

Heterogeneous Fenton-like degradation of Rhodamine 6G in water using CuFeZSM-5 zeolite catalyst prepared by hydrothermal synthesis

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ABSTRACT

In this study, heterogeneous Fenton-like degradation of reactive azo dye Rhodamine 6G in water was investigated over a CuFeZSM-5 zeolite catalyst prepared by hydrothermal synthesis. At initial pH of 3.4, a color removal of 100% was achieved after a reaction time of 45 min. TOC elimination was measured to be 51.8% after 2 h of oxidation. Initial decolorization rate was described by an equation of $-r_{A0} = 4.56 \times 10^2 e^{-24.83/RT} C_{R6G,0}^{0.35} C_{H_2O_2,0}^{0.35}$ where R is in kJ/mol. The leaching of iron and copper cations from zeolite structure into the solution during oxidation was dependent on pH strongly. The regulation of pH from 6.5 (dye solution pH) to 3.4, increased leaching for iron from 0.7 to 0.8 mg/dm³ and for copper from 1.4 to 2.1 mg/dm³. The copper was totally leached from the catalyst during the process at pH 3.4.

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1. Introduction

Large quantities of waste water are discharged into the environment during the textile dyeing process. These effluents are intensely colored and contaminated with high concentrations of chemical oxygen demand. They not only deteriorate the aesthetics of receiving waters, but also pose significant threat to aquatic life because of the hindrance of the penetration of oxygen and formation of some toxic products by hydrolysis of dyes in the waste water.

Most of textile dyes are designed to produce long-lasting colors and are resistant to mild oxidation conditions. Therefore, stronger oxidation agents such as Fenton's reagent are needed to degrade these structures.

The Fenton-like processes are used as a powerful source of hydroxyl radicals from H₂O₂ in the presence of transitional metal cations, such as iron, Fe²⁺/Fe³⁺/H₂O₂, to decompose many organic compounds including dyes. However, the usage of homogeneous Fenton process has a number of disadvantages such as impossible regeneration of catalyst, requirement of narrow range of pH values for reaction and necessity of the treatment of the sludge containing iron before discharging it to receiving waters. These drawbacks can be overcome by using heterogeneous Fenton-type catalysts,

in particular, zeolites, whose recovery from water is not difficult. Iron and copper containing zeolites show redox properties because these metals can change their oxidation states [1–14]. Recently, high catalytic activity of iron containing zeolites for phenol oxidation [15,16] and for degradation of dyes [2,3] has been reported. Supported Fe-saponite clay catalysts revealed to be quite active in the Fenton-like oxidation of Orange II [4]. FeZSM-5 prepared by ion-exchange was tested in wet oxidation with hydrogen peroxide of diluted formic, acetic and propionic acid [17].

In literature it was reported that copper containing catalysts such as Al-Cu catalyst supported on pillared clay and CuO catalyst supported on γ -Al₂O₃ showed high catalytic activity during oxidation of phenol dissolved in water [18] and isolated Cu²⁺ sites grafted to Al-MCM-41 also gave relatively high catalytic activity in ethane oxidation [19]. On the other hand, it is well known that copper exchanged zeolites such as CuZSM-5 have been widely studied for selective catalytic reduction of NO_x to N₂ with ammonia or propane [20–22].

Although many studies were present in literature on wet peroxidative removal of textile dyes on Fe-containing zeolites, no study has been reported on iron and copper containing zeolites for heterogeneous Fenton-like degradation of textile dyes.

The aim of this paper is to assess the catalytic performances of iron and copper containing ZSM-5 zeolites prepared by hydrothermal synthesis on the Fenton-like degradation of Rhodamine 6G, which is an important reactive azo dye used in textile industry.

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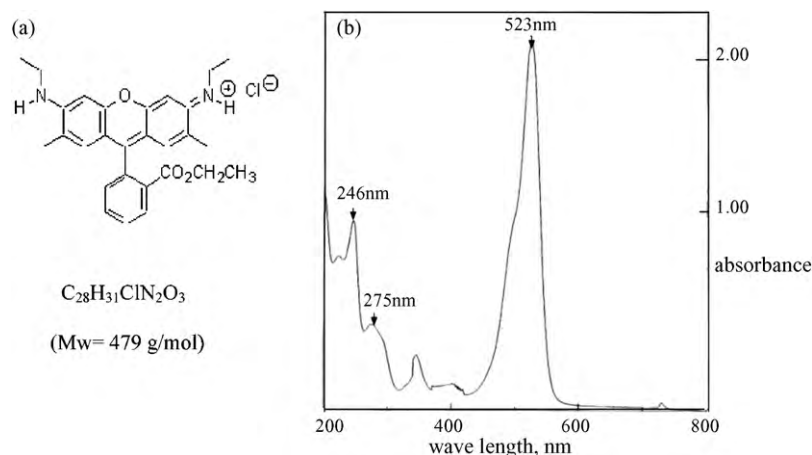


Fig. 1. Chemical structure of Rhodamine 6G (R6G) (a) and UV-vis. Absorption spectra of aqueous solutions of Rhodamine 6G (b).

2. Experimental

2.1. Materials

The reactive azo dye Rhodamine 6G was obtained from Sigma–Aldrich and used without further purification. The absorption spectra of Rhodamine 6G is characterized by three main bands, one in the visible region ($\lambda_{\text{max}} = 523 \text{ nm}$) which is responsible for the chromophoric components (for the color of dye arising from aromatic rings connected by azo groups) and the others in the UV region ($\lambda_{\text{max}} = 246 \text{ nm}$ and $\lambda_{\text{max}} = 275 \text{ nm}$) which represent the absorption of benzene-like and naphthalene-like structures in the molecule, respectively [4]. Rhodamine 6G is also called as R6G, Rh6G, C.I. Pigment Red 81, C.I. Pigment Red 169, C.I. 45160 where C.I. is color index. The hydrogen peroxide solution (35%) of analytical grade was obtained from Merck. Aqueous solutions containing 0.1 g/dm^3 azo dye were prepared with deionized water from a Millipore Direct Q purification unit.

