Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21509

95 (2017) 170–179
November

Degradation of 4-nitrophenol (4-NP) using Fe-loaded fly ash brick clay as a heterogeneous Fenton catalyst

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Received 19 May 2017; Accepted 29 September 2017

ABSTRACT

Fly ash is one of the solid wastes generated from thermal power plants. Fly ash has certain catalytic capacity because of the possessions of porous structure. 4-Nitrophenol (4-NP) is considered to be toxic, non-biodegradable organics and it is recognized by Environmental Protection Agency as a priority pollutant. 4-NP was selected as model organic compound and fly ash making brick clay was used as raw material to prepare catalyst in this work. The catalyst consists of iron which is loaded on fly ash brick clay (FABC). The catalyst was prepared by impregnation method using fly ash clay support matrix. The prepared catalyst was used to study the performance of heterogeneous catalyst on degradation of 4-NP. The prepared catalyst was characterized by X-ray diffraction, scanning electron microscope coupled with energy dispersive X-ray, Fourier transform infrared spectroscopy. The influence of operating parameters such as the iron loading on matrix, dosage of H_2O_2, dosage of catalyst, initial concentration of 4-NP, initial pH and temperature was investigated on percentage degradation of 4-NP. The stability of prepared catalyst was also investigated by reusing the catalyst applying for four consecutive experiments. All the experiments were performed with 100 ppm of initial concentration. With operating condition of 10% Fe-FABC catalyst dosage of 2 g/L, pH 3.0, oxidant (H_2O_2) dosage 30 mM, reaction time of 40 min and room temperature, % degradation was more than 92% within these operating conditions.

Keywords: Advanced oxidation process; Environmental pollution; Fenton process; Fly ash brick clay

1. Introduction

The pursuit for innovative products and technological developments has led to the generation of large amount of wastewater which seriously affects our ecosystems. Approximately 23% of the world's population live in developed countries, consume 78% of the resources and produce 82% of the waste products [1]. Due to the evolution of industrialization, both the amount and categories of hazardous pollutants are increasing [2,3]. Typical non-biodegradable, toxic and bio-refractory pollutants are nitroaromatic compounds. 4-Nitrophenol (4-NP) from the phenol family belongs to this category of pollutant, which is largely present in the wastewater as a by-product of pesticide, herbicide and synthetic dyes production [4]. 4-Nitrophenol (4-NP) is present in agricultural irrigation effluents and industrial effluents discharged from chemical plants producing pesticides, explosives, dyestuffs, etc. Due to the presence of a nitro group in the aromatic ring, 4-NP is toxic, non-biodegradable and highly persistent in the environment, so it has been considered to be priority toxic pollutant by U.S. Environmental Protection Agency (EPA) in 1976 [5,6]. 4-NP can cause considerable damage to the human health, causing alterations in the central nervous system, liver, kidney, and blood of humans and animals even at low concentration [4].

The poor biodegradability of 4-NP wastewater does not allow the direct application of biological processes. On the other hand, chemical treatments are usually expensive and could produce intermediates, which is similar to the original pollutant [7]. The conventional methods in industrial wastewater treatment are biological oxidation [8]

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and physico-chemical processes [4], these are not efficient enough to actually provide a real degradation of the pollutants. For this reason, the research community focused on the development of processes for pollutants degradation innocuous and reasonable approach based on physical operation: biodegradation, adsorption, membrane separation, solvent extraction, photo-catalytic degradation and wet air oxidation degradation [4]. However, above mentioned traditional degradation methods still exists with some disadvantages such as long reaction time, high operating costs and lower ability to degrade high concentration of 4-NP. Hence, an efficient and energy saving approach to deal with the 4-NP wastewater is needed for degradation of 4-NP wastewater by an advanced oxidation processes (AOP) such as heterogeneous Fenton process [9]. A few researchers have reported the degradation of 4-NP by AOP including O_3, Fenton reagent, photo-Fenton and electro-Fenton methods, UV/H_2O_2, UV/TiO_2/H_2O_2, UV/TiO_2 and ultrasonic irradiation [10–12]. The main drawbacks in homogeneous Fenton and photo-Fenton processes are: the removal of dissolved iron from the treated water, mainly as iron oxyhydroxide sludge.

The following reactions show basic Fenton reactions:

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

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\circ} + H^{+} \tag{3}$$

$$OH^{-} + H_2O_2 \rightarrow HO_2^{\circ} + H^{+} \tag{4}$$

$$H_2O_2 + OH \rightarrow H_2O + HO_2 \tag{5}$$

To overcome the disadvantages in Fenton process, many efforts have been made in the last years in the field of heterogeneous Fenton process, which has the convenience of reuse of the catalyst [13]. In the literatures, Fe ions have been loaded on various kinds of substrates, such as zeolite [13,14], clays [15], membrane [16], mesoporous silica [17] and C-fabrics [18] to form Fe-based Fenton-like catalysts for the degradation of organic compounds. Pereira et al. [19,20] and Yu et al. [3] investigated that Fenton heterogeneous catalysts can be synthesized on the basis of minerals or iron-containing solid waste products such as kaolin, pyrite ash, fly ash, red mud, etc. In many places, fly ash can be used as additives or construction materials, sorbents or catalysts for the oxidation of H_2S, methane and sodium sulfite. Duc [21] studied a heterogeneous Fenton technique using modified fly ash/H_2O_2 for removing Reactive Blue 181 from aqueous solution. Dao et al. [22] found Fe-FA as a promising catalyst for the degradation of organic dyes (RB182) in aqueous solutions and 93% removal of RB182 was achieved within 50 min of reaction. The high concentration of iron oxide, present mostly in hematite and pyrite ash, gives the basis for its application as a source of catalytic iron in a modified Fenton process for anthraquinone dye reactive blue 4 degradation. Acid-modified coal fly ash (CFA) was tested for use as a catalyst of a Fenton-like process in *p*-nitrophenol (*p*-NP) wastewater treatment [23].

