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Immobilized Fe(III)-HY: an efficient and stable photo-Fenton catalyst☆

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Abstract

This article presents preparation, characterization and evaluation of an efficient heterogeneous Fe(III)-HY catalyst for photo-assisted Fenton reaction. Fe(III) ions are immobilized on HY zeolite using different loadings by impregnation, calcination and the activity of the catalyst is evaluated by the degradation of phenol. To initiate a photo-Fenton reaction, suspended Fe(III)-HY in solution is irradiated using UV light to form Fe(II)-HY necessary for the reaction to go. The effect of Fe loadings, H_2O_2 concentration, pH and quenching on photo-Fenton reaction are studied. The results obtained clearly show that 0.25 wt.% Fe(III)-HY is efficient in the degradation of phenol at pH = 6. Further the efficiency of Fe(III)-HY is compared with that of a homogeneous photo-Fenton reaction and the increased rate of reaction on Fe(III)-HY highlights the synergistic role of zeolite. Heterogeneous Fe(III)-HY in photo-Fenton reaction allows a wide range of pH for reaction against the narrow pH range in homogeneous system. The system is further subjected to evaluate its stability in solid state. Firstly the reaction solution containing Fe(III)-HY catalyst on irradiation is analyzed for Fe ions with atomic absorption spectroscopy (AAS) and also by calorimetry using 1,10-phenanthroline (*o*-phen) to find out any Fe leaching from the catalyst and the results show insignificant leaching of Fe (<0.3 ppm) at maximum loading of Fe under experimental conditions. Secondly, the irradiated Fe(III)-HY is complexed with *o*-phen and it is subjected to Fourier transform infrared spectroscopy (FT-IR), diffuse reflectance spectroscopy (DRS) and electron spectroscopy for chemical analysis (ESCA) studies to detect and confirm the oxidation state of Fe in solid state. Critical analysis of these studies clearly show that Fe(III)-HY on irradiation changed to Fe(II)-HY and it is intact with the surface during the course of the reaction. The DRS spectra further evidences complexation of Fe(II) with *o*-phen. The stability of the catalyst is established by recycling studies.

Keywords: Heterogeneous photo-Fenton; Homogenous photo-Fenton; Fe(III)-HY; Phenol degradation

1. Introduction

Homogeneous photo-Fenton system is widely studied and reported to be a promising method for wastewater treatment [1]. But the major disadvantage of such a system is, reactions are to be studied at acidic pH < 3 and it is difficult to remove the sludge containing Fe ions after the treatment. The latter step is laborious and not economical. In this context photocatalytic degradation of organic contaminants using photo-Fenton system can become more effective when carried out in heterogeneous method [2–4]. Development of supported Fenton catalysts is gaining much importance recently in advanced oxidation technologies (AOTs) [5].

In literature photochemical studies on immobilized Fe ions involved different supports. Bozzi et al. [6,7] reported immobilization of Fe(III) ions on silica fabrics to degrade oxalates under visible light. They observed the existence of Fe^{3+}/Fe^{2+} mixed complex with oxalic acid on the surface of the catalyst with time and reported the formation and disappearance of Fe-carboxylates by infra-red attenuated total reflection (IRATR) Fourier transform spectroscopy and concomitant recycling of the resulting Fe(III) ions back to the catalyst surface. Fernandez et al. [8] reported photo-assisted degradation of non-biodegradable Orange-II catalyzed by Fe-exchanged nafion membranes in the presence of

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H_2O_2/visible light. The Fe-redox reactions in the nafion membranes were studied by XPS and spectrophotometric techniques. Yuranova et al. [9] immobilized Fe(III) ions on carbon fabric for discoloration of Orange-II under visible light. It was observed that surface iron oxide and iron hydroxide are the catalytically active sites on C-fabric during the reaction. Some covalent iron-organic compounds like Fe/tetra-sulfophthalocyanine (FePcS) show high activity in mixed solvents of acetonitrile/H_2O for the degradation of substituted phenols by H_2O_2 at neutral pHs [10]. Collins [11] reported an efficient catalyst Fe(II)-tetraamidomacrocyclic iron ligand (Fe-TAMIL) for degradation of organic pollutants in aqueous H_2O_2. It was found that the ligand moiety of the complex was found to decompose during the reaction. But, these Fe-complexes can sustain only in co-solvents and show low activity in aqueous systems. Ma et al. [12] reported immobilization of Fe(III) ions on cationic exchange resin (Amberlite IRA200) as a photocatalyst for degradation of organic pollutants in aqueous H_2O_2 and XPS studies revealed the presence of mixed Fe^{3+}/Fe^{2+} ionic states before and after the reaction. Li et al. [13] explored the supported $(Fe(bpy)_3)^{2+}$ complex on cationic exchange resin as a photocatalyst for degradation of organic pollutants by activating with molecular oxygen under visible light and suggested the involvement of active super-oxide species $\{Fe(bpy)_3{}^{3+}O_2{}^{\bullet -}\}$ by EPR studies. Thus any support can be chosen for the immobilization of Fe ions that should resist the oxidative attack during Fenton process without loss in catalytic performance.