Fig. 1 presents the chemical structure of Rhodamine 6G (R6G) (a) and UV-vis absorption spectra of aqueous solutions of Rhodamine 6G (b).

2.2. Catalysts

Hydrothermal synthesis method given by Szostak et al. [23] was applied to prepare FeZSM-5 sample. The same method was used for CuFeZSM-5. The prepared catalysts were characterized by nitrogen adsorption, XRD, SEM and FTIR measurements. The precise procedures for preparation and characterization of the catalysts were described in Ref. [24]. Metal contents and Si/Fe ratios of the catalysts were determined by ICP-AES method. BET-surface area (S_{BET}), total pore volume (V_p), average pore diameter (d_{ave}) and chemical composition of CuFeZSM-5 and FeZSM-5 catalysts are given in Table 1. CuFeZSM-5 catalyst contains 1.7% iron and about 0.2% copper. Iron content of FeZSM-5 catalyst is about 2.5%.

Table 1
Surface characteristics and physicochemical properties of FeZSM-5 and CuFeZSM-5 catalysts.

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	d_{ave}^a (nm)	Si/Al	wt%Fe	wt%Cu	Si/Fe	Si/Cu
CuFeZSM-5	390.0	0.254	2.60	No aluminum	1.7	0.2	52.02	600.52
FeZSM-5	344.4	0.192	2.23	No aluminum	2.5	–	35.88	No copper

^a By BET method.

2.3. Heterogeneous Fenton-like degradation

Heterogeneous Fenton-like degradation of Rhodamine 6G (R6G) was performed under isothermal conditions in a temperature-controlled shaded glass batch reactor equipped with a mechanic stirrer and a pH electrode. In a typical run, 0.15 dm^3 of aqueous dye solution ($0.1 \text{ g-dye/dm}^3\text{-soln.}$) was placed into the reactor and the temperature was adjusted to 323 K. When the temperature reached to 323 K, pH of the solution was measured and 0.15 g of catalyst ($1 \text{ g-cat/dm}^3\text{-soln.}$) was introduced into the solution under continuous stirring. After stabilization of the temperature at 323 K, pH of the solution was again measured and the solution was analyzed in order to determine whether the dye is adsorbed by the catalyst. Then a solution of 35% H_2O_2 ($40 \text{ mmol H}_2\text{O}_2/0.15 \text{ dm}^3$ solution, the amount of H_2O_2 used was in excess, which was equal to 1.34 times of the H_2O_2 amount necessary to completely oxidize dye to CO_2 and H_2O) was added into the dye solution. After the addition of H_2O_2 , pH of the solution was again measured (pH 6.1). This time was recorded as the starting time of the reaction. For the experiments with initial pH of 3.4, pH was regulated by addition of H_2SO_4 into the dye solution. The samples taken periodically at every 15 min were diluted in 1:10 ratio. After centrifugation for 0.5 h to remove the catalyst, the samples were analyzed with UV spectrophotometer (Jasco 7800 UV/Vis).

The decrease of the intensity of the band at 523 nm was used as a measure of decolorization degree. The absorbance peak at 275 nm is due to the naphthalene ring of R6G and the decrease of the intensity of this band was taken as a measure of degradation degree. The decrease in the intensity of the band at 275 nm is attributed to the formation of intermediates resulting from the degradation of the azo dye, which still contain benzoic and naphthalene type rings [17].

In addition to these measurements, total organic carbon (TOC) removal was determined using a TOC Shimadzu Vcph spectrophotometer for each run after a reaction time of 2 h for the evaluation of the mineralization of R6G dye. TOC was calculated as the difference between the total carbon (TC) and inorganic carbon (IC) in the liquid sample.

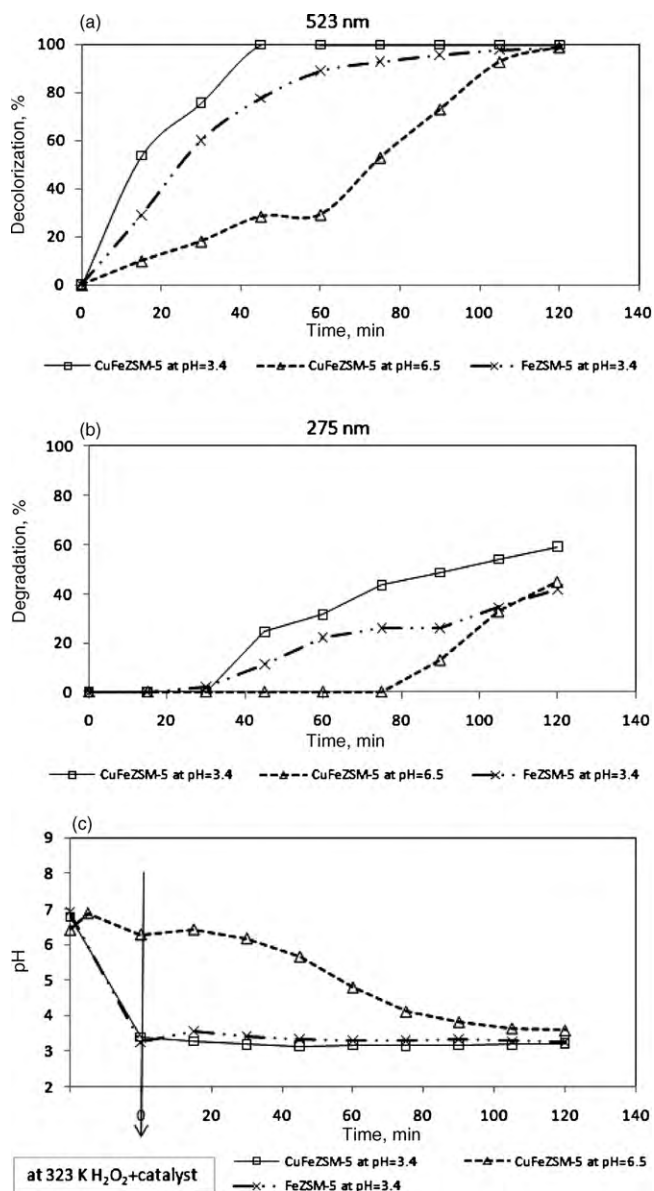


Fig. 2. The influence of catalyst type and pH on the oxidation of R6G (a) decolorization, (b) degradation %, (c) pH value (Initial concentration of R6G = 0.1 g/dm³, temperature = 323 K, catalyst amount = 0.15 g, solution volume = 0.15 dm³, H₂O₂ amount = 40 mmol).