Fly ash being a solid waste obtained from thermal power plants, steel mills, etc. needed specific attention pertaining to its utilization for controlling air, land and water pollution. Due to rich source of silica, alumina and other oxides, it has been explored as a catalyst to remove color from wastewater [24]. Chang et al. [25] investigated that COD removal of rhodamine B by the combined Fenton oxidation and fly ash sorption process was 98%. Fly ash is a solid waste which is produced from coal-burning power plants or steel mills. It is estimated that over 300 billion tons of fly ash are produced every year in the world [26]. Traditionally, most of fly ash is disposed of through landfill which is causing serious environmental concerns. Recently, fly ash has been used as low-cost adsorbent for the removal of pollutants in gaseous and liquid residues [27,25]. Some studies have demonstrated that fly ash is an interesting heterogeneous catalyst, which could cause catalytic oxidation reactions of H_2S, ethanethiol and methane in exhaust gases, sodium sulfide in water and esterifiable reactions [26,28,29]. Catalytic wet peroxide oxidative degradation of *p*-nitrophenol and *p*-nitroaniline in aqueous solution was studied using CFA converted and nano CuO fringes incorporated zeolite X material [30].

These catalysts have been proved to possess the similar catalytic activities as that of homogeneous Fenton systems (AOP). Therefore the aim of this study is to investigate the applicability of Fe-loaded fly ash brick clay (FABC) as heterogeneous Fenton catalyst for the degradation of the organic content in the synthetic wastewater containing 4-NP. The effect of Fe content in Fe-FABC (3, 5, 10 and 15 wt% Fe) on the catalytic activity was investigated and the Fe content was optimized. The influence of various parameters such as amount of Fe-FABC catalyst, oxidant (H_2O_2) dose and initial pH of 4-NP solution on the efficiency of the process was assessed.

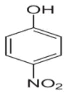
In this work, a simplified technique of catalyst preparation was developed by impregnation of ferrous ion on the solid matrix FABC to form a heterogeneous Fenton-like catalyst. The prepared catalyst was reused/regenerated three to four times per cycle of experiments. The catalyst was tested on degradation of 4-NP pollutant. The effect of various experimental parameters such as iron loading on support matrix, catalyst dosages, pH, oxidant (H_2O_2) dosages, temperature and initial pollutant (4-NP) concentration on the degradation efficiency was investigated. A kinetic model was also developed to evaluate the selectivity of the developed catalyst and the effect of initial concentration on the degradation of 4-NP.

2. Material and methods

2.1. Chemicals and reagents

Iron sulfate $FeSO_4.7H_2O$ was purchased from Merck India limited. All the reagents used for this experiment were of analytical grade and used without further purification. Distilled water was used for all the experiments. The pH was adjusted by addition of sodium hydroxide (0.1 M) and sulfuric acid (0.1 M) to the 4-NP solutions. The concentration of hydrogen peroxide was 30% (w/v). 4-Nitrophenol (LOBA Chemie, India, and LR grade) was chosen as the target compound, and its chemical structure is as follows:

Target compound properties

Pollutant	4-Nitrophenol (4-NP)
Molecular formula	$C_6H_5NO_3$
Chemical structure	
Other names	Para-nitrophenol (*p*-NP), 4-hydroxynitrobenzene
Molecular weight (g/mol)	139.11

The clay used as the support of catalyst had the following chemical composition: SiO_2 45%–65%; Al_2O_3 14%–31.10%; Fe_2O_3 13%–15%; TiO_2 0.5%–2.42%; CaO 0.1%–22.31%; MgO 0.2%–2.3%; Na_2O 0.1%–3.4%.

2.2. Catalyst support preparation

The catalyst support is FABC. Fly ash as one of the solid wastes is generated from thermal power plants. Fly ash has certain catalytic properties because of the possessions of porous structure and activated metallic oxide. Prior to its use, the gray-colored FABC was crushed to powder using laboratory mortar and vessel and washed several times with distilled water to remove impurities. The samples were dried in an oven at 100°C for overnight, to obtain FABC purity [31]. Fineness of powder is 62 mm in size.

Fly ash was used as raw material for cement and concrete manufacture. Fly ash contains alkali oxides and plant nutrients that are useful in agriculture, so this material has been used as soil additive to decrease soil acidity and promote root growth and as a sulphur fertilizer. Nevertheless, a series of other applications should be investigated in order to more effectively recycle the large fly ash output [32]. Low % fly ash substitution in clay bricks is possible without significantly deteriorating the mechanical performance, while porosity progressively increases [33].