The aim of the present study is to highlight the preparation of a stable heterogeneous photo-Fenton catalyst based on zeolites. In continuation of our earlier reports [14,15] the addition of zeolite induces synergism due to the adsorption properties with respect to pollutant molecules and thus facilitates the photodegradation. The role of zeolite is clear as it not only pools the pollutant molecules to the vicinity of photocatalyst but also stabilizes Fe(III)/Fe(II) ions through interaction in zeolite cavity. The catalyst was characterized to understand the stability and the red-ox chemistry of iron during the photo-Fenton reaction. The activity of Fe(III)-HY was studied by taking phenol as model compound. Different experimental parameters were studied to arrive at the optimal conditions for this reaction. Further the work also highlights the efficiency of Fe(III)-HY catalyst on recycling.

2. Experimental

2.1. Materials and chemicals

Phenol (purity grade >98%) from Merck, Ferric nitrate nona hydrate, $Fe(NO_3)_3 \cdot 9H_2O$ 98% and H_2O_2 (30% w/w) were from Qualigens and 1,10-phenanthroline from Fluka were obtained. All the chemicals were used as such without further purification. HCl and NaOH (0.1 M) were used to adjust pH and methanol (HPLC) from Rankem was used as a quenching solution. All the solutions were prepared with de-ionized water. HY (Si/Al $\simeq$ 2.6; surface area = 500 $m^2\,g^{-1}$) zeolite was purchased from PQ (Philadelphia Quartz) Corporation, USA.

2.2. Preparation of catalysts

Fe(III)-HY zeolite, a heterogeneous photo-Fenton catalyst was prepared by a method described in our earlier report [16].

2.3. Catalyst characterization

The diffraction patterns of the Fe(III)-HY catalysts were recorded with Siemens D-5000 X-ray diffractometer using Cu Kα radiation at a scan rate of $0.09^\circ\,s^{-1}$ (2θ). UV–vis-diffuse reflectance spectroscopy measurements integrated with a sphere reflectance accessory using 50 mg catalyst sample ground with 2.5 g of KBr. Infrared spectra of the Fe(III)-HY catalysts were recorded on a Nicolet 740 FT-IR Spectrometer using the KBr self supported pellet technique in the frequency range of 400–4000 cm^{-1}. The electron spectroscopy for chemical analysis (ESCA) was carried out on KRATOS AXIS 165 Photoelectron Spectroscopy using the Mg Kα (150 W) anode. For energy calibration Carbon 1s photoelectron line was used. Spectra were deconvoluted using the Sun Solaris based vision 2 curve resolver. The location and full width at half maximum (FWHM) for a species was first determined using the spectrum of a pure sample. Symmetric Gaussian shapes were used in all cases for fitting the experimental curves. BE for identical samples were in general reproducible within ±0.1 eV.

2.4. Photocatalytic experiments

Phenol solutions of concentration (10^{-4} M) were freshly prepared from the stock solution for the Fenton and photo-Fenton experiments. A UV source of 250 W mercury vapor lamp of wavelengths greater or equal to 254 nm was used. Prior to the start of light experiments dark adsorption experiments were carried out for 1 h under continuous stirring. In a typical experiment a phenol solution of 50 ml (10^{-4} M) was taken in a quartz reactor and 25 mg of catalyst is added and required pH of the solution is maintained by adding HCl or NaOH. Fenton reactions were initiated by addition of known concentration of H_2O_2 obtained by diluting 30% (w/w) H_2O_2 prior to the start of experiment. Samples of the suspensions were taken at regular intervals and the radical reaction in the samples was quenched with 0.5 ml methanol and then subjected to analysis.

2.5. Analyses

The concentration of phenol was determined by HPLC using C-18 phenomix (5 μm), 250 mm × 4 mm column and methanol/water mobile phase of ratio 50/50 (v/v) and at a flow rate of 1 ml min^{-1}. UV absorbance was measured in the range of 190–500 nm. Phenol is normally quantified at $\lambda = 220$ nm.

2.5.1. Detection of Fe in solution

The elemental analyses of Fe in a solution during an experiment were determined by atomic absorption spectroscopy (AAS) using Perkin-Elmer 300A spectrophotometer. Any formation of Fe(II) during photo-Fenton reaction in solution is estimated by complexing Fe(II) with 1,10-phenanthroline (*o*-phen) calorimetrically. The irradiated samples were taken and quenched with methanol, filtered and filtrate is added to a standard volumetric flask, which contains *o*-phen solution and acetate buffer and this was kept in dark for 30 min. Absorbance was measured at the maximal absorption of Fe(II)-*o*-phen complex i.e., at $\lambda_{max} = 510$ nm and $\varepsilon_{510} = 10{,}476\ M^{-1}\ cm^{-1}$ was determined by a calibration curve. Absorbance of Fe(II)-*o*-phen complex solutions were recorded on Cintra 10_e spectrophotometer.

2.5.2. Stabilization and characterization of Fe(II) in solid state

To the irradiated Fe(III)-HY catalyst, 1,10-phenanthroline and acetate buffer was added and kept under stirring for 2 h for complexation and the catalyst was filtered, washed, dried and characterized by techniques mentioned in Section 2.3.