3. Results and discussion

3.1. The influence of pH on catalytic oxidation

Catalytic activity tests were performed under the conditions indicated in Section 2.3 for initial pH of 3.4. No noticeable dye removal by adsorption (blank run in the same conditions but without H₂O₂) took place during experiments over the prepared catalysts. Fig. 2 presents the results. A color removal of 100% was achieved after a reaction time of 45 min and degradation of naphthalene-like structures (hereafter it is called as degradation) was obtained to be 59.1% after 2 h oxidation when CuFeZSM-5 was used as catalyst, Fig. 2a and b. Addition of H₂O₂ to solution at the beginning of the reaction caused an increase in pH of the solution because of the oxidation of some Fe²⁺ species present in the zeolite. As the reaction proceeded, solution pH decreased to about 3.6. This phenomenon can be explained by the fragmentation of the

azo dye molecules into organic acids which lead to a drop of pH. For the same reaction duration, lower color and naphthalene ring removals were achieved with FeZSM-5 catalyst, 98.7% and 41.7%, respectively. The difference in catalytic activity between CuFeZSM-5 and FeZSM-5 catalysts can be attributed to the introduction of copper into zeolite structure for CuFeZSM-5 catalyst. This sample had a larger surface area (390.0 m²/g) and average pore diameter (2.60 nm) than those of FeZSM-5. Higher activity obtained may also arise from the fine dispersion of iron and copper in structure of CuFeZSM-5 zeolite. TOC elimination on CuFeZSM-5 was measured to be 51.8% after an oxidation time of 2 h. At initial pH of 3.4, the pH value remained almost unchanged during the oxidation. When the catalytic oxidation runs were performed at initial pH of 6.5 which was the pH of dye solution, 99% color removal was obtained after 2 h of reaction with CuFeZSM-5 catalyst. The achieved decolorization degree after 45 min was only 28.5%. Initial rate of color removal was much lower, than that with initial pH of 3.4. Degradation at 275 nm and TOC removal after 2 h oxidation were measured to be 45% and 34%, respectively.

There was a great difference in color (Fig. 2a) and naphthalene ring removal (Fig. 2b) for different initial pH values (pH 6.5 and pH 3.4) during the early stage of the reaction for CuFeZSM-5 catalyst. But this difference diminished after a reaction time of 2 h for decolorization. Decolorization after 2 h was complete, independent of pH. However, degradation and TOC abatement were affected significantly from the initial pH of dye solution. Degradation showed a decrease from 59.1% to 45% and TOC reduction decreased from 51.8% to 34% with the increase of pH from 3.4 to 6.5, respectively. This is likely due to the formation of intermediates at nearly neutral pH whose mineralization is hindered [3].

Initial decolorization rate decreased with the increase in initial pH value, likely due to the accelerated formation of less reactive peroxy radicals, H₂O^{*}, rather than OH^{*} radicals [2].

On the other hand, an induction period was seen for degradation of dye over CuFeZSM-5 and FeZSM-5 catalysts, beyond which there was degradation of Rhodamine 6G. Induction period was about 30 min at pH 3.4 and about 75 min at pH 6.5. This indicates that a certain minimum number of free radicals are required for the onset of the degradation process. Induction period was also reported by Gogate et al. [25] in sonolytic degradation of Rhodamine B.

During the CWPO runs of CuFeZSM-5 catalyst, amount of iron and copper loss into the solution was determined by measuring the iron and copper concentration in the solution after a reaction time of 2 h with atomic absorption spectrophotometer (Varian 10 plus). Iron leached was measured to be 0.7 mg/dm³ (loss % = 4) at initial pH of 6.5 and 0.8 mg/dm³ (loss % = 4.6) at pH 3.4. Copper loss was more significant, 1.4 mg/dm³ (loss % = 82.4) at pH 6.5 and 2.1 mg/dm³ (loss % = 100) at pH 3.4. It means that at pH 3.4 the copper was totally leached from the catalyst during the process. Consequently, the leaching of iron and copper cations from zeolite structure into the solution was strongly dependent on pH [17]. Even though iron leaching increased with the regulation of pH to about 3.4, leached amount of iron was below the EU directives (<2 mg/dm³).

In order to determine the homogeneous contribution of leached ions to total activity, a couple of runs were performed with homogeneous catalysts at the concentration of dissolved ions and no color removal and degradation of dye were obtained. This result supported the idea that introduction of copper into the FeZSM-5 zeolite had a synergetic effect rather than catalytic degradation of dye.

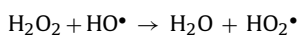
The highest color removal, degradation and TOC elimination were obtained with CuFeZSM-5 catalyst at initial pH of 3.4. The effects of amount of H₂O₂, concentration of the catalyst and temperature were investigated on R6G oxidation and kinetics of the oxidation reaction was studied over this catalyst.

3.2. The influence of H₂O₂ amount on oxidation

Before investigating the influence of H₂O₂ amount on oxidation of Rhodamine 6G (R6G), blank experiments were carried out. In the absence of the catalyst, when H₂O₂ was present alone, a color removal of 91% was recorded, but no degradation was achieved. In the presence of CuFeZSM-5 catalyst alone (without H₂O₂) neither color removal nor degradation was obtained at initial pH of 3.4 after a reaction time of 2 h. These results show that CuFeZSM-5 catalyst is effective when it is present in the dye solution with H₂O₂ together.

