



Catalytic wet peroxide oxidation of azo dye (Congo red) using modified Y zeolite as catalyst

Arun Kumar Kondru, Pradeep Kumar, Shri Chand*

Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee 247667, India

ARTICLE INFO

Article history:

Received 6 July 2008

Received in revised form 7 November 2008

Accepted 11 November 2008

Available online 24 November 2008

Keywords:

Catalytic wet peroxide oxidation

Y zeolite

Hydrogen peroxide

Azo dye

Congo red

ABSTRACT

The present study explores the degradation of azo dye (Congo red) by catalytic wet peroxide oxidation using Fe exchanged commercial Y zeolite as a catalyst. The effects of various operating parameters like temperature, initial pH, hydrogen peroxide concentration and catalyst loading on the removal of dye, color and COD from an aqueous solution were studied at atmospheric pressure. The percent removals of dye, color and COD at optimum pH₀ 7, 90 °C using 0.6 ml H₂O₂/350 ml solution and 1 g/l catalyst was 97% (in 4 h), 100% (in 45 min) and 58% (in 4 h), respectively. The % dye removal has been found to be less in comparison to % color removal at all conditions, e.g. dye removal in 45 min and at above conditions was 82%, whereas the color removal was 100%. The results indicate that the Fe exchanged Y zeolite is a promising catalyst for dye removal. Fe exchanged catalyst is characterized using XRD, SEM/EDAX, surface area analyzer and FTIR. Though the dye, color and COD removals were maximum at pH₀ 2 but as the leaching of Fe from the catalyst was more in acidic pH range, pH₀ 7 was taken as operating pH due to almost comparable removals as of pH₀ 2 and no leaching of Fe ions.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Reactive azo dyes from textile and dyeing industries pose grave environmental problem. An estimate shows that textiles account for 14% of India's industrial production and around 27% of its export earnings [1]. Production during 2006 registered a growth of about 3.5% at 29,500 tonnes and the textile industry accounts for the largest consumption of dyestuffs at nearly 80% [2]. The waste containing these azo dyes is non-degradable. The process of dyeing is a combination of bleaching and coloring, which generates huge quantities of wastewaters causing environmental problems. The effluents from these industries consist of large quantities of sodium, chloride, sulphate, hardness, carcinogenic dye ingredients and total dissolved solids with very high BOD and COD values over 1500 mg/l and over 5000 mg/l, respectively [3].

Various methods have been used for dye removal like adsorption, coagulation, electrocoagulation, Fenton's reagent and combination of these processes. Though these treatment processes are efficient in dye removal, they generate adsorbed waste/sludge, etc. which further causes a secondary pollution. In wet oxidation the sludge is disposed off to a great extent by oxidizing the organic pollutant. Catalytic wet oxidation method (CWAO and CWPO) is gaining more popularity. CWPO process using H₂O₂, in particular has advantages like better oxidation ability than using oxygen,

as the former is carried out at lower pressure (atmospheric pressure).

WAO usually acts under high temperatures (200–325 °C) and pressure (50–150 bar). A comparable oxidation efficiency is obtained at a less temperature of 100–120 °C when using hydrogen peroxide as the oxidizing agent instead of oxygen [4]. WAO is capital intensive whereas WPO needs limited capital but generates little higher running costs [4].

Rivas et al. [5] showed that the addition of H₂O₂ (as a source of free radicals) enhanced wet air oxidation of phenol, a highly non-degradable substance and found that the combined addition of H₂O₂ and a bivalent metal (i.e. Cu, Co or Mn) enhanced the rate of phenol removal. Various oxidation catalysts have been studied for the removal of different compounds like phenol, benzoic acid, dyes, etc. by CWPO process. Catalysts like Fe₂O₃/CeO₂ and WO₃/CeO₂ in the removal of phenolic solution, (Al–Fe) pillared clay named FAZA in the removal of 4-hydroxybenzoic acid, mixed (Al–Fe) pillared clays in the removal of organic compounds have been used [6–8].

Removal of dyes by CWPO process is gaining importance in recent times with a large number of catalysts. Kim and Lee [9] used Cu/Al₂O₃ and copper plate in treatment of dye house effluents. Liu and Sun [10] removed acid orange 52, acid orange 7 and reactive black 5 using CeO₂ doped Fe₂O₃/γ-Al₂O₃ from dye waste water. Kim and Lee [11] reported the treatment of reactive dye solutions by using Al–Cu pillared clays as catalyst.

Among these catalysts, modified zeolites are preferred for improved efficiency, lower by-product formation and less severe experimental conditions (temperatures and pressures). The

* Corresponding author. Tel.: +91 1332 285217; fax: +91 1332 276535.
E-mail address: schanfch@iitr.ernet.in (S. Chand).