3. Results and discussion

3.1. Catalytic activity

To check the catalytic activity of photo-Fenton catalysts, 25 mg of Fe(III)-HY catalyst was taken in 50 ml of phenol (10^{-4} M) solution in a quartz reactor open to air under continuous stirring. The initial pH of the solution was pH 5.6 and it was not controlled during the process. Prior to start of the light experiments, adsorption properties of Fe(III)-zeolite were studied in dark for 30 min under continuous stirring. For normal photo-Fenton reaction a known volume of H_2O_2 is added in order to maintain a desired concentration in solution. The solution was irradiated by UV-light of 250 W mercury vapor lamp for 3 h and samples taken at regular intervals were quenched with methanol to arrest the radical reactions. These samples were filtered and analyzed by HPLC to study the rates of phenol degradation with time.

In order to check the effect of various parameters on the reaction like the presence of light, H_2O_2, Fe(III) with and without immobilization have been studied and shown in Fig. 1. A preliminary experiment on photolysis (UV light) shows 5–10% degradation of phenol. Whereas in the presence of catalyst and UV light about 25–30% phenol degradation is observed which may be seen as due to the photocatalytic reaction of Fe(III). In the presence of light and H_2O_2 the rate of reaction was very fast and reaction was completed in 60 min. This enhanced rate of reaction is due to generation of $^{*}OH$ radicals by the action of Fe(II) formed during the light irradiation (photo-Fenton). In dark with addition of H_2O_2 there is no change in the concentration and remained at the same level of adsorption.

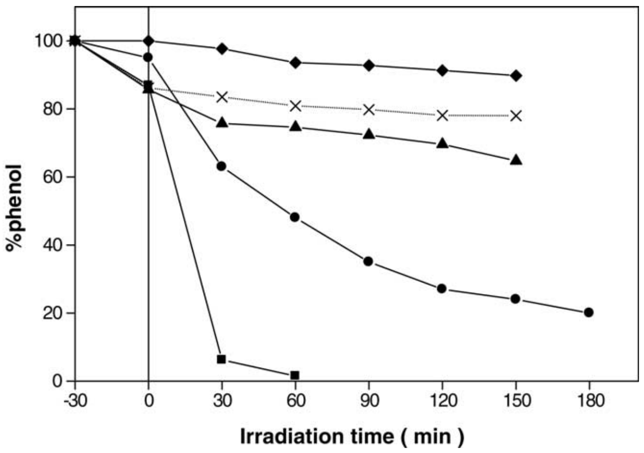


Fig. 1. Effect of various experimental parameters on photo-Fenton degradation of phenol (10^{-4} M): (■) UV + Fe(III)-HY + H_2O_2; (●) homogeneous photo-Fenton; (▲) UV + Fe(III)-HY; (×) dark + Fe(III)-HY + H_2O_2; (◆) photolysis.

In order to compare the heterogeneous photo-Fenton reaction with that of the homogenous system we have taken same amount of Fe, which is present on zeolite in phenol solution and homogenous photo-Fenton reaction is studied. Fig. 1 clearly shows that heterogeneous system is faster than the homogenous reaction. This difference in the rate of reaction may be seen as due to the synergistic effect resulting by the adsorption property of zeolite. Wherein the adsorbed pollutant molecules in the immediate vicinity of immobilized Fe-ions are easily attacked by the generated $^{*}OH$ radicals. Thus, heterogeneous photo-Fenton system accounts for the enhanced rate of reaction and is not because of Fe in solution as only trace amounts of Fe(II) is detected during the reaction. The heterogeneous photo-Fenton reaction shows degradation of phenol in less irradiation time when compared to homogeneous system under similar reaction conditions.

3.1.1. Effect of Fe(III) loading on zeolites

Table 1 shows the correlation between the Fe and the Al amounts. The Fe/Al ratio of the catalyst prepared ranges from 0.00321 to 0.135. As the Si/Al ratio of HY is low (Si/Al $\simeq$ 2.6), the available bronsted acid protons for Fe cations to exchange are high. The maximum Fe concentration used in the present course is only 1/13th of the Al concentration. In an experiment only 25 mg of the catalyst is used for photo-Fenton reaction. In our experiments the Fe concentration varied from a minimum of 0.4 to 18 ppm. Fig. 2 shows the effect of Fe(III) loading on HY in photo-Fenton reaction. It was observed that 0.25 wt.% Fe(III)-HY shows

Table 1
Characterization of the Fe(III)-HY catalysts

Fe_2O_3 (wt.%)	Fe/Al ratio	Fe concentration[a] (ppm)	% Fe detected in the solution[b]
0.125	0.00321	0.44	No traces
0.25	0.00643	0.87	No traces
0.5	0.01289	1.75	No traces
1.0	0.0258	3.5	No traces
2.0	0.0524	7.0	No traces
5.0	0.135	17.6	<2.0

[a] Fe concentration in an experiment.