Research efforts increasingly focus on added-value physico-chemical treatment of organic matter applications based on fly ash. The fly ash obtained from thermal power plant contains total and leachable concentration of highly volatile elements. These elements are strongly influenced by the interaction with ubiquitous free lime which may cause several environmental problems when used in construction. The availability and mobility of trace pollutants contained in ash is a key issue [34]. Thus, it is important to take extra care in preparation of FABC heterogeneous catalyst. Catalyst was washed several times with distilled water to remove impurities before use. The heat treatment in wet impregnation method of catalyst synthesis removes the volatile elements from the catalyst.

2.3. Catalyst preparation

The catalyst iron-FABC was prepared by supporting the metal onto the matrix using impregnation method [35]. In this process, specific amount of $FeSO_4.7H_2O$ (3–15 wt% of iron ions in the catalyst) were dissolved in a beaker containing 50 mL of distilled water. Then, 10 g of clay was added to this aqueous solution in the beaker and stirred constantly at 150 rpm and heated at 100°C until all water was evaporated. After impregnation, the sample was dried at 105°C for overnight in oven, followed by calcinations at 500°C for 4 h [36]. The obtained catalysts are denoted as *x*Fe-FABC, where *x* is the weight percentage of Fe in the mixture, based on [Fe/(Fe + clay) × 100%].

2.4. Experimental procedure

A batch Fenton reactor essentially consists of a non-pressurized stirred reactor with the addition of acid, base, a Fe-loaded fly brick clay (Fe-FABC) catalyst and industrial strength (30 w/v%) hydrogen peroxide [37]. It is recommended that the reactor vessel be coated with an acid-resistant material, because the Fenton reagent is very aggressive, and corrosion can be a serious problem. Addition of reactants is done in the following sequence: wastewater followed by dilute sulfuric acid (for maintaining acidic conditions) catalyst in acidic solutions, base or acid for the adjustment of pH at a constant value (must be added slowly with proper maintenance of temperature).

For the 4-NP degradation study on Fe-FABC, a stock solution of 100 ppm was prepared. In each degradation (experiment), 30 mM H_2O_2 (30% w/v) and 2 g/L Fe-FABC was added to 1 L of the stock solution. After 60 min of adsorption, H_2O_2 was added into the reactor throughout the process. Solutions of 4-NP were prepared by using ultrapure water (MILLIPORE, Direct-Q, UV3 with Pump) and the solution was adjusted to constant pH with dilute aqueous H_2SO_4 0.1 M or NaOH 0.1 M solutions. The samples were taken by using a syringe and samples were collected in every 5 min intervals. The 4-NP concentrations were measured using an 1800-type ultraviolet-visible spectrophotometer. λ_{max} for the 4-Np solution was found to be 318 nm [38]. Percentage degradation was calculated using the formula: $(C_0 - C_t)/C_0 \times 100$, where C_0 is the initial concentration of the 4-NP synthetic wastewater and C_t is the concentration at time t. In order to check the reproducibility of the results, experiments were conducted in duplicate to confirm the results.

3. Result and discussion

3.1. Characterization of prepared catalyst

The phase compositions of the prepared sample were characterized by X-ray diffraction (XRD) techniques using Cu K_α (λ = 1.54060 nm) radiation, functioning to 40 kV and 30 mA. The data were collected with 2θ range of 10°–80°. XRD was used to ascertain the Fe_2O_3 loaded on catalyst. This component is indicative of the presence of iron in the impregnated catalyst. The results are shown in Fig. 1. Fig. 1 shows the characteristic peaks of Fe_2O_3 (version match 3.0.3 build 37) at 27.81°, 40.52°, 50.23°, 56.62°, 60.15°, 69.21°, respectively, [39] and this intensity increased with increase in iron content. This indicates that higher loading of iron in prepared catalyst which led to form the higher levels of iron oxide on the catalyst.

3.2. Scanning electron microscopy

The scanning electron microscopy (SEM) image is used to probe the change in morphological features of FABC and clay impregnated by different wt% of iron sulfate heptahydrate. It can be seen from Fig. 2 that surface morphology of the FABC is different from the impregnated one.

After impregnation of iron in the catalyst, the clay became more porous and fluffy. This porous and fluffy appearance probably is due to the change in the surface of the particle as a result of impregnation process and reduction of certain amorphous phase originally associated with the clay [40].

3.3. Energy dispersive X-ray analysis

The energy dispersive X-ray (EDX; microanalysis) was employed to perform elemental analysis in the FABC and catalysts. The EDX analysis confirms the 10 wt% of Fe loaded in the catalyst (as shown in Table 1). The results are shown in Fig. 3 and Table 1.

3.4. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. Infrared

Table 1
Chemical composition of fly ash brick clay and 10 wt% Fe-FABC evaluated by EDX

Elements	Weight%	
	FABC	10% Fe-FABC
Mg	4.33	1.45
Al	11.85	5.68
Si	23.70	9.18
S	–	29.28
K	2.16	
Ca	47.15	26.57
Ti	1.33	
Fe	*9.48*	*27.83*
Total	100	

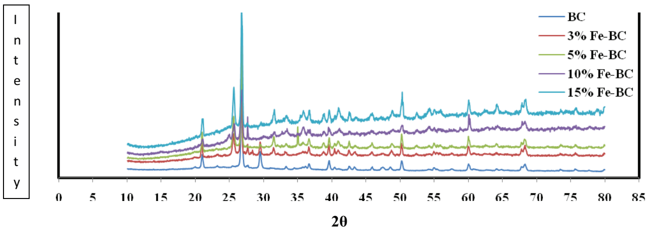


Fig. 1. Powder XRD patterns of Fe-fly ash brick clay catalyst with different Fe wt% and that of fly ash brick clay.