Nomenclature

COD	chemical oxygen demand (kg/m ³)
CWAO	catalytic wet air oxidation
CWPO	catalytic wet peroxide oxidation
pH ₀	initial pH
pH _f	final pH
PCU	platinum cobalt unit (Pt–Co)
<i>t</i>	time
WAO	wet air oxidation
WPO	wet peroxide oxidation

improved efficiency of the catalyst is ascribed to its structure and large surface area with the ability of forming complex compounds. Zeolites can be ion exchanged using transition metal ions like Fe, Cu, Mn and others like Ca, Ba, etc. Zeolites are negatively charged because of the substitution of Si(IV) by Al(III) in the tetrahedral accounts for a negative charge of the structure and hence the Si/Al ratio determines the properties of zeolites like ion exchange capacity [12]. These metal ions neutralize the negative charge on zeolites and their position, size and number determine the properties of zeolite. These metal ions are fixed to the rigid zeolite framework which prevents leaching and precipitation in various reactions [13–21].

In this work, catalytic wet peroxide oxidation of Congo red azo dye using Fe exchanged Y zeolite has been presented. Effect of variables like temperature, initial pH, peroxide concentration and catalyst loading on catalytic wet peroxide oxidation were examined and the optimum conditions evaluated.

2. Materials and methods

2.1. Chemicals

Hydrogen peroxide (30% analytical grade), manganese dioxide, sodium hydroxide pellets (AR) and hydrochloric acid were obtained from RFCL limited (Mumbai), India. Congo red was obtained from Loba Chemie Pvt. Ltd. (Mumbai) and were obtained from RFCL limited (Mumbai), India.

Commercial Na–Y zeolite was obtained from Sud chemie Pvt. Ltd. (Baroda), India. Commercial catalyst was iron exchanged with excess 1 M Fe(NO₃)₃ at 80 °C for 6 h. The process was repeated three times and the sample was thoroughly washed with distilled water and dried in oven in air at 60 °C for 10–12 h. The amount of iron exchanged was 1.53 wt% estimated by A.A.S.

2.2. Apparatus and procedure

The experimental studies were carried out in a 0.5 l three-necked glass reactor equipped with a magnetic stirrer with heater and a total reflux (Fig. 13). Water containing Congo red dye was transferred to the three-necked glass reactor. Thereafter, the catalyst was added to the solution. The temperature of the reaction mixture was raised using heater to the desired value and maintained by a P.I.D. temperature controller, which was fitted in one of the necks through the thermocouple. The raising of the temperature of the reaction mixture to 90 °C from ambient took about 30 min. The total reflux prevents any loss of vapor and magnetic stirrer to agitate the mixture. Hydrogen peroxide was added, the runs were conducted at 90 °C and the samples were taken at periodic intervals. The samples after collection were raised to pH-11 by adding 0.1N NaOH (so that no further reaction takes place) and the residual hydrogen peroxide was removed by adding MnO₂ which catalyzed the decomposition of peroxide to water and oxygen. The samples

were allowed to settle for overnight or one day (or centrifuged) and filtered. The supernatant was tested for color and COD. After the completion of the run, the mixture was allowed to cool and settle overnight.

2.3. Characterization

The determination of structure of the heterogeneous catalyst was done by X-ray diffractometer (Bruker AXS, Diffraktometer D8, Germany). The catalyst structure was confirmed by using Cu K α as a source and Ni as a filter. Goniometer speed was kept at 1°/min and the chart speed was 1 cm/min. The range of scanning angle (2 θ) was kept at 3–60°. The intensity peaks indicate the values of 2 θ , where Bragg's law is applicable. The formation of compounds was tested by comparing the XRD pattern using JCPDS files (1971). The determination of images and composition of catalyst were done by SEM/EDAX QUANTA 200 FEG. Scanning for zeolite samples was taken at various magnifications and voltage to account for the crystal structure and size. From EDAX, the composition of the elements in weight percentage and atomic percentage were obtained along with the spectra for overall compositions and particular local area compositions. BET surface area of the samples was analyzed by Micromeritics CHEMISORB 2720. The FTIR spectra of the catalyst was recorded on a FTIR Spectrometer (Thermo Nicolet, USA, Software used: NEXUS) in the 4000–480 cm⁻¹ wave number range using KBr pellets. The internal tetrahedra and external linkage of the zeolites formed are identified and confirmed by FTIR. The IR spectra data in Table 2 is taken from literature [22].

2.4. Analysis

The amount of the dye present in the solution was analyzed by direct reading TVS 25 (A) Visible Spectrophotometer. The visible range absorbance at the characteristic wavelength of the sample at 497 nm was recorded to follow the progress of decolorization during wet peroxide oxidation.

The COD of the dye solution was estimated by the Standard Dichromator Closed Reflux Method (APHA-1989) using a COD analyzer (Aqualytic, Germany). The color in Pt–Co unit was estimated using a color meter (Hanna HI93727, Hanna Instruments, Singapore) at 470 nm and the pH was measured using a Thermo Orion, USA make pH meter. The treated dye solutions were centrifuged (Model R24, Remi Instruments Pvt. Ltd., Mumbai, India) to obtain the supernatant free of solid MnO₂.

A.A.S (Avanta GBC, Australia) was used to find the amount of iron exchanged and leached.