[b] % Fe detected in the solution after the experiment determined by AAS.

higher efficiency than the catalysts with high loading of Fe. With further increase in the iron content no increase in the activity is observed. This may be seen as due to the interaction of Fe ions with the available cationic sites in the zeolite, thus decreasing the acid sites for adsorption of pollutant molecules affecting the photo-Fenton reaction. Thus the effect of Fe loading clearly shows that one has to optimize the Fe content simultaneously retaining the acid sites for adsorption to result in affective synergism.

3.1.2. *Effect of quenching*

In a photo-Fenton reaction on irradiation Fe(III) reduces to Fe(II) and these active species decompose H_2O_2 to form the *OH radicals, a reaction similar to a Fenton reaction, which is continuous even in the absence of light [1c]. If this radical reaction is not stopped after the sample collection the reaction continuous in the sample vial in presence of Fe(II) and H_2O_2. In order to arrest this radical reaction a *OH scavenger like methanol is added.

Samples collected at regular intervals were quenched with methanol and for comparison another experiment was done without quenching and the results are shown in Fig. 3. Without quenching the degradation appears to be fast and 99% degradation is observed in 60 min. But the real degradation is observed when the solution was quenched with methanol. So in all our experiments the samples were quenched before the analysis in order to avoid the radical reaction.

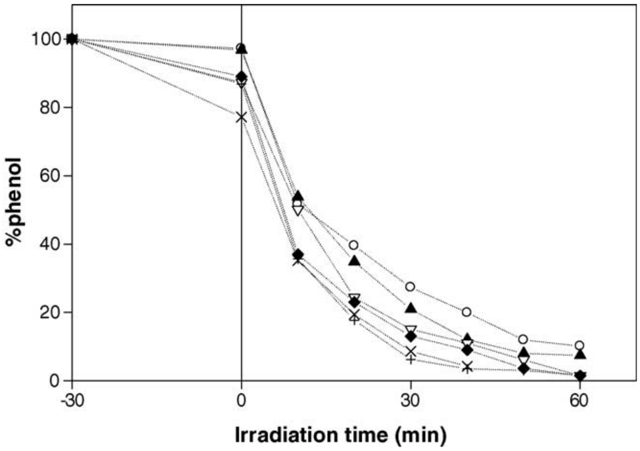


Fig. 2. Effect of Fe(III) loading over HY on heterogeneous photo-Fenton degradation of phenol (10^{-4} M): $H_2O_2 = 10^{-3}$ M; pH = 6: (○) 5 wt.%; (▲) 2 wt.%; (▽) 1 wt.%; (◆) 0.5 wt.%; (+) 0.25 wt.%; (×) 0.125 wt.%.

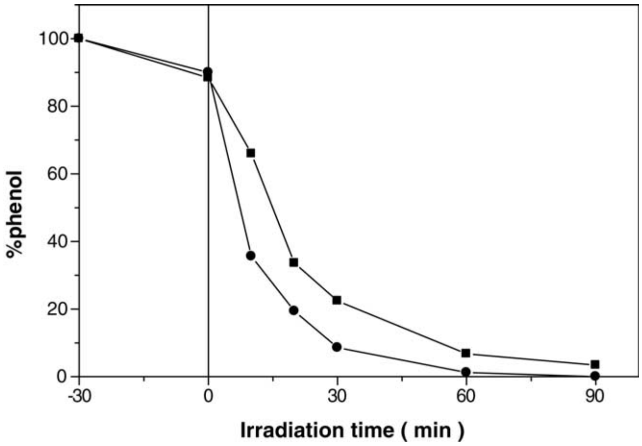


Fig. 3. Influence of *OH scavenger on photo-Fenton mediated phenol degradation over 0.125 wt.% Fe(III)-HY: (●) without methanol and (■) with methanol.

3.1.3. *Effect of pH*

The influence of pH on phenol degradation on heterogeneous Fe(III)-HY/UV/H_2O_2 was shown in Fig. 4.

The experiments were done at pH = 3.0, 6.0 and 8.0 respectively and the pH was not adjusted during the process. The maximum degradation of phenol is observed within 60 min at pH = 3. It was observed that at pH = 6 initial rate was slow and latter it followed the same pattern of pH = 3. In case of pH = 8, the rate of reaction was very slow and complete conversion of phenol was observed over a period of 3 h. In homogenous systems pH = 3–4 is known to be the optimal value for phenol degradation by H_2O_2/iron [1]. As the degradation proceeds the formation of organic acids, lead to a drop of pH of the solution. In that case at pH = 3 there will be no change in the pH of the solution during the reaction. In case of pH > 3 there is decrease of pH during the

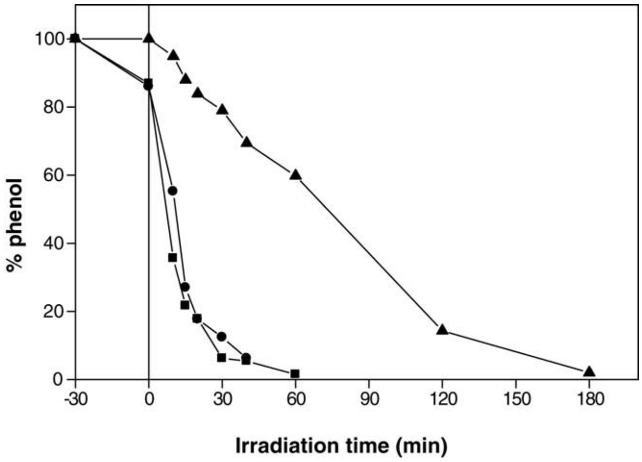


Fig. 4. Influence of pH on the percentage removal of phenol over Fe (III)-HY during photo–Fenton reaction: (■) pH = 3; (●) pH = 6; (▲) pH = 8.