The catalytic oxidation runs for different H₂O₂ concentrations were carried out using the following operational conditions: Initial pH of 3.4, catalyst amount of 0.15 g/0.15 dm³, initial concentration of R6G of 0.1 g/dm³, temperature of 323 K. The results are presented in Fig. 3. The increase in H₂O₂ concentration from 10 to 80 mmol accelerated the initial decolorization rate of Rhodamine 6G from 4.72×10^{-6} to 9.26×10^{-6} mol/dm³ min. This phenomenon can be explained by the effect of OH• radicals produced additionally. However, color removal after 2 h of reaction duration was not altered significantly with the increase in the mole ratio of H₂O₂ and dye from 9:1 to 75:1 for a reaction time of 120 min. At H₂O₂ initial concentration of 10 mmol/0.15 dm³ 97.7% and at 20 mmol/0.15 dm³ 100% decolorization were obtained after 2 h of reaction. However, at doses of 40 and 80 mmol H₂O₂, almost complete color removal was achieved after 45 min of reaction time. Similar result has been reported by Chaliha and Bhattacharyya [16] in the wet oxidative removal of 2,4,6-trichlorophenol in water using Fe (III), Co (II), Ni (II) supported MCM41 catalysts. This could be explained by different by-products coming from the partial oxidation of the dye.

For the intermediate H₂O₂ concentrations (20 and 40 mmol), a similar behavior in term of degradation was observed (60.4% and 59.1%). Whereas the reaction took place more slowly when the concentration was the lowest (10 mmol) or the highest (80 mmol). The increase of the oxidant concentration from 10 mmol to 40 mmol led to an increase in degradation from 52.9% to 59.1%, because more radicals would be formed. Nevertheless, for the highest H₂O₂ concentration (80 mmol) degradation of naphthalene ring decreases to 48%. This was because of the scavenging of HO• radicals which occurs by the following reaction:



Produced hydroperoxyl radicals (HO₂•) are less reactive than OH• species. The existence of an optimum H₂O₂ concentration is well known in Fenton's oxidation. The selection of the optimum value is important from the commercial point of view (due to the cost of H₂O₂). This optimum value, for the conditions used in this study, seems to be 40 mmol rather than 20 mmol because initial decolorization rate at 40 mmol of H₂O₂ is much higher than that at 20 mmol of H₂O₂ (Fig. 3a). Solution pH was not affected significantly by H₂O₂ concentration used in the run, Fig. 3c. TOC removal at different H₂O₂ concentrations are presented in Fig. 3d at an initial pH of 3.4. The increase of H₂O₂ amount from 20 to 80 mmol causes a drastic enhancement in TOC removal from 1.7% to 69.6%. The increase of TOC elimination and the decrease of naphthalene ring removal with hydrogen peroxide concentration indicate that benzene ring removal is enhanced by the increase of H₂O₂ concentration. The effect of H₂O₂ on degradation and TOC removal being similar to those reported by Ramirez et al. [4] in the Fenton-like oxidation of Orange II solutions over heterogeneous catalysts based on saponite clay, by Dutta et al. [26] in the chemical oxidation of methylene blue using a Fenton-like reaction, by Guedes et al. [27] in the Fenton oxidation of cork cooking waste water and by Stoljarova et al. [3] in oxidative degradation of Rhodamine 6G over FeZSM-5 zeolites.