3. Results and discussion

Due to the iron present after the exchange process, the Y peaks diminished along with the rise in Fe peaks. Similar phenomena has also been observed by Yee and Yaacob [23] who obtained zeolite iron oxide by adding NaOH and H₂O₂ (drop wise) at 60 °C to Na–Y zeolite. XRD pattern (Fig. 2) showed diminishing zeolite peaks along with evolution of peaks corresponding to γ -Fe₂O₃ with increasing NaOH concentration. The IR assignments from FTIR (Fig. 3) remain satisfied even after iron exchanging. The EDAX data (Table 1) show clearly an increase in the value of Fe conc. after ion exchange of Y-zeolite. The BET surface area (Table 1) has been found to decrease from 433 to 423 m²/g after Fe exchange. SEM image is shown in Fig. 1. Table 2 presents FTIR specifications of zeolites (common to all zeolites).

The effect of temperature, initial pH, hydrogen peroxide concentration and catalyst loading on catalytic wet peroxide oxidation of azo dye Congo red were investigated in detail.

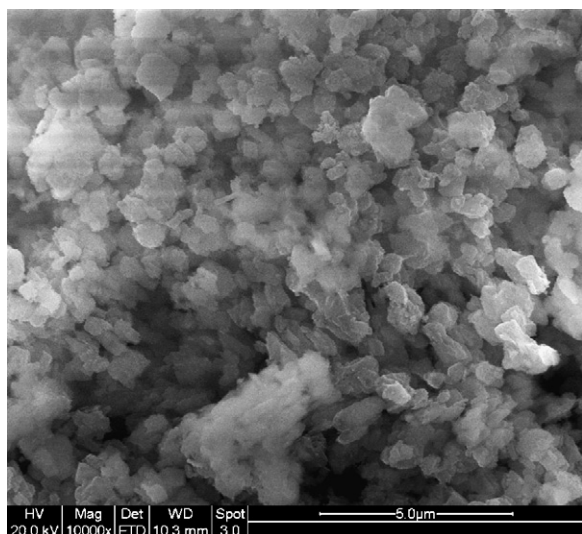


Fig. 1. SEM image of Fe-exchanged Y zeolite.

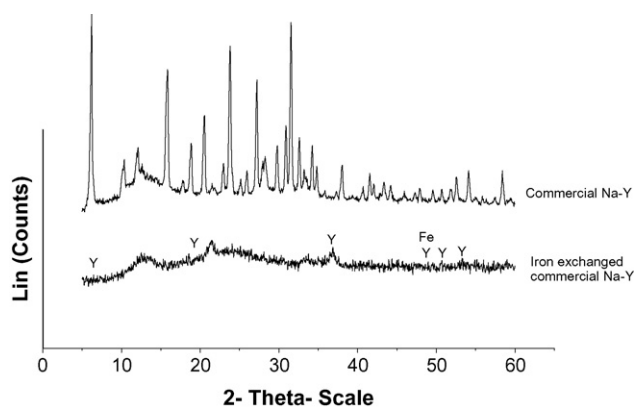


Fig. 2. XRD of commercial and Fe-exchanged commercial Y zeolite.

3.1. Effect of temperature on dye, color and COD removal

The temperatures during the experiments were varied from 50 °C to 100 °C. A maximum conversion of dye of 99.1% was observed at 100 °C in 4 h (and 97% at 90 °C). The dye removals at

Table 1
Surface area and composition of commercial and Fe exchanged Y zeolite from EDAX.

	Fe commercial Y (wt%)	Commercial Y (wt%)
C	08.03	08.22
O	44.31	43.72
Na	00.35	04.60
Mg	00.39	00.35
Al	00.58	8.69
Si	34.34	30.84
P	00.27	00.26
S	00.51	00.51
K	00.15	00.17
Ca	00.17	00.18
Ba	00.00	00.00
Ti	00.48	00.45
Mn	00.68	00.67
Fe	09.74	01.34

BET surface area (commercial Na-Y): 433.4 m²/g.

BET surface area (Fe exchanged commercial Na-Y): 423 m²/g.

Table 2
Zeolite IR assignments (common for all zeolites) from FTIR.

Internal tetrahedral:	
Asymmetric stretch (cm ⁻¹)	1250–950
Symmetric stretch (cm ⁻¹)	720–650
T–O bend (cm ⁻¹)	420–500
External linkage:	
Double ring (cm ⁻¹)	650–500
Symmetric stretch (cm ⁻¹)	750–820
Asymmetric stretch (Sharp) (cm ⁻¹)	1050–1150

80 °C, 70 °C, 60 °C and 50 °C and at 4 h are 56%, 52%, 42% and 30%, respectively. Fig. 4 shows that at a particular temperature, the dye concentration gradually decreases with time. The initial red color of the dye solution decreased into brown color in due course and finally the brown color disappeared into a colorless solution. Dye concentration decreases at faster rates with temperatures for initial 30 min and thereafter it decreases from 1 h to 2 h. The initial concentrations of dye did not change after a brief contact period of dye solution with the Fe-exchanged zeolite catalyst (before CWPO) confirming that there is negligible adsorption of the dye by the catalyst.