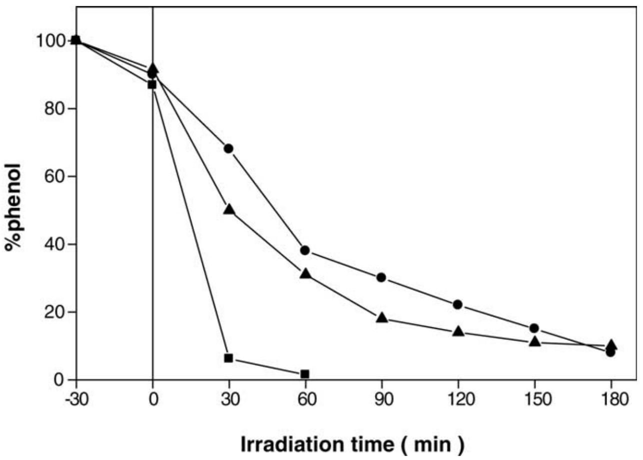


Fig. 5. Effect of hydrogen peroxide concentration on photo-Fenton assisted degradation of phenol (10^{-4} M) over Fe(III)-HY catalyst at pH = 6: (■) 10^{-3} M; (▲) 10^{-2} M; (●) 5×10^{-4} M.

reaction. At pH = 8 precipitation of iron hydroxide occurs. Thus, the observed rate of reaction at pH = 8 is slow as mentioned above. Whereas in the case of heterogeneous Fenton catalysts due to the immobilization of Fe(III) on the surface of zeolite no precipitation of iron is seen even at pH > 5. It is known that leaching of Fe out of zeolite or amorphous silica depends on pH [17,18]. As the rates at pH = 6 or 3 are almost same to avoid the leaching of iron, the experiments in the present study are conveniently carried out at pH > 5 where no leaching of Fe is observed.

3.1.4. Effect of H_2O_2

The degradation of phenol over 0.25 wt.% Fe(III)-HY at pH = 6 with different hydrogen peroxide concentrations were studied and it is shown in Fig. 5. It was observed that with increase in H_2O_2 concentration from 10^{-4} to 10^{-3} M the percent removal of phenol increases due to increased *OH radicals in solution. Further increase in the concentration of H_2O_2 to 10^{-2} M, decreased the phenol degradation. This may be seen as due to the reaction of generated *OH radicals with H_2O_2 to form hydroperoxyl radicals, which are less reactive than *OH radicals and thus not suitable for degradation of pollutants in solution.

3.2. Characterization

3.2.1. Chemical analysis of the catalysts after reaction

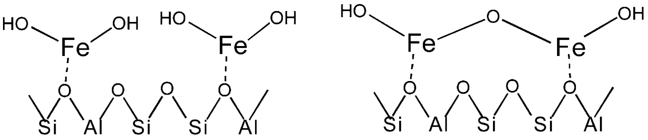
To check the loss of iron from zeolite during the degradation reaction, the catalyst after use was digested in aquaregia and analyzed by AAS for the Fe content. It was observed that the amount was nearly equal to original Fe content on zeolite.

3.2.2. Analysis of Fe during the reaction

In order to check whether Fe(II) ions are coming into the solutions during the reaction on irradiation, the solutions were analyzed by AAS and calorimetrically. Fe(II) is complexed with 1,10-phenanthroline as described in experimental. The absorbance of thus obtained Fe(II)-*o*-phen complex corresponds to a Fe(II) concentration of 0.3 ppm for 5 wt.% Fe(III)-HY calculated from calibration graph. The amount of Fe in the solution is counter checked by AAS and the results show that at high loadings of Fe only ≃ 2% of the total Fe amount used in an experiment is detected as shown in Table 1.

3.2.3. IR-characterization of Fe(III)-HY before and during the course of reaction

The Fe(III)-exchanged/impregnated zeolite may form the following structure on calcination [19] as follows:



Monomers Dimer

As per this structure the IR spectra of Fe(III)-HY shown in Fig. 6a, should exhibit characteristic peaks at 895 cm^{-1} Fe–O–Fe asymmetric stretch and Fe–O at 606 cm^{-1} [20]. These characteristic bands are not clearly seen as they overlap with zeolite characteristic stretching frequencies, which are predominant in this region. However the stretching frequencies of zeolite in this region are intensified due to presence of Fe–O–Fe and Fe–O stretching frequencies in the Fe(III)-HY catalyst.