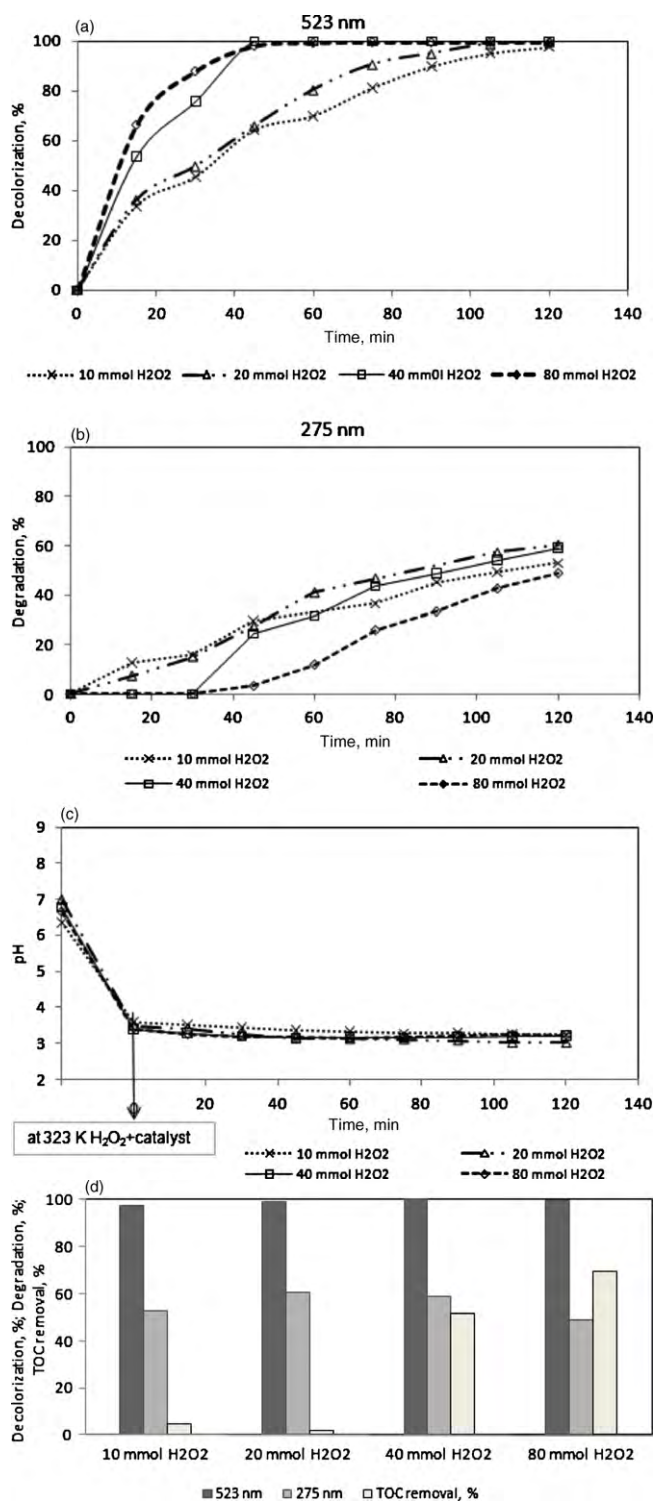


Fig. 3. Catalytic oxidation runs for different H₂O₂ concentrations on CuFeZSM-5 catalyst (a) decolorization, (b) degradation %, (c) pH value, (d) TOC % removal (Initial concentration of R6G = 0.1 g/dm³, temperature = 323 K, catalyst amount = 0.15 g, solution volume = 0.15 dm³, pH 3.4).

3.3. The influence of catalyst concentration

The influence of catalyst concentration on azo dye R6G removal using CuFeZSM-5 catalyst was studied by using 0.15 g (1 g-cat./dm³-soln.) and 0.3 g catalyst (2 g-cat./dm³-soln.) for 0.15 dm³ dye solution under the following reaction conditions: Initial R6G concentration of 0.1 g/dm³, temperature of 323 K, initial pH of

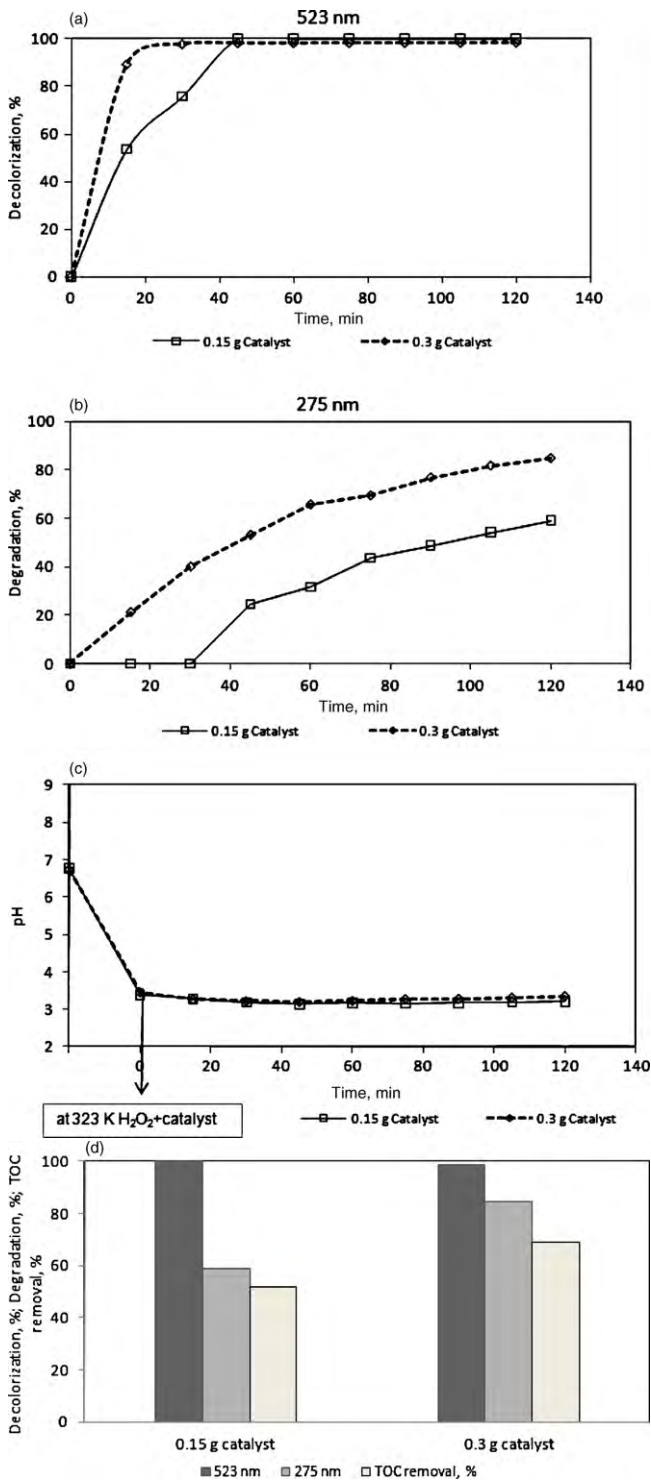


Fig. 4. Catalytic oxidation runs for different catalyst concentrations on CuFeZSM-5 catalyst (a) decolorization, (b) degradation %, (c) pH value, (d) TOC % removal (Initial concentration of R6G = 0.1 g/dm³, temperature = 323 K, H₂O₂ amount = 40 mmol, solution volume = 0.15 dm³, pH 3.4).