Fig. 5 shows the results obtained for color removal as a function of time and temperature. The maximum color removal (100%) is obtained at 100 °C in 30 min and also at 90 °C in 45 min. At a particular temperature, the color continuously decreases with time at

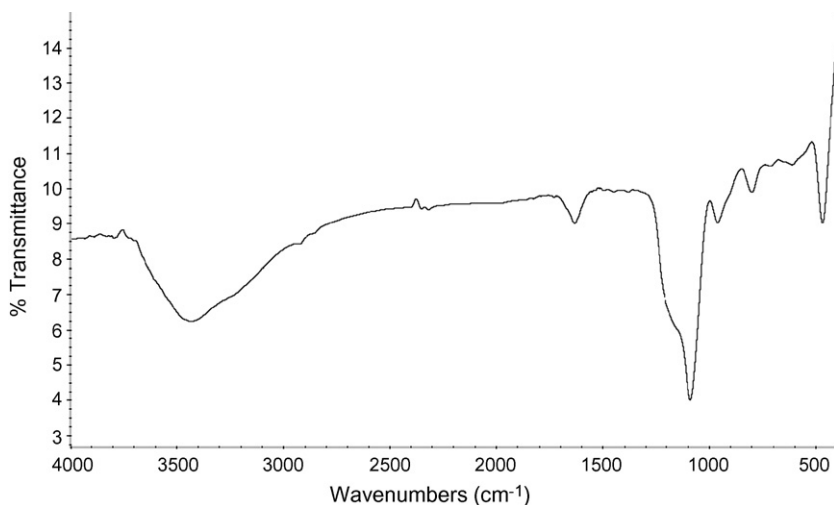


Fig. 3. FTIR of Fe-exchanged Y zeolite.

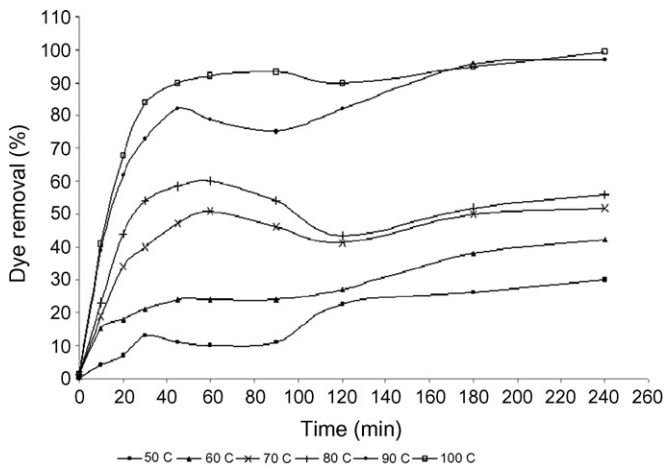


Fig. 4. % dye removal as function of temperature.

faster rate in first few minutes until a certain point ($t = 45$ min) and then remaining almost unchanged. At 50 °C, the color removal is very low, whereas at 60 °C, there is a sudden shift towards its greater removal. The color removal is much higher at higher temperatures (70–100 °C).

Fig. 6 depicts the results obtained for %COD removal as a function of time and temperature. A maximum COD removal of 66% was obtained at 100 °C (at 4 h) followed by 58% at 90 °C (at 4 h). Until 60 °C, the rate of COD removal is less and during 70–100 °C, the rate is much faster.

3.2. Effect of initial pH on dye, color and COD removal

The influence of initial pH on dye (Congo red) removal was studied at different pH (pH_0 2, 4, 7, 8, 9 and 11) without any adjustment of pH during the experiments. A maximum conversion of 99% was obtained at pH_0 2 followed by 97% at pH_0 7. The dye removal at pH_0 4, 8, 9 and 11 were 94%, 29%, 5% and 0.6%, respectively. All the runs were conducted for 4 h duration. The color of the solution is violet blue at pH_0 2 (a colloidal solution) and greenish blue at pH_0 4 (colloidal solution). In neutral and basic pH_0 (7, 8, 9 and 11) range, color of the solution did not change during treatment and was same as original solution, i.e. red color.

Fe cations can leach out from zeolite structure into the solution causing secondary pollution. Leaching of Fe cations out of zeolites

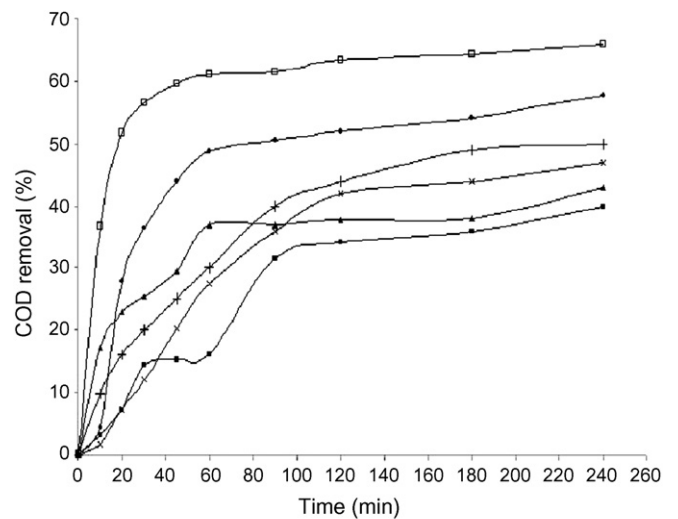


Fig. 6. %COD removal as function of temperature.

