71 %) to 40 mg/L (23.82%) and then it was decreased to 23.8% at 50 mg/L. The initial increase in dye removal may be explained due to the presence of fixed active fresh sites of catalyst at a certain catalyst dose for adsorption until all the active sites become saturated and further increase in initial dye concentration decreases the decolorization efficiency [14,21].

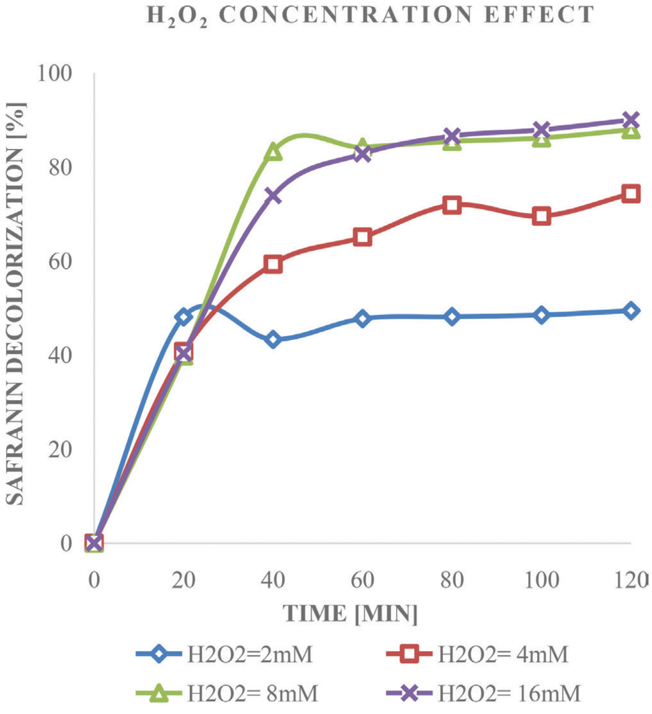


Fig. 7. Effect of H_2O_2 concentration on the decolorization of safranin for RHA-Fe/UV/H_2O_2 process ($C_{o\,(SAF)}$ =15 mg/L; T = 30°C; pH = 3.0; catalyst amount = 0.1 g; V = 100 mL).

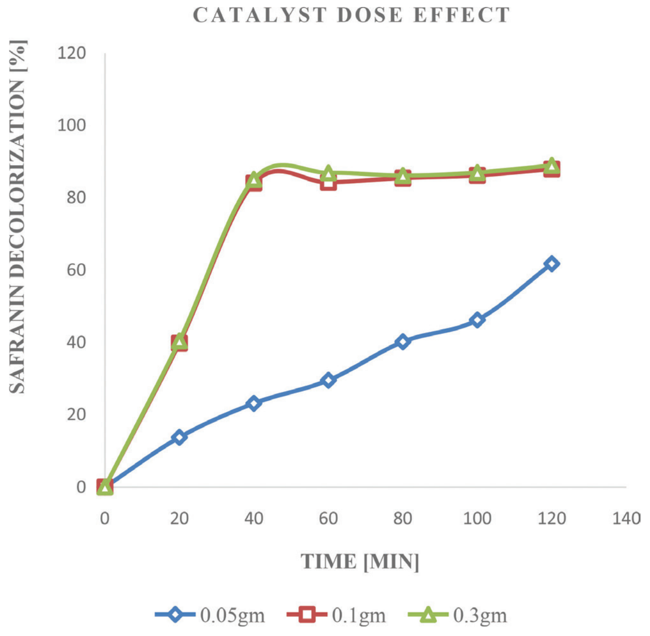


Fig. 8. Catalyst dose effect on the decolorization of safranin for RHA-Fe/UV/H_2O_2 process ($C_{o\,(SAF)}$ =15 mg/L; H_2O_2 = 8 mM; T=30°C; pH=3.0; catalyst amount=0.05, 0.1 and 0.3 g; V=100 mL).

3.2.5. Effect of temperature

The results presented in Fig. 10 show that the rate of safranin removal increased with the increase in temperature in synergic process. For example, the removal efficiency was 68.3%, 87.1% and 95% at 20°C, 30°C and 40°C, respectively, in 120 min. This may be because, at higher temperature the rate of generation of hydroxyl radicals may increase due to the increase in reaction rate between catalyst and H_2O_2 [14,15].

3.2.6. Catalyst reuse performance

Catalyst reuse performance has been studied at optimum conditions to investigate catalyst stability in synergic process (H_2O_2/UV/Fe-RHA process). The experimental results show that catalyst reuse performance for decolorization of safranin, decreases from 82.1% in cycle 1 to 79.6% in cycle 2 and 77.6% in cycle 3 (Fig. 11). The decolorization efficiency of the catalyst was significantly low after three successive runs. Slight decrease in decolorization efficiency may be due to iron leach out effect of iron from catalyst [14]. The leach out test was also conducted and leach out of iron was found to be less than European Standards (2 mg/L) [14].