The Fe(III)-HY catalyst is irradiated by photon to form Fe(II)-HY and is complexed with 1,10-phenanthroline. The solid obtained out of this experiment was dried and characterized by IR spectra to confirm the formation of

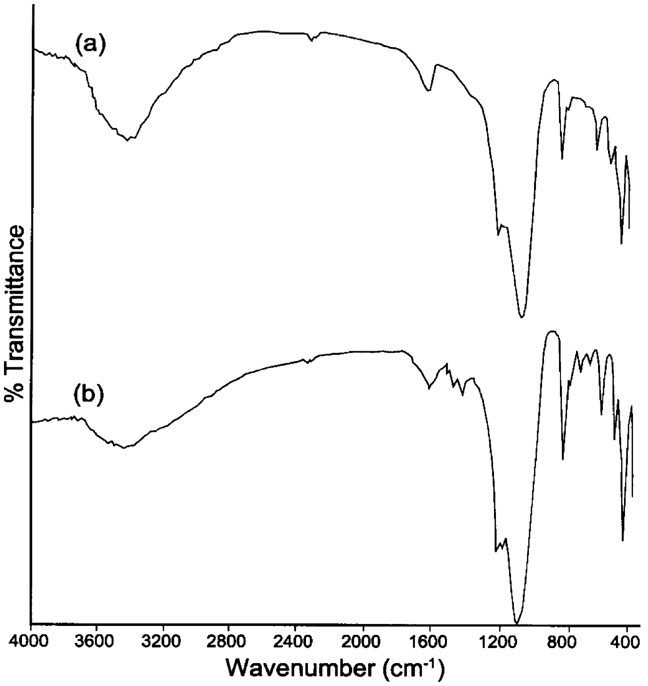


Fig. 6. IR spectra of 1 wt.% Fe(III)-HY catalyst (a) before reaction and (b) after irradiation and complexation with *o*-phen.

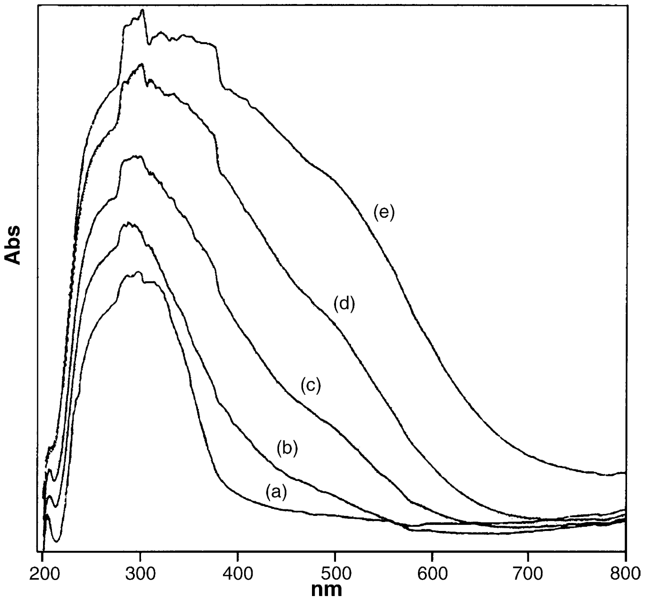


Fig. 7. UV–vis diffuse reflectance spectra of Fe(III) on HY with different loadings over HY zeolite. (a) HY, (b) 0.25 wt.%, (c) 1 wt.%, (d) 2 wt.% and (e) 5 wt.%.

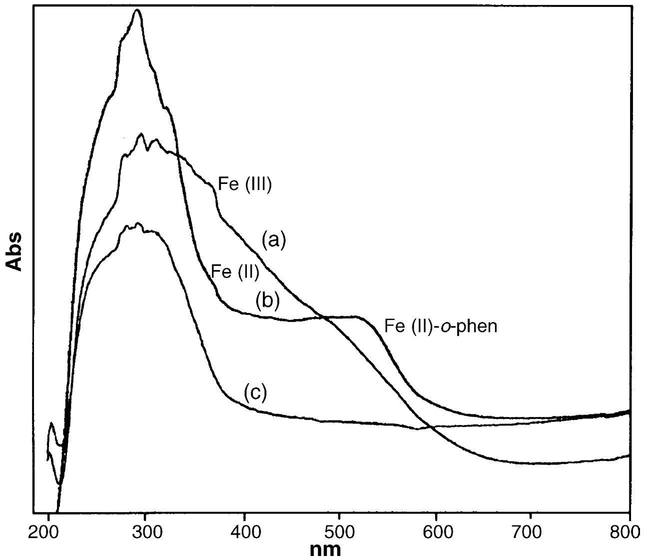


Fig. 8. UV–vis diffuse reflectance spectra of (a) Fe(III)-HY catalyst, (b) Fe(II)-(*o*-phen)-HY and (c) HY.

Fe(II) in the solid state. The characteristic peaks of $[\mathrm{Fe(phen)}]^{2+}$ that range from 400 to 1600 $\mathrm{cm}^{-1}$and Fe–O–Fe stretching frequency shift to 841 cm^{-1} [21], are not observed on the surface due to overlap with zeolite stretchings in this region. However in the 1400–1600 cm^{-1} region less intense peaks of 1,10-phenanthroline in Fe(II)-*o*-phen complex are observed (Fig. 6b). The broad OH frequency in Fe (III)-HY in turn found to be decreased and this may be seen as due to the lone pair of electrons of nitrogen atom in *o*-phenantholine interacting with the surface silanols through hydrogen bonding. These results are in confirmation with the earlier studies [22]. Thus our IR studies clearly show that Fe(III)-HY on irradiation with a photon is converted into Fe(II)-HY that would be complexed with *o*-phen in solid state.