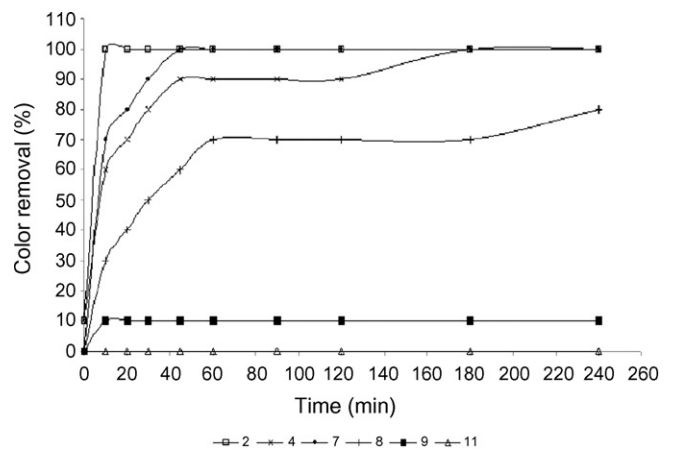


Fig. 7. % color removal as function of pH_0 .

depends strongly on pH of the solution. The leaching of iron ions was enhanced at low pH values [24,25]. In order to determine dissolved Fe concentration, final pH values of the solutions were analyzed by A.A.S. At initial pH_0 2 and 4, Fe detected in the solution was 7.8 ppm and 3.9 ppm, respectively. At pH_0 7 and in alkaline range, there was

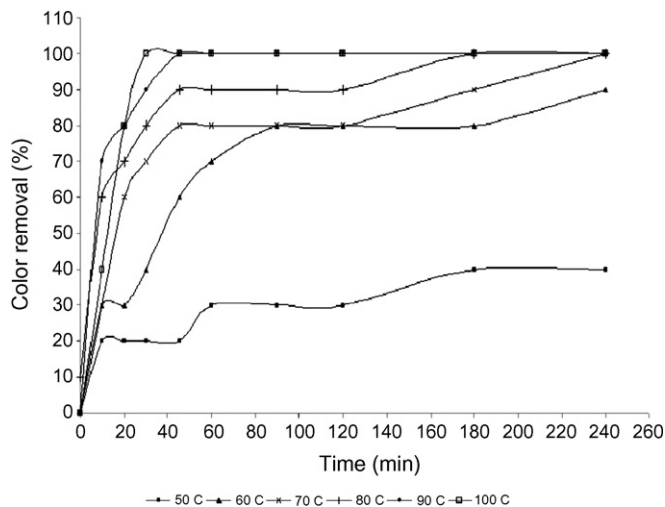


Fig. 5. % color removal as function of temperature.

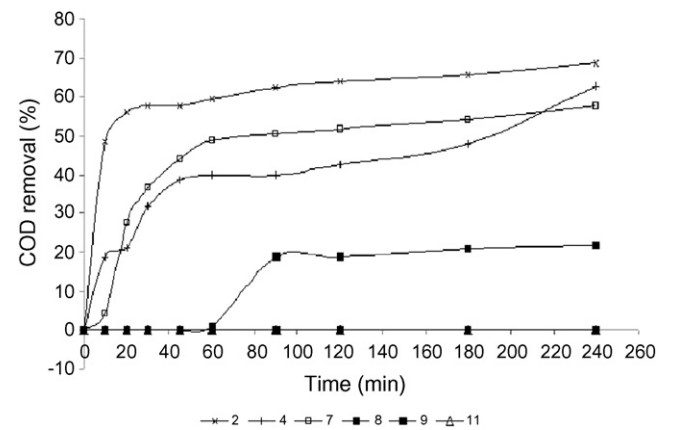


Fig. 8. %COD removal as function of pH_0 .

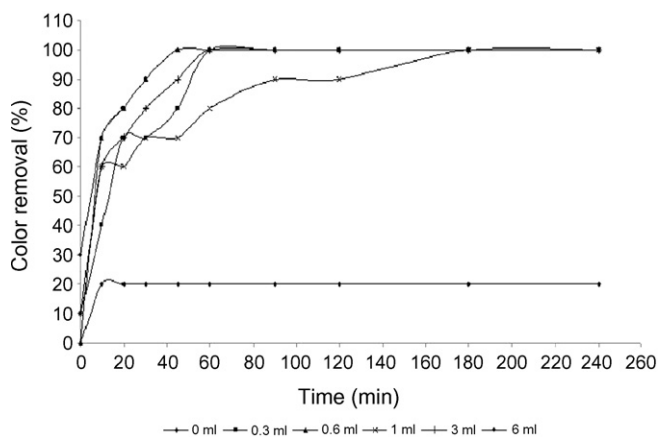


Fig. 9. % color removal as function of peroxide concentration.