3.4. Results are presented in Fig. 4. A significant increase in initial color removal rate was observed when catalyst concentration was increased from 1 to 2 g/dm³. A complete color removal was achieved after 45 min of reaction time for both of the catalyst concentrations. Nevertheless, degradation was more efficient than color removal throughout the catalytic process with 2 g/dm³ catalyst concentration; 84.6% removal with 2 g/dm³ catalyst, but 59.1%

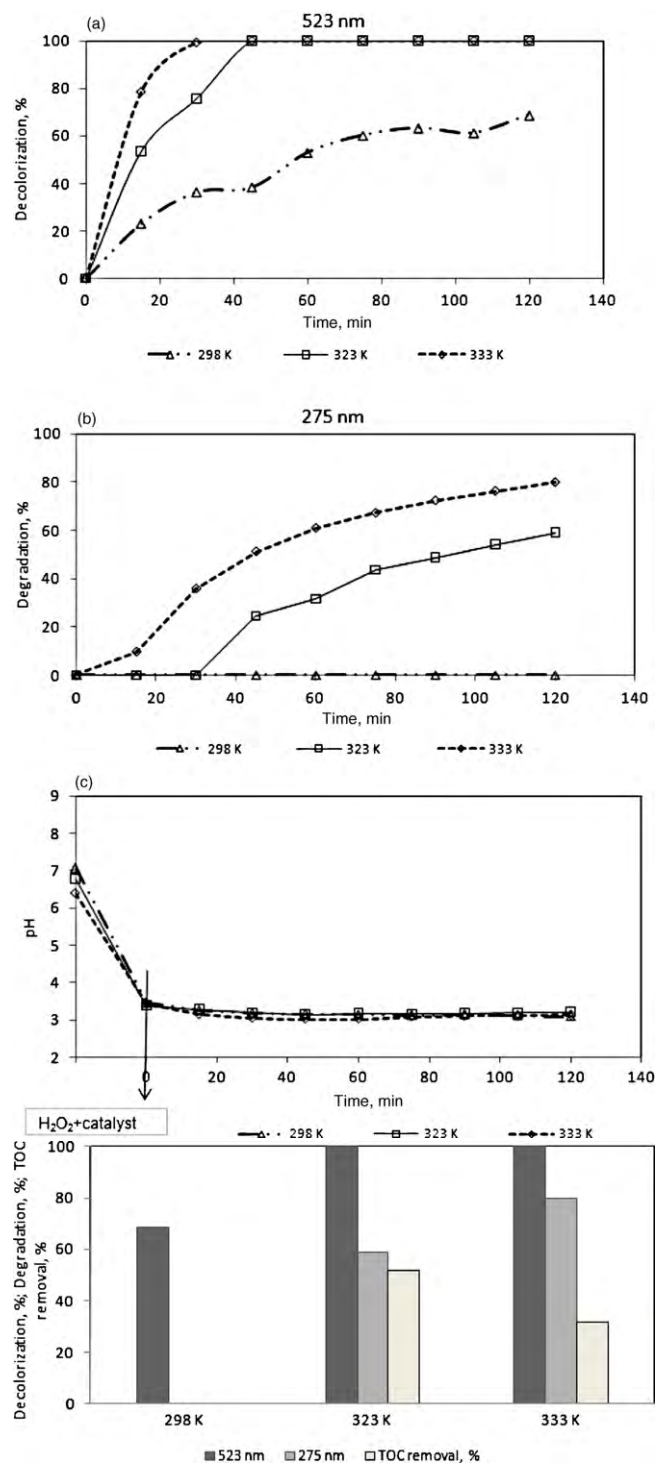


Fig. 5. Catalytic oxidation runs for different temperatures on CuFeZSM-5 catalyst (a) decolorization, (b) degradation %, (c) pH value, (d) TOC % removal (Initial concentration of R6G = 0.1 g/dm³, catalyst amount = 0.15 g, H₂O₂ amount = 40 mmol, solution volume = 0.15 dm³, pH 3.4).

with 1 g/dm³ of catalyst. Solution pH was not affected by catalyst concentration, Fig. 4c. Iron and copper loss by leaching from the catalyst in the 2 g of catalyst/dm³ experiment were measured to be 3.45% and 100%, respectively. This result was very similar to that obtained by 1 g of catalyst/dm³ experiment.

TOC removal increased with increasing amount of catalyst, Fig. 4d. When the catalyst amount was doubled, TOC elimination changed from 51.8% to 68.8%. Similar trend for the influence of cat-