3.2.7. Degradation and decolorization efficiency

The COD of the dye solution was also investigated to verify the effectiveness of UV/H_2O_2/iron loaded rice husk ash based advanced oxidation process. The experimental data indicate that decolorization efficiency of safranin

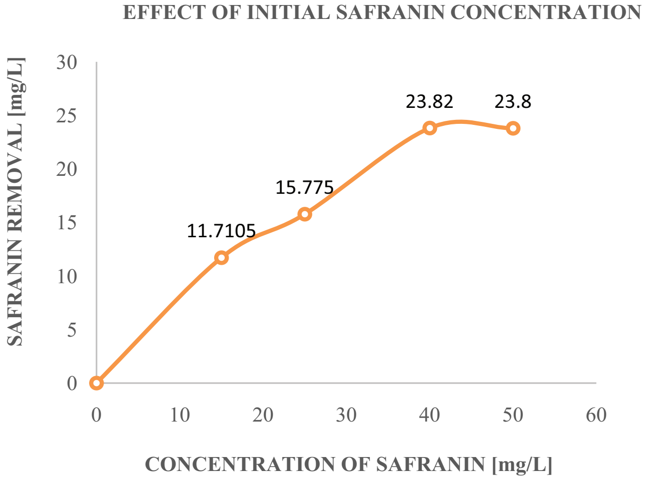


Fig. 9. Effect of initial dye concentration on the amount of safranin removed in RHA-Fe/UV/H_2O_2 process ($C_{o\,(SAF)}$ = 15–50 mg/L; H_2O_2 = 8 mM; T = 30°C; pH = 3.0; catalyst amount = 0.1 g; V = 100 mL.

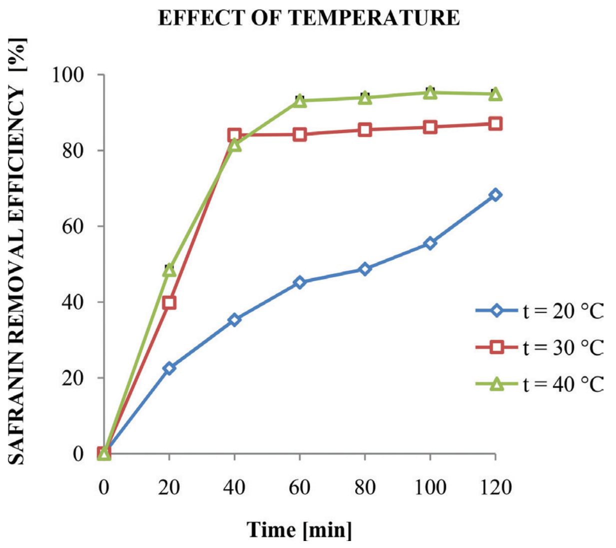


Fig. 10. Effect of temperature on safranin removal efficiency in RHA-Fe/UV/H_2O_2 process ($C_{o\,(SAF)}$ = 15 mg/L; H_2O_2 = 8 mM; T = 20°C, 30°C and 40°C; pH = 3.0; catalyst dose = 0.1 g; V = 100 mL.

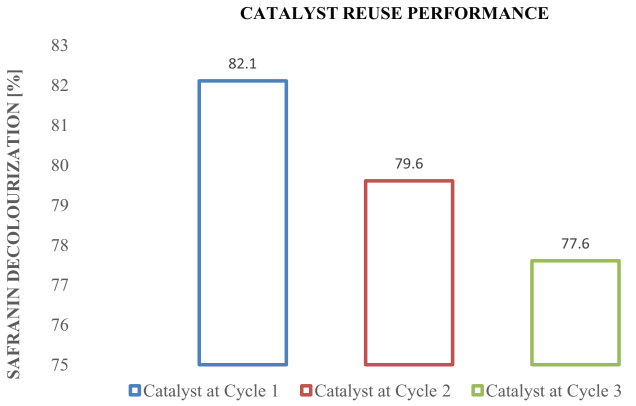


Fig. 11. Reuse performance of RHA-Fe/UV/H_2O_2 process ($C_{o\,(SAF)}$ =15 mg/L; T = 30°C; pH = 3.0; T = 120 min; H_2O_2 = 8 mM; catalyst = 0.1 g; V = 100 mL.

was higher as compared to degradation. The maximum of 65% COD removal efficiency was obtained in 120 min (Fig. 12). The results show that the UV/H_2O_2/Fe-RHA process was an effective method for the degradation of dyes in wastewater.

4. Conclusions

The UV/H_2O_2/Fe-RHA based catalyst was tested and used in Fenton-like process for the removal of safranin. Following findings have been drawn based on all the experimentation:

- The rice husk ash/UV/H_2O_2 system was effective for the removal of safranin.
- The activity of the catalyst was pH dependent and decolourization was the highest at pH 3.
- The rice husk ash/UV/H_2O_2 process significantly removes COD.
- The catalyst has good reuse performance.

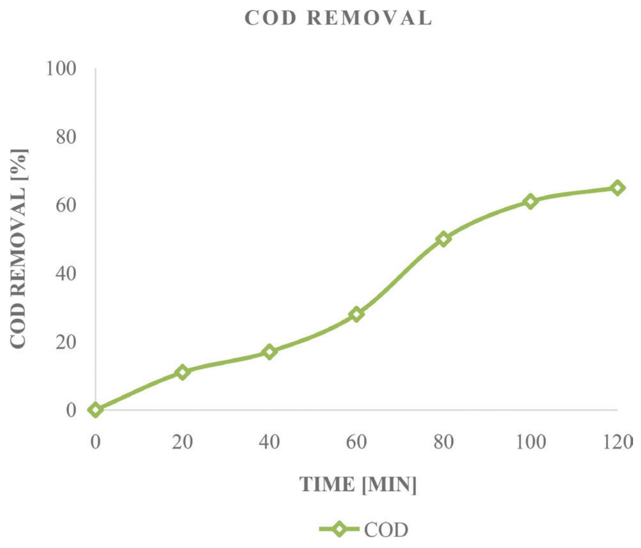


Fig. 12. COD removal of safranin solution for UV/H_2O_2/Fe-RHA ($C_{o\,(SAF)}$ = 15 mg/L; pH = 3.0; catalyst dose = 0.1 g; T = 30°C; H_2O_2 = 8 mM; V = 100 mL).

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