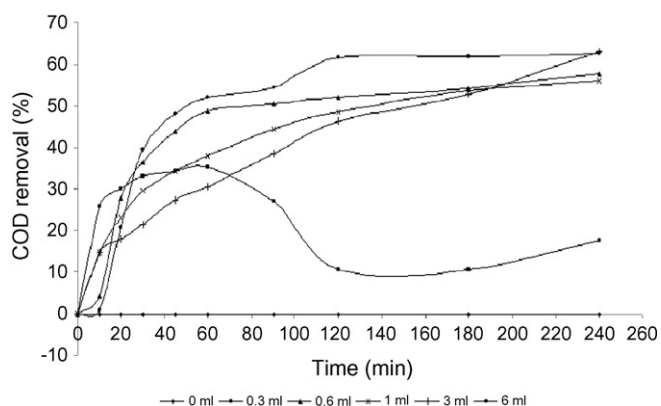


Fig. 10. %COD removal as function of peroxide concentration.

almost no leaching. pH_0 7, therefore, was chosen to be optimum pH for future experiments. The final pH values pH_f after the reaction corresponding to pH_0 2, 4, 6, 8, 9 and 11 were 2.1, 4.2, 7.2, 7.7 and 8.7, respectively. This shows that the pH_f tend to reach to neutral pH for all starting pH values.

Fig. 7 presents the results obtained for color removal as a function of time and pH_0 . A maximum color removal of 100% was obtained at pH_0 2 (in 10 min) and also at pH_0 7 (in 45 min). The color removal at a particular pH_0 decreases at a faster rate initially (0–1 h) and thereafter it has a slower rate. The lowest removal was observed at pH_0 11 with almost no removal.

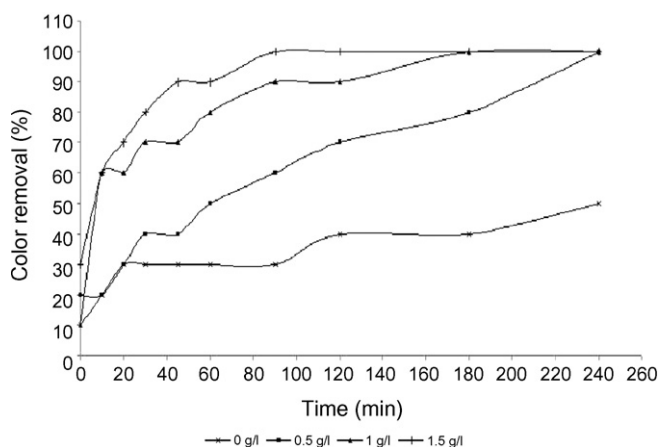


Fig. 11. % color removal as function of catalyst loading.

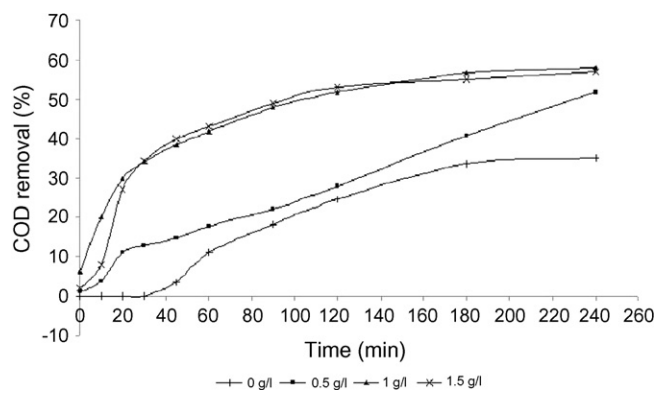


Fig. 12. %COD removal as function of catalyst loading.

The results obtained for COD removal as a function of time and pH_0 are shown in Fig. 8. A maximum COD removal of 69% was obtained at pH_0 2 in 4 h followed by 63% at pH_0 4 and 58% at pH_0 7 in 4 h. Fig. 8 shows maximum decrease in COD value in the initial 30 mins at all pH_0 . The decrease in COD is not appreciable thereafter. The COD removal is more in acidic range with a maximum removal of 69%, moderate in neutral region and least in basic region.

3.3. Effect of peroxide concentration on dye, color and COD removal

The influence of H_2O_2 concentration on dye removal was investigated at different concentrations of hydrogen peroxide (in the range 0–6 ml). A maximum removal of 99.02% was obtained at H_2O_2 concentration of 3 ml per 350 ml of solution, followed by 98.3% at 1 ml and 97% at 0.6 ml. The dye removal at H_2O_2 concentrations of 6 ml, 0.3 ml and 0 ml (and at 4 h) were 94%, 82% and 8%, respectively. The dye removal rate at 90 °C temperature is gradual at all concentrations of peroxide. At peroxide concentration of 0 ml, there is very little removal of dye, hardly 8%. Hence, it can be inferred that catalytic thermolysis (a process of effluent treatment by heating the effluent with/without catalyst) is not active and cannot be applied for dye removal.