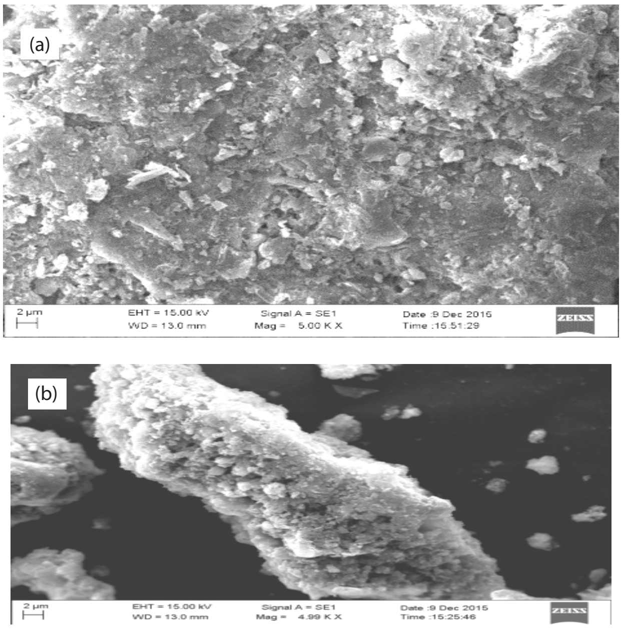


Fig. 2. SEM images of (A) fly ash brick clay and (B) 10% Fe-FABC.

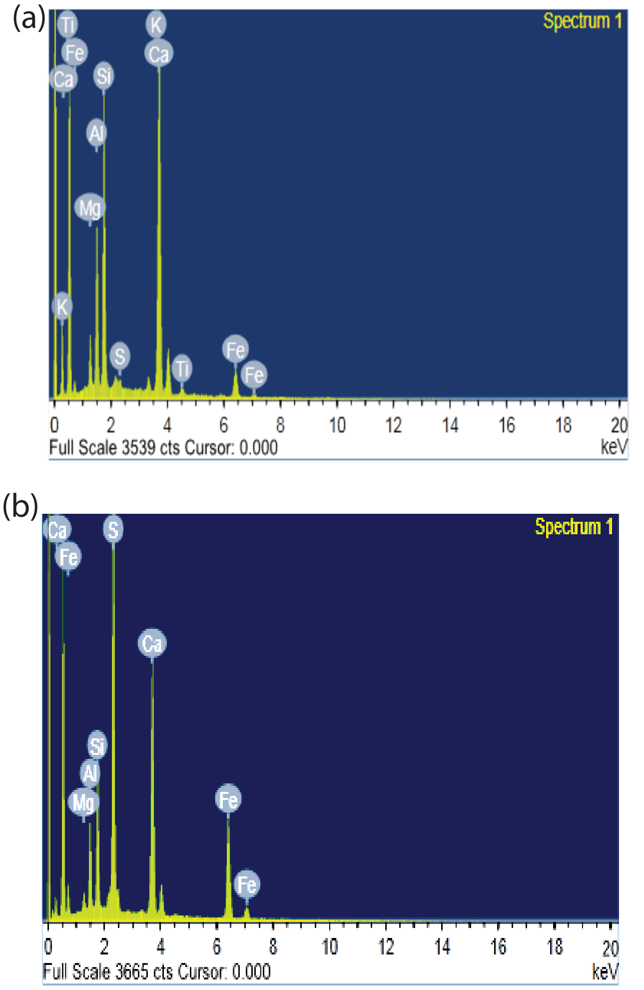


Fig. 3. EDX analysis of the fly ash brick clay and Fe-FABC at 10% wt Fe (a) fly ash brick clay and (b) 10% Fe-FABC.

spectroscopic analysis (Fig. 4) indicates the presence of hydroxyl groups due to superficially adsorbed and interlayer water (bands at 3,448.62 and 1,638.39 cm^{-1}). The band centered at 1,047 cm^{-1} may be typically assigned to (due to) the Si–O stretching [41].

FABC shows band at 3,448.62 and 1,639 cm^{-1} which is due to OH stretching of interlayer water; an OH bending band at 1,639 cm^{-1} confirms the presence of hydration of water. Typical bands of the silicate framework contributions were also confirmed: at 1,047 cm^{-1} due to in-plane band stretching of Si–O bonds; at 531 and 465 cm^{-1}, corresponding to Si–O–Si and Al–O–Si vibrations, respectively [42].