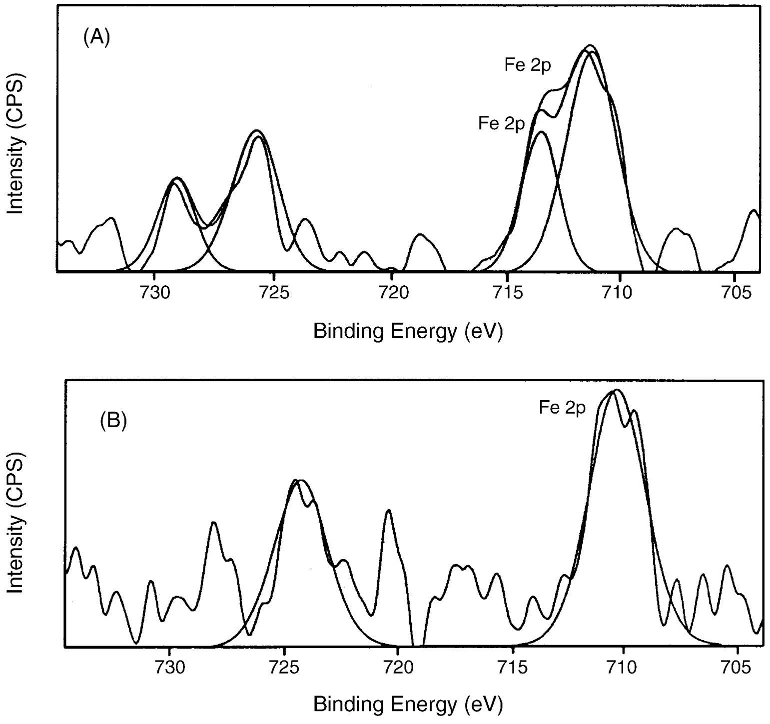


Fig. 9. XPS spectra of the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ regions for 1 wt.% Fe(III)-HY catalysts. The Gaussian–Lorentzian fitting of the experimental curves are also shown: (A) Fe(III)-HY and (B) Fe(II)-*o*-phen-HY.

Table 2
XPS results of Fe(III)-HY catalysts showing the binding energies of various elements before and after irradiation

Spectral peaks	BE (eV)	
	Before irradiation	After irradiation
Fe (2p)	711.3, 713.5	710.3
O (1s)	532.7	531.9
Si (2p)	103.6	102.8
Al (2p)	75.4	74.25

3.2.4. *UV–vis-DRS*

The UV–vis diffuse reflectance absorption spectra of Fe(III)-HY show wide range of characteristic Fe–O charge transfer bands in the range of 380–570 nm as shown in Fig. 7. The band gap of HY is high and lies around 280 nm. At low loadings, Fe(III) establishes an interaction with HY creating different energy levels in this band gap. With an increase in the Fe concentration there is an increase in the number of energy levels resulting in a decrease in the band gap falling closer to that of pure Fe-oxide. Thus Fig. 7 clearly depicts a gradual red shift of the band gap as well as an increase in absorption intensity proportional to the concentration of Fe(III). Thus as the percentage of Fe(III) on zeolite increases, the band edge is shifted towards 500–570 nm, which may be accounted for the formation monomers $[Fe(OH)_2]^+ \rightarrow$ dimers $[(HO)Fe–O–Fe(OH)]^{2+} \rightarrow$ agglomeration of iron oxide particles.