At the beginning of the reaction, the OH^* radicals which are produced additionally when peroxide concentration is increased, speeds up the azo dye degradation. After a particular peroxide concentration, on further increase of the peroxide, the dye removal is

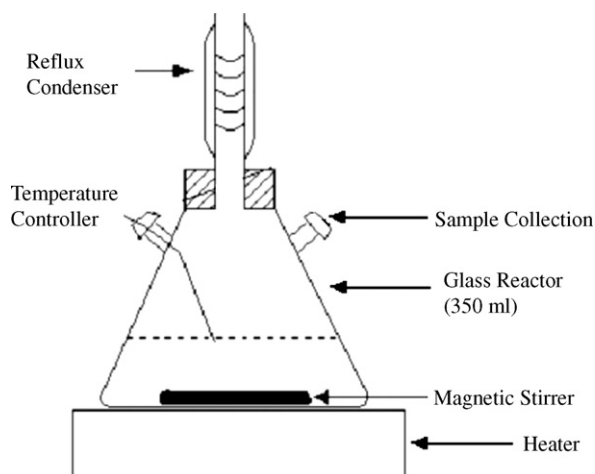


Fig. 13. Schematic diagram of the reactor.

not increased. This may be because of the presence of excess peroxide concentration, hydroperoxyl radicals (HO_2^\bullet) are produced from hydroxyl radicals that are already formed. The hydroperoxyl radicals do not contribute to the oxidative degradation of the organic substrate and are much less reactive. The degradation of the organic substrate occurs only by reaction with HO^\bullet [26].

The % color removal at a particular peroxide concentration increases at a faster rate in the initial 45 min and then at slower rates afterwards (Fig. 9). As H_2O_2 concentration increases, the rate of removal is much faster, reaching 100% in 45 min using 6 ml H_2O_2 per 350 ml solution, whereas it is 100% in 1 h for both 0.3 ml and 3 ml.

Fig. 10 shows the results obtained for COD removal as a function of time and H_2O_2 concentration. The maximum COD removal, 63% is obtained for H_2O_2 conc. 3 ml at 90 °C, pH_0 7 and 2 h duration.

3.4. Effect of catalyst loading on dye, color and COD removal

The influence of catalyst concentration on dye removal was investigated at different concentrations (in the range 0.5–1.5 g/l). A maximum dye removal of 98.6% was observed at 1.5 g/l followed by 98.3% at 1 g/l and 87.3% at 0.5 g/l in 4 h duration. The % dye removal without catalyst was very low with only 36% dye removal in 4 h. By comparing the results for the dye removal without catalyst and 1.5 g/l catalyst, the removal for 1.5 g/l is approximately three times to that of without catalyst. The rate of removal is also more for higher concentrations of catalyst and increases with it.

Fig. 11 shows the results obtained for color removal as a function of time and catalyst concentration. The maximum color removal of 100% was obtained using 1.5 g/l catalyst conc. in 1.5 h and also using 1 g/l catalyst in 3 h.

Fig. 12 presents the results obtained for %COD removal as a function of time and catalyst concentration. A maximum COD removal of 58% was obtained at catalyst conc. 1 g/l, 51.8% at 1.5 g/l and 50.5% at 0.5 g/l in 4 h. Without catalyst, the COD removal was only 35%.

4. Conclusions

The % removals of dye, color and COD by catalytic wet peroxide oxidation obtained at 100 °C, 4 h duration using 0.6 ml H_2O_2 /350 ml solution, 1 g/l Fe–Y catalyst and pH_0 7 were 99.1%, 100% (30 min) and 66%, respectively. As at 100 °C the solution has tendency to vaporize during the operation, 90 °C was taken as operating temperature. The corresponding % removals at 90 °C were 97% dye, 100% color (in 45 min) and 58% COD.

Acidic range gave higher % removals in comparison to neutral and alkaline range. At pH_0 2, the dye, color and COD removals of 99%, 100% (in 10 min) and 69% were observed after 4 h duration. As at pH_0 2, the leaching of Fe ions from Y zeolite catalyst is predominant, pH_0 7 was taken as operating pH. Fe concentration of 7.8 ppm was observed in the solution at pH_0 2. The values of removals, however, are comparable to pH_0 2, with dye removal of 97%, color removal of 100% (in 45 min) and COD removal of 58% in 4 h.

The H_2O_2 concentration was found to be optimum at 3 ml/350 ml solution giving dye, color and COD removals of 99%, 100% (in 1 h) and 63%, respectively.

The study on the effect of catalyst loading revealed 1.5 g/l as best among the catalyst concentrations studied. The results with 1 g/l and 1.5 g/l catalyst concentration were almost comparable.