4. Effect of various factors on % degradation

4.1. Effect of catalyst dosages (g/L) on degradation of 4-NP

A number of reports have demonstrated that catalyst dosage has a large influence on the % degradation of substrate [31]. To investigate the effect of catalyst (Fe-FABC) dosage on 4-NP degradation, five different catalyst loadings (500, 1,000, 1,500, 2,000 and 2,500 mg) were tested. Fig. 5 displays the decomposition rate of 4-NP with different catalyst dosages. There was a critical dosage (2,000 mg) of the catalyst, at which the degradation efficiency was the maximum (92%). A maximum 4-NP degradation of 92% was observed at 2,000 mg of catalyst dosage, followed by 90% at 2,500 mg and 86%, 82%, 79% at 1,500, 1,000 and 500 mg, respectively, in 40 min of duration. The % degradation initially increases with catalyst dosage after that again it starts to fall. This can be explained as up to certain level of dosage, the catalyst gets well dispersed in the reaction medium and thus all active surface sites are available for the reaction. Accordingly, the % degradation increased with catalyst dosage. At dosage of 2,000 mg/L, the adsorption of 4-NP onto the catalyst surface reached an optimum state. Beyond 2,000 mg/L, there was decrease in % degradation.

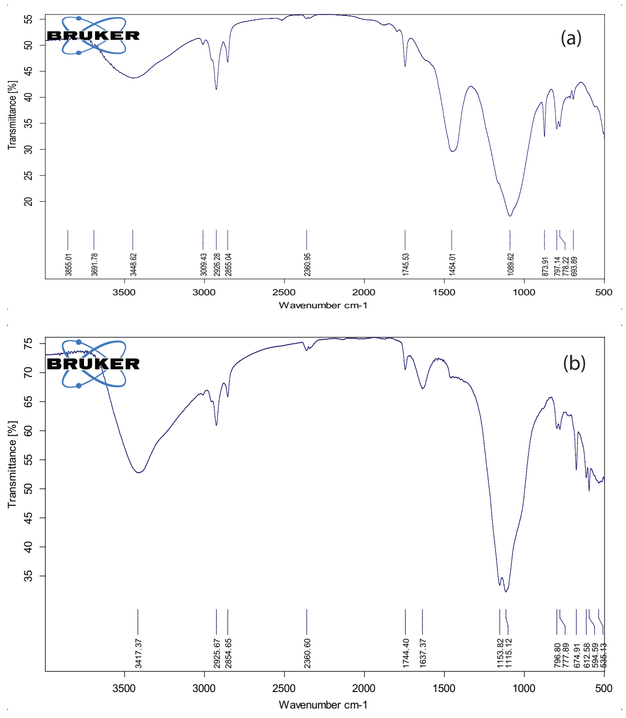


Fig. 4. FTIR analysis of the fly ash brick clay and Fe-FABC at 10%wt Fe (a) fly ash brick clay, (b) 10% Fe-FABC.

The decrease of catalytic activity at higher catalyst dosages may be due to the fact that all 4-NP molecules are already adsorbed on the catalyst surface and the addition of a larger amount of Fe_2O_3 would have no effect on the % degradation [43]. Excess amount of Fe^{2+} reacts with hydroxyl radicals (OH) by scavenging reaction ($Fe^{2+} + OH \rightarrow Fe^{3+} + OH^-$) and the progressive fall of OH concentration can induce a gradual drop in the degradation of contaminants, indicating that a suitable iron ion content for a certain Fenton process was significant.

4.2. Effect of pH on degradation of 4-NP

The effect of initial pH solutions on the degradation of 4-NP was studied in the pH range of 1.0–7.0 and the result is shown in Figs. 6 and 7. The results indicated that the degradation of 4-NP is significantly influenced by the pH of the solution.

The optimum solution pH for degradation of 4-NP was achieved at pH 3 with 92% degradation efficiency within 40 min reaction time. At low pH (pH < 2.0), the reaction of hydrogen peroxide with Fe^{2+} (ferrous ion) could be slowed down because H_2O_2 can stay stable probably by solvating a proton to form an oxonium ion (e.g., $H_3O_2^+$) as presented by Eq. (6). An oxonium ion ($H_3O_2^+$) makes H_2O_2 electrophilic

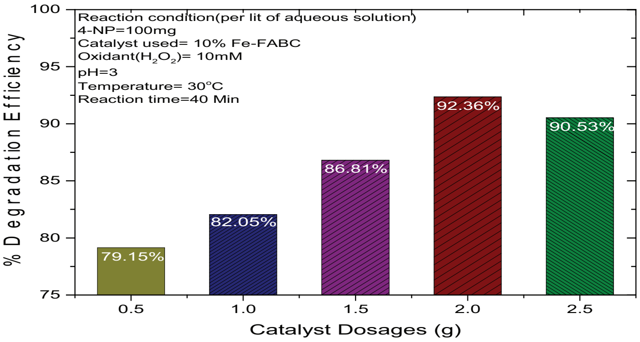


Fig. 5. Effect of catalyst dosages on degradation of 4-NP.

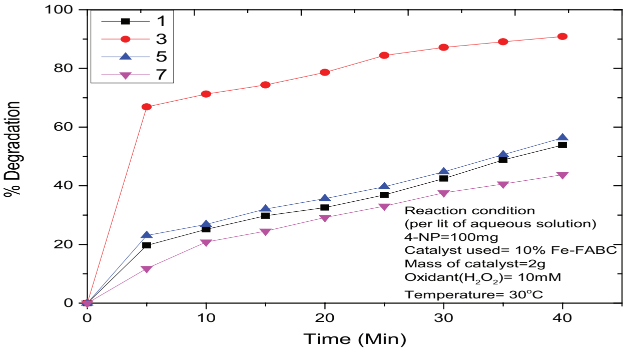


Fig. 6. Effect of pH on degradation of 4-NP.