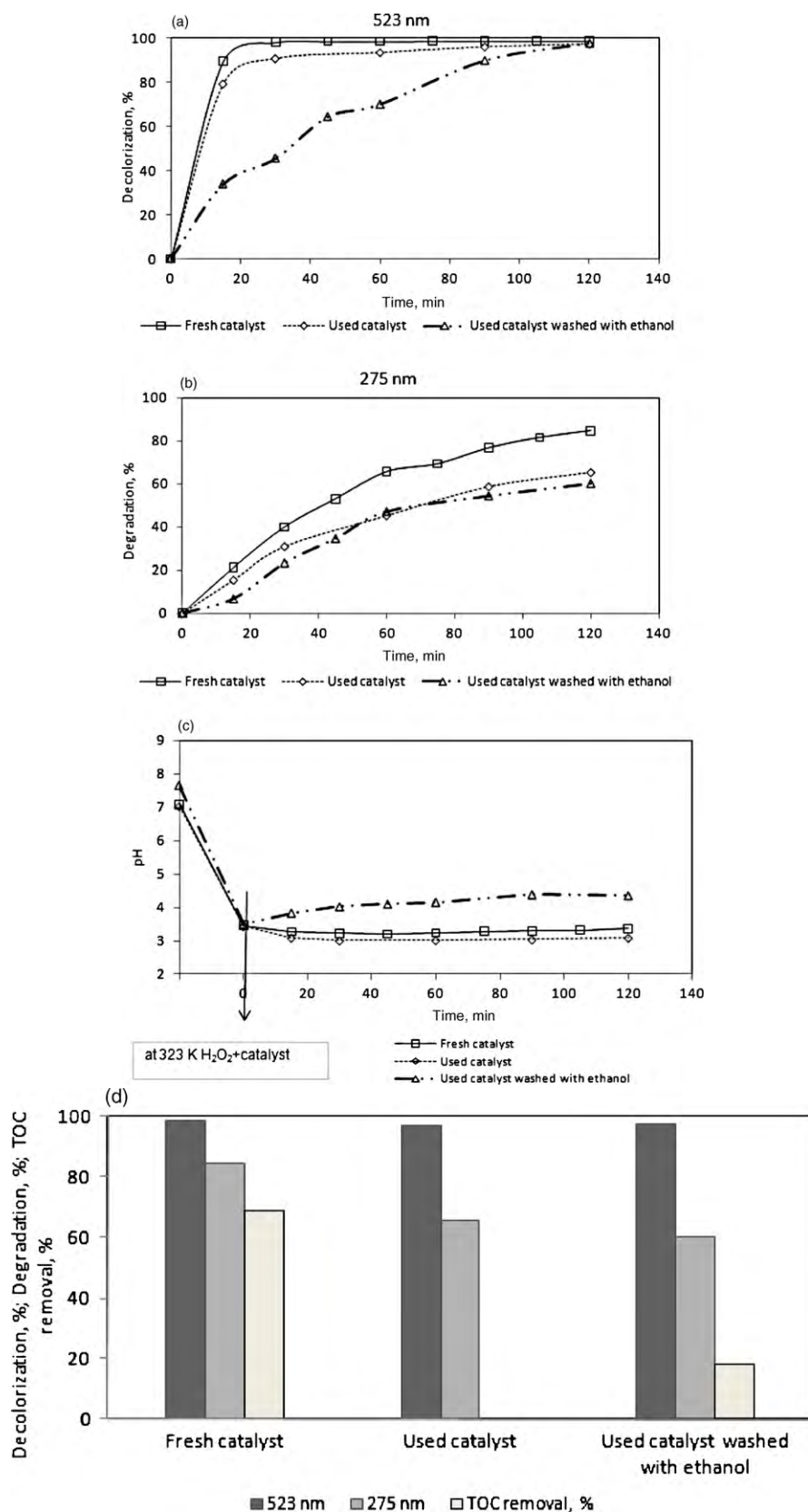


Fig. 6. Oxidation of Rhodamine 6G over CuFeZSM-5 at an initial pH of 3.4 with fresh and used catalyst (a) decolorization, (b) degradation %, (c) pH value, (d) TOC % removal (Initial concentration of R6G = 0.1 g/dm³, catalyst amount = 0.3 g, temperature = 323 K H₂O₂ amount = 40 mmol, solution volume = 0.15 dm³, pH 3.4).

alyst concentration on dye oxidation was reported by Neamtu et al. [2] for CWPO of reactive azo dye Procion Marine H-EXL over Fe-exchanged Y zeolite.

3.4. Temperature effect

The degradation kinetics of aqueous dye solution was investigated for different temperatures, 298, 323 and 333 K under the following conditions over CuFeZSM-5 catalyst: initial R6G concentration of 0.1 g-dye/dm³, catalyst amount of 0.15 g/0.15 dm³ dye solution, initial pH of 3.4. The results presented in Fig. 5 showed clearly that the color removal rate and degradation rate increased with increasing temperature, which was expected due to the exponential dependency of the rate constant with the reaction temperature. The lowest decolorization degree was measured at a temperature of 298 K. Nevertheless, complete color removal was obtained after 45 min of reaction time at 323 and 333 K.

As expected, degradation increased with the temperature being 59.1% at 323 K and 79.8% at 333 K. No degradation was observed at 298 K.

Fig. 5d presents the effect of temperature on TOC abatement. No TOC removal was obtained at 298 K and TOC elimination was enhanced with the increase in temperature from 298 to 323 K where it was 51.8%. Nevertheless, the TOC elimination obtained at 333 K was lower (31.8%) than that at 323 K (51.8%). Similar result has been found during CWPO of Orange II over Fe-saponite catalysts [4]. The lower performance achieved than expected at high temperatures was attributed to the accelerated decomposition of H₂O₂ into oxygen and water which causes a decrease in degradation degree of dye. On the other hand, the low TOC removal at higher temperature (333 K) may be explained by the production of small organic molecular fragments which are not completely mineralized under the oxidation conditions used [2].

3.5. Stability and recycling of the catalyst

For a practical implementation of a heterogeneous catalytic system, it is crucial to evaluate the stability of the catalysts. To recover the catalyst, the final effluent was filtrated and dried or washed with ethanol. These catalysts were called as used catalyst and used catalyst washed with ethanol, respectively. The latter one was calcined by heating to 423 K and keeping there for 15 min then heating to 873 K and keeping at this temperature for 2 h to remove the adsorbed organic species from the active sites [4,28]. The activities of these catalysts in R6G decolorization and degradation were presented in Fig. 6. Eventhough initial decolorization rate became lower than with fresh catalyst, no significant decay in decolorization degree of the dye solution was observed after a reaction time of 2 h when used catalyst or used catalyst washed with ethanol were tested. However, an appreciable activity decay, from 84.6% with fresh catalyst to 65.5% with used catalyst and to 60.2% with used catalyst washed with ethanol was measured in naphthalene ring removal of Rhodamine 6G dissolved in water. A pronounced decay in initial degradation rate was obtained on used catalyst washed with ethanol. The results showed that the loss of activity could not be attributed to poisoning of the catalytic sites due to the adsorbed organic species as thermal treatment was applied. The lower activity of the used and washed catalyst could be due to copper leaching from the catalyst. There was no copper in the used catalyst. Thus, synergetic effect of copper was not included in the reactions with used catalyst and used catalyst washed with ethanol.

Solution pH was not affected (around 3.1–3.4) by the presence of fresh and used catalyst in the system. However, when catalyst washed with ethanol was used in oxidation, reaction was preceded at a higher pH of 4.4.

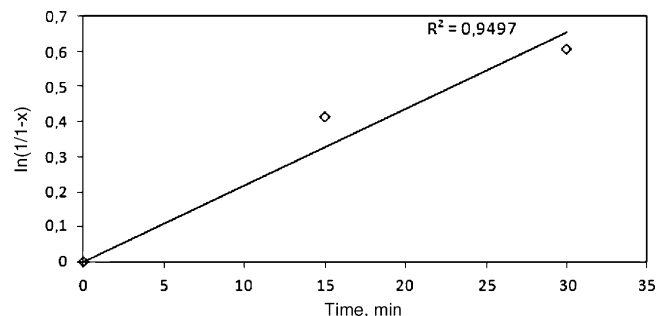


Fig. 7. $\ln(1/(1-x))$ vs. time plot at 323 K in the presence of 10 mmol H₂O₂.