References

- [1] P. Kumar, B. Prasad, I.M. Mishra, S. Chand, Decolorization and COD reduction of dyeing wastewater from a cotton textile mill using thermolysis and coagulation, *Journal of Hazardous Materials* 153 (1/2) (2008) 635–645.
- [2] K. Ranganathan, K. Karunakaran, D.C. Sharma, Recycling of wastewaters of textile dyeing industries using advanced treatment technology and cost analysis—case studies, *Resources, Conservation and Recycling* 50 (2007) 306–318.
- [3] Annual Report 2006–07, Ministry of Chemicals & Fertilisers, Department of Chemicals & Petrochemicals, Government of India.
- [4] H. Debellefontaine, M. Chakchouk, J.N. Foussard, D. Tissot, P. Striolo, Lab ingenierie procedes environment, complexe Scientifique Rangueil, Toulouse, Fr, treatment of organic aqueous wastes: wet air oxidation and wet peroxide oxidation, *Environmental Pollution* 92 (2) (1996) 155–164.
- [5] F.J. Rivas, S.T. Kolaczowski, F.J. Beltran, D.B. McLurgh, Hydrogen peroxide promoted wet air oxidation of phenol: influence of operating conditions and homogeneous metal catalysts, *Journal of Chemical Technology & Biotechnology* 74 (5) (1999) 390–398.
- [6] P. Massa, A. Dafinov, F.M. Cabello, R. Fenoglio, Catalytic wet peroxide oxidation of phenolic solutions over $\text{Fe}_2\text{O}_3/\text{CeO}_2$ and WO_3/CeO_2 catalyst systems, *Catalysis Communications* 9 (7) (2008) 1533–1538.
- [7] A.N. Nikolopoulos, O.I. Markopoulou, N. Papayannakos, Degradation of 4-hydroxybenzoic acid by combined ultrasound irradiation and catalytic wet peroxide oxidation, *Ultrasonics Sonochemistry* 11 (2004) 183–186.
- [8] J. Barrault, J.M. Tatiboue, N. Papayannakos, Catalytic wet peroxide oxidation of phenol over pillared clays containing iron or copper species, *Comptes Rendes de l'Academie des Sciences Paris, Seirie IIc, Chimie: Chemistry* 3 (2000) 777–783.
- [9] S.C. Kim, D.K. Lee, Catalytic wet peroxide oxidation of dye house effluents with $\text{Cu}/\text{Al}_2\text{O}_3$ and copper plate, *Studies in Surface Science and Catalysis* 159 (2006) (New Developments and Application in Chemical Reaction Engineering), 393–396.
- [10] Y. Liu, D. Sun, Effect of CeO_2 doping on catalytic activity of $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst for catalytic wet peroxide oxidation of azo dyes, *Journal of Hazardous Materials* 143 (2007) 448–454.
- [11] S.C. Kim, D.K. Lee, Preparation of Al–Cu pillared clay catalysts for the catalytic wet oxidation of reactive dyes, *Catalysis Today* 97 (2004) 153–158.
- [12] A. Dyer, *An Introduction to Zeolite Molecular Sieves*, Wiley, New York, 1988.
- [13] R. Aravindhan, N.N. Fathima, J.R. Rao, B.U. Nair, Wet oxidation of acid brown dye by hydrogen peroxide using heterogeneous catalyst Mn–salen–Y zeolite: a potential catalyst, *Journal of Hazardous Materials B138* (2006) 152–159.
- [14] C. Schüth, M. Reinhard, Hydrodechlorination and hydrogenation of aromatic compounds over palladium on alumina in hydrogen-saturated water, *Applied Catalysis B* 18 (1998) 215.
- [15] K. Fajerwerg, T. Castan, J.–N. Foussard, A. Ferrard, H. Debellefontaine, Dependency on some operating parameters during wet oxidation of phenol by hydrogen peroxide with Fe–ZSM-5 zeolite, *Environmental Technology* 21 (3) (2000) 337.
- [16] K.S. Lin, H.P. Wang, Supercritical water oxidation of 2-chlorophenol catalyzed by Cu^{2+} cations and copper oxide clusters, *Environmental Science & Technology* 34 (22) (2000) 4849.
- [17] P. Laidlaw, D. Bethell, S.M. Brown, G.J. Hutchings, Benzoylation of substituted arenes using Zn- and Fe-exchanged zeolites as catalysts, *Journal of Molecular Catalysis A* 174 (2001) 187.
- [18] S.K. Mohapatra, S.U. Sonavane, R.V. Jayaram, P. Selvam, Reductive cleavage of azo dyes and reduction of nitroarenes over trivalent iron incorporated hexagonal mesoporous aluminophosphate molecular sieves, *Applied Catalysis B* 46 (2003) 155–163.
- [19] E. Guelou, J. Barrault, J. Fournier, J.–M. Tatibouet, Active iron species in the catalytic wet peroxide oxidation of phenol over pillared clays containing iron, *Applied Catalysis B* 44 (2003) 1.
- [20] J.G. Carriazo, E. Guelou, J. Barrault, J.M. Tatibouet, S. Moreno, Catalytic wet peroxide oxidation of phenol over Al–Cu or Al–Fe modified clays, *Applied Clay Science* 22 (2003) 303.
- [21] K. Ojha, N.C. Pradhan, S. Amarnath, Zeolite from fly ash: synthesis and characterization, *Bulletin Materials Science* 27 (December (6)) (2004) 555–564.
- [22] M. Yee, I.I. Yaacob, Synthesis and characterization of iron oxide nanostructured particles in Na–Y zeolite matrix, *Materials Research Society* 19 (2004) 930–936.
- [23] K. Fajerwerg, H. Debellefontaine, Wet oxidation of phenol by hydrogen peroxide using heterogeneous catalysis Fe–ZSM-5: a promising catalyst, *Applied Catalysis B: Environment* 10 (1996) 229.
- [24] J. Barrault, M. Abdellaoui, C. Bouchoule, A. Majeste, J.M. Tatibouet, A. Louloudi, N. Papayannakos, N.H. Gangas, Catalytic wet peroxide oxidation over mixed (Al–Fe) pillared clays, *Applied Catalysis B: Environment* 27 (2000) 225.
- [25] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($-\text{OH}/\text{O}-$) in aqueous solution, *Journal of Physical and Chemical Reference Data* 17 (2) (1988) 513.