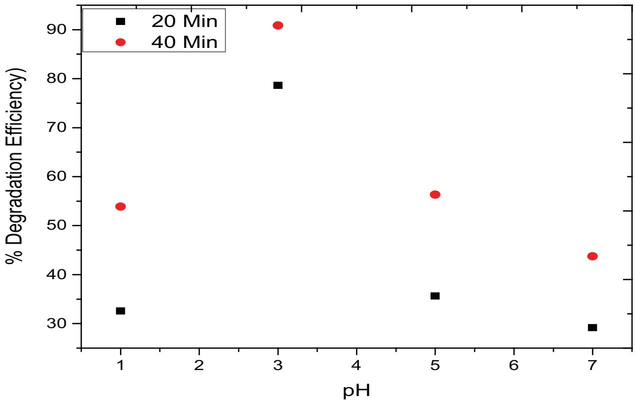


Fig. 7. % Degradation with different pH and change in time (20 and 40 min, respectively).

which enhance the stability and presumably reduce substantially the reactivity with ferrous ion [44].

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \quad (6)$$

$$\bullet OH + H^+ + e^- \rightarrow H_2O \quad (7)$$

At the same time, the formed complex species $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ also react more slowly with H_2O_2. In addition, the scavenging effect of the •OH radical by H^+ is severe (Eq. (7)) [44]. On the other hand, in case of pH > 3.00, the oxidation efficiency decreased rapidly due to the stability of H_2O_2 which starts to rapidly decompose into molecular oxygen without formation of appreciable amounts of hydroxyl radical. It is expected that the formed O_2 is not capable to efficiently oxidize the organics in the mild operating conditions [44].

4.3. Effect of temperature on degradation of 4-NP

The influence of temperature on the 4-nitrophenol degradation using catalyst was studied by varying the temperature from 30°C to 70°C [45]. The results are shown in Fig. 8. As can be seen from Fig. 8, rising temperature significantly enhanced the catalytic activity of 4-NP degradation. At 70°C, the degradation efficiency of 4-NP reached to 80% and 92% in 20 and 40 min. respectively.

The 4-NP degradation is much higher at higher temperatures (70°C). This is because higher temperature increased the reaction rate between hydrogen peroxide and the catalyst, thus increasing the rate of generation of oxidizing species such as •OH radical or high-valence iron species [46]. Erlenmeyer flask was immersed in a water bath in order to control the working temperature using a thermostat (Julabo Labortechnik GMBH, Seelbach, Germany) [47]. The degradation efficiency after 20 min was 78%, 79% and 80% at 30°C, 50°C and 70°C, respectively (shown in Fig. 9). Complete degradation can be achieved in 1 h at 70°C. This shows that higher temperature can be employed in cases where a faster rate of degradation is required. But we got significant degradation of 4-nitrophenol, at room temperature for cost-effective system of 4-NP degradation. So we did not go high temperature for all the experiments.

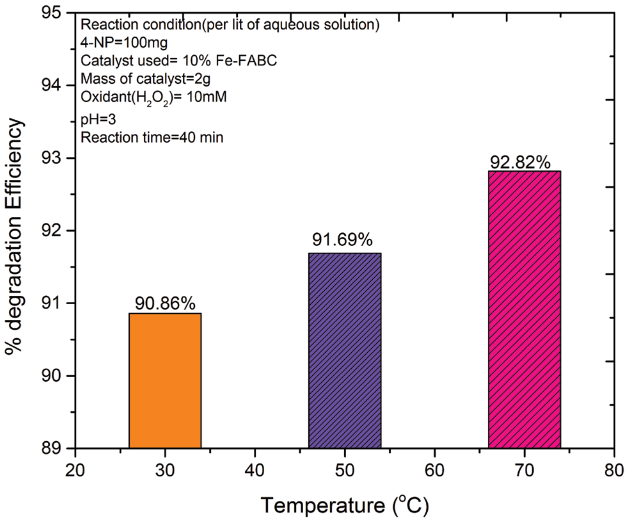


Fig. 8. Effect of temperature variation on the catalytic degradation of 4-NP.

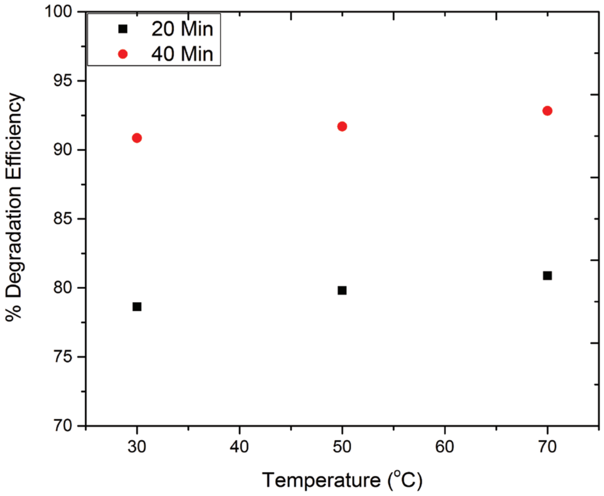


Fig. 9. % Degradation on different temperature with change in time (20 and 40 min, respectively).