TOC elimination measured with used catalyst is shown in Fig. 6d. There was no TOC removal with used catalyst. However, after the used catalyst was washed with ethanol and then calcined, a TOC removal of 18.3% was measured which was much lower than that with fresh catalyst (68.8%).

3.5.1. Decolorization kinetics of catalytic oxidation of Rhodamine 6G

The decolorization kinetics was determined for initial rate, $-r_{A0}$, over CuFeZSM-5 catalyst at initial pH of 3.4. Data at reaction times of 0, 15 and 30 min were used for initial rate calculations. For determining the reaction order, several orders were tested and first order rate equation best fit the initial data. For this purpose, a plot of $\ln(1/(1-x))$ vs. time (where x is decolorization degree) was drawn by using decolorization data in the range of 0–30 min for a known amount of H₂O₂ added to the solution initially. Fig. 7 presents that plot for R6G initial concentration of 0.1 g/dm³ (2.087×10^{-4} mol/dm³) at 323 K in the presence of 10 mmol H₂O₂.

First order dependency of decolorization rate was in a good accordance with those reported in literature for dyes [2,29,30].

The order with respect to H₂O₂ concentration was determined by plotting $\ln(-r_{A0})$ against $\ln(C_{H_2O_2,0})$. The slope of the straight line obtained was equal to the order with respect to concentration of H₂O₂. Fig. 8 presents the variation of initial rate with respect to initial concentration of H₂O₂ for R6G initial concentration of 0.1 g/dm³ over CuFeZSM-5 catalyst at initial pH of 3.4 and 323 K. As seen from Fig. 8, order was equal to 0.3481–0.35 in the range of 10–80 mmol initial concentration of H₂O₂.

Fig. 9 presents the Arrhenius plot of $\ln k$ vs. $1/T$ obtained by using the decolorization data for 40 mmol (0.267 mol/dm³) H₂O₂ and 2.087×10^{-4} mol/dm³ R6G at different temperatures, namely 298, 323 and 333 K.

From the slope of Arrhenius plot in Fig. 9, $-E/R$, where R is universal gas constant (8.314×10^{-3} kJ/molK), activation energy (E) was calculated to be 24.83 kJ/mol. Consequently, initial decoloriza-

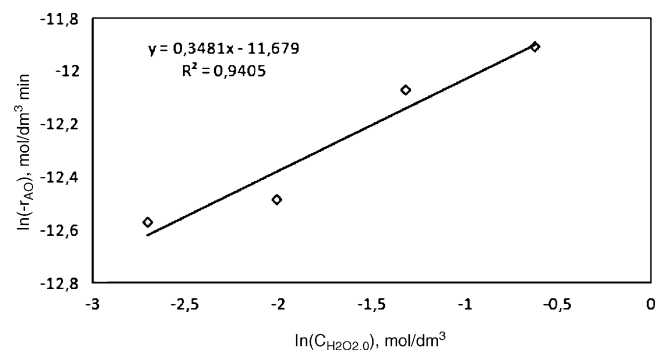


Fig. 8. Variation of initial rate with respect to initial concentration of H₂O₂.

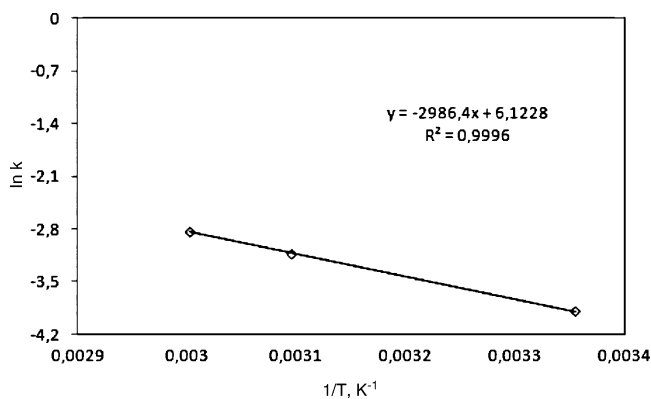


Fig. 9. Arrhenius plot of $\ln k$ vs. $1/T$.

tion rate can be expressed by the following equation;

$$-r_{A0} = 4.56 \times 10^2 e^{-24.83/RT} C_{R6G,0}^{0.35} C_{H_2O_2,0}$$

Activation energy of 35.9 kJ/mol was reported for the rapid decolorization of azo dye methyl orange in aqueous solution by nanoscale zerovalent iron particles [31]. Moreover, activation energy of homogeneous catalytic Fenton oxidation of Reactive Brilliant Blue X-BR azo dye was given in literature to be 25.21 kJ/mol [32]. The activation energy obtained in this study for oxidation of R6G was very close to that given for the latter azo dye oxidation.

4. Conclusions

Higher activities were obtained over CuFeZSM5 catalyst compared to FeZSM-5. This was due to the presence of Cu. Higher color removal and degradation were observed at initial solution pH of 3.4 compared to pH of 6.5. A color removal of 100% was obtained after a reaction time of 45 min over CuFeZSM-5 catalyst at low pH. Degradation and TOC elimination were measured to be 59.1% and 51.8% after an oxidation time of 2 h. The decrease of color removal and degradation at high pH was attributed to the accelerated formation of less reactive hydroperoxyl radicals, HO_2^* , rather than OH^* radicals. The increase in H_2O_2 concentration from 10 to 80 mmol increased initial decolorization rate of Rhodamine 6G. Initial color removal rate increased significantly with the catalyst amount. TOC elimination changed depending on the temperature of the solution. It first increased and then decreased. This phenomenon was explained by the accelerated decomposition of H_2O_2 into oxygen and formation of small organic molecules which were not completely mineralized under the reaction conditions studied. Reaction activation energy was calculated as 24.83 kJ/mol.

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