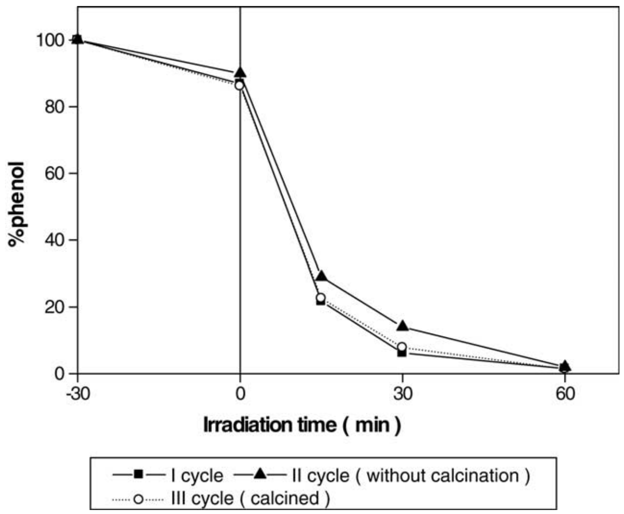
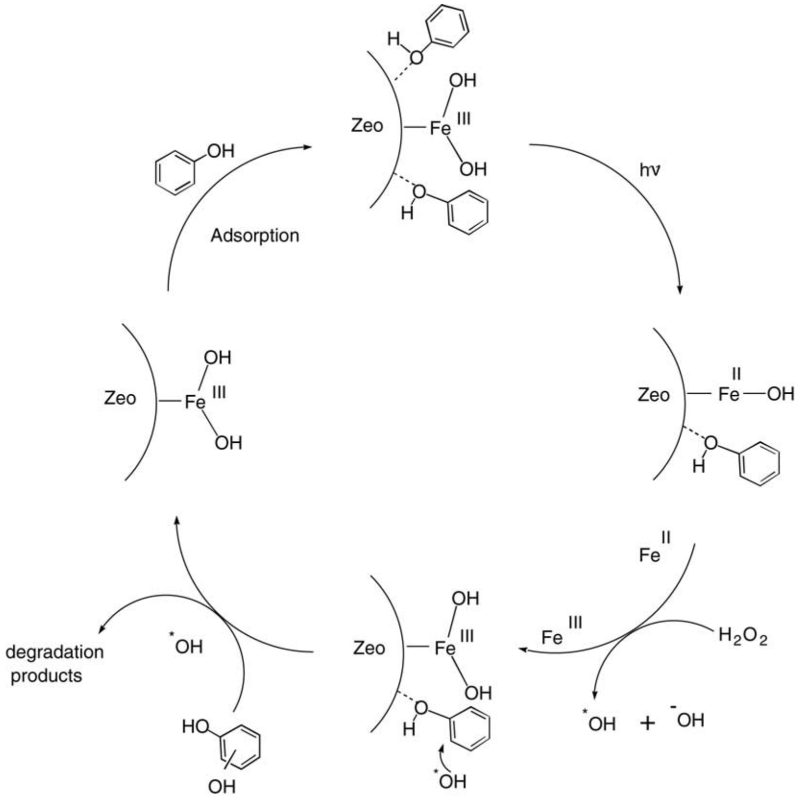


Fig. 10. Effect of recycling studies over Fe(III)-HY on phenol degradation.

On the other hand, Fig. 8 shows the DRS spectra of Fe(III)-HY on irradiation and complexation with *o*-phen. On irradiation, the band edge of Fe(III)-HY is blue shifted which may be seen as due to reduction of Fe(III) to colorless Fe(II) [8]. The DRS of complexed Fe(II)-HY catalyst (Fig. 8b) shows a new broad absorption band at 520–530 nm which is characteristic band of $[Fe(o\text{-phen})]^{2+}$ complex [21].



Scheme 1. A pictorial representation of photo-Fenton degradation of phenol over Fe(III)-HY.

3.2.5. XPS

The reduction of Fe(III) to Fe(II) during photo-Fenton reaction is also characterized by ESCA. Fe(III)-HY after irradiation in solution is complexed with 1,10-phenanthroline under the specified conditions as given in the experimental to stabilize the Fe(II) oxidation state and these samples were subjected to ESCA studies as shown in Fig. 9 and Table 2. It is observed that the binding energy (BE) of the Fe_{2p} doublet slightly shifted to lower BE value after the irradiation, which may be seen as due to the transformation of Fe(III) to Fe(II). The ESCA signal observed at 710.3 eV (after irradiation) is shown due to the abundance of Fe(II) compared to the original signal (before reaction) at 711.3 eV of Fe(III). The ESCA of Fe(III)-HY (Fig. 9A) also shows the presence of mixed oxidation states [7] in the form of Fe_3O_4 as given in Table 2.

3.3. Recycling of Fe(III)-HY

Fig. 10 shows the recycling studies of Fe(III)-HY catalyst. When the catalyst is reused without calcination (II cycle) there is slight difference in degradation rate and the completion of the reaction is almost taking the same time. The difference in the rates may be seen as due to the accumulated organic intermediates in the zeolite cavities, affecting the adsorption in turn reducing the degradation rate. When the same catalyst is reused after calcination (III cycle), the original degradation rate is restored. Thus calcination of the reused catalyst is necessary to maintain the activity.

Based on the activity studies and other spectral evidences a pictorial representation of photo-Fenton degradation of phenol on an immobilized Fe(III)-HY is depicted in Scheme 1.

4. Conclusions

The present investigation illustrates the following:

- An easy and simple preparation of Fe(III)-HY catalysts by impregnation and calcination.
- Optimization of reaction parameters like effect of loading of Fe(III), pH, H_2O_2 concentration and quenching.
- 0.25 wt.% Fe(III)-HY is active for the degradation of phenol at $pH = 6$.
- Heterogeneous Fe(III)-HY efficiency over homogenous photo-Fenton system, that can be applied at $pH > 3$.
- The enhanced activity of heterogeneous Fe(III)-HY system due to the synergistic effect of zeolite by adsorption of pollutant molecules facilitating the rate of degradation.
- No leaching of Fe from the solid catalyst into the solution.
- IR, DRS and XPS confirm the red-ox states of Fe in solid state.
- The present work opens an eco-friendly method by heterogenizing the homogenous photo-Fenton system to achieve a stable and efficient photo-Fenton catalyst for wastewater treatments.

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