4.4. Effect of initial concentration of 4-NP

Fig. 10 shows the % degradation for different initial concentration of 4-NP with the reaction time. The results indicate that degradation efficiency increased when the initial 4-NP concentration increased. Initial concentration plays a very important role in reactions according to the collision theory of chemical reactions. The collisions theory state that for a chemical reaction to occur, the reacting particles must collide in correct orientation with each other so that the breaking and formation of chemical bonds can occur and they also should possess energy that is equal to or more than minimum energy called activation energy.

By increasing the concentration, the frequency of collisions between reactants molecules is increased and the frequency of effective collisions that causes a reaction to occur will also be high. The lifetime of hydroxyl radicals is very short (only a few nanoseconds) and they can only react

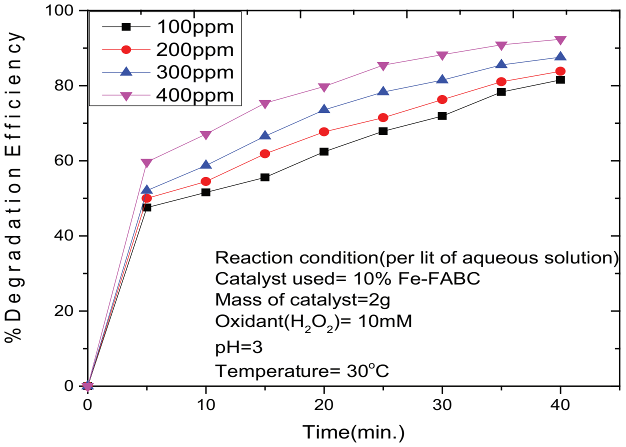


Fig. 10. Effect of initial concentration of pollutant (4-NP).

when they are formed. Therefore, as increasing the quantity of 4-NP molecules per volume unit, logically enhances the probability of collision between organic matter and oxidizing species, leading to an increase in the degradation efficiency. Similar result was shown by Daneshvar et al. [48], in their study of degradation of Acid Blue 74 by using Fe-ZSM5 zeolite as heterogeneous photo-Fenton catalyst.

4.5. Effect of hydrogen peroxide concentration on 4-NP degradation

The influence of H_2O_2 concentration on 4-nitrophenol degradation (4-NP) is shown in Fig. 11. A maximum degradation of 92% was obtained at H_2O_2 concentration of 30 mM at 40 min, followed by 89% at 40 mM, 85% at 20 mM and 79% at 10 mM. The 4-NP degradation at H_2O_2 concentrations of 40 mM at 40 min was 89% (Fig. 12). Beyond 30 mM H_2O_2 concentration there was decrease in % degradation.

This means that there is an optimal concentration of H_2O_2 to degrade organic contaminants. The addition of H_2O_2 is known to increase the rate of 4-NP degradation by allowing the formation of more amount of hydroxyl radical. Consequently, the degradation rate is expected to be enhanced. But at high dosage, H_2O_2 is a powerful HO• scavenger.

Addition of excess of H_2O_2 results in a decrease in reaction rate. This phenomenon can be explained by the scavenging effect of excess H_2O_2, which decreases the number of hydroxyl radicals in the solution.

4.6. Effect of iron loading on fly ash brick clay

The performance in degradation of aqueous 4-nitrophenol (4-NP) solution using Fe-FABC was examined over a period of time as shown in Fig. 13. This figure shows the effect of iron loading on FABC on the degradation of 4-nitrophenol. The results indicated that the degradation of 4-nitrophenol is remarkably dependent on the iron ions concentration at fixed initial concentration of hydrogen peroxide and 4-nitrophenol.

It is observed that with an increase in the amounts of iron ions concentration from 3 to 15 wt%, the degradation of

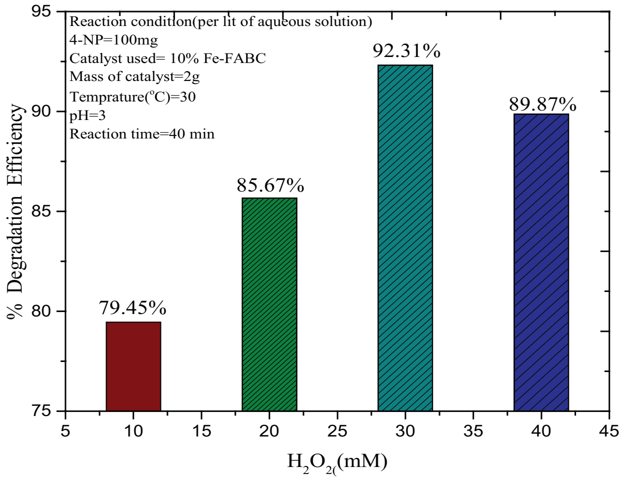


Fig. 11. Effect of hydrogen peroxide concentration on 4-NP degradation.

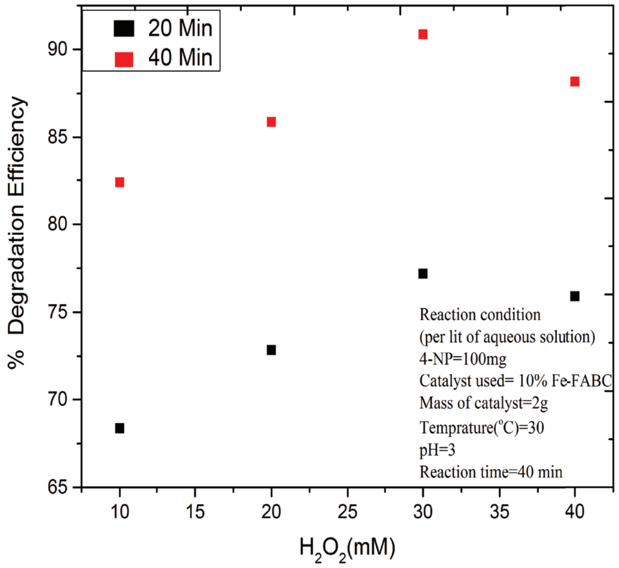


Fig. 12. % Degradation on different H_2O_2 dosages with change in time (20 and 40 min, respectively).

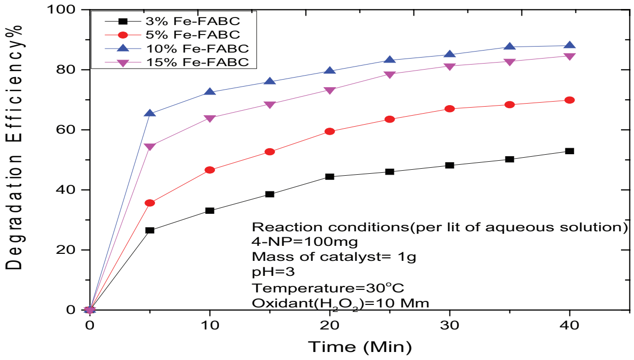


Fig. 13. Effect of iron loading on fly ash brick clay.

4-nitrophenol increased until it reached the maximum value. This can be attributed to the increased production of more •OH radicals in the system. Around, 92% degradation was achieved for 10 wt%, catalyst loading within 40 min.

However, with further increase in the amount of iron ions beyond the 10 wt%, the degradation efficiency of 4-nitrophenol was reduced. This may be explained by the fact that higher concentration of iron ions could lead to the scavenging of •OH radicals by iron ions which is responsible for the decrease in degradation of 4-nitrophenol.

4.7. Comparative study for degradation of 4-NP with different catalyst and without catalyst

The removal efficiency of 4-NP in absence of catalyst was found to be very low. It was maximum 23% in 40 min of reaction time. By comparing the results for the 4-NP degradation without catalyst and with 2 g catalyst, the degradation for 2 g catalyst is approximately three times to that of without catalyst. The rate of degradation is also more for higher concentrations of catalyst and increases with it. The clay with initial percentage of iron ions gave higher percentage degradation without catalyst but it was less than the percentage with catalyst of 10% Fe. Because it contains sufficient quantity of iron percentage. Degradation of 4-NP with 2 g of reactant was found to be around 92% and with FABC was 47% only.

4.8. Effect of catalyst stability

The stability tests were conducted to assess the catalytic activity of Fe-FABC catalyst through four consecutive experiments with the same catalyst load under the same reaction conditions which show that the degradation efficiency of 4-NP decreased with recycle number. At the end of each cycle, the catalyst was washed with distilled water three times followed by drying in an oven. As can be seen from Fig. 14, the degradation efficiency of 100 ppm of 4-NP in 40 min decreases from 90% for the first cycle to 84% for the second cycle. Nevertheless, when the catalyst was further reused without treatment in the third cycle, it was found that the 4-NP degradation efficiency dropped from 90% to about 70% as reported in Fig. 14. Therefore, the used catalyst after the third run requires suitable regeneration prior to further use.

Several possible regeneration methods include refluxing, calcination under a suitable atmosphere, rinsing by appropriate solvent or some combinations of processes. The deactivated 10% Fe-FABC catalyst was regenerated by drying at 100°C for 1 h followed by calcinations at 500°C for 1 h, to remove the unreacted 4-NP, the catalytic activity of fresh catalyst was compared with the catalytic activity of regenerated catalyst under the same conditions. Calcination of 10% Fe-FABC is an effective regeneration method, gave the degradation efficiency of 85% (Fig. 14). The catalytic activity of regenerated catalyst is very close to its initial activity.

5. Kinetic study on degradation of 4-NP

Fig. 15 shows a plot of ln(C_0/C_t) vs. time for the catalytic degradation of 4-NP in the presence of the Fe-FABC. The first-order kinetic model (Eq. (8)) was used to measure the efficiency of Fe-FABC. It was used to calculate the respective first-order rate constant (*k*) according to following equation:

$$\ln\left(\frac{C_0}{C}\right) = kt \tag{8}$$

where C_0 is the initial concentration and C is concentrations of 4-NP at time *t*. The linear regression plots fitted well (as shown in Fig. 16), from which the slopes of each plot were calculated and used to obtain the first-order rate constants (*k*). The *k* value for different wt% of catalyst was found as in Table 2:

The higher the *k* value, the faster the degradation of 4-NP, hence better the catalytic activity of the Fe-FABC.

6. Reaction mechanism

The degradation of 4-NP might be characterized as two unique plans as shown in Fig. 17 (Plan 1 and Plan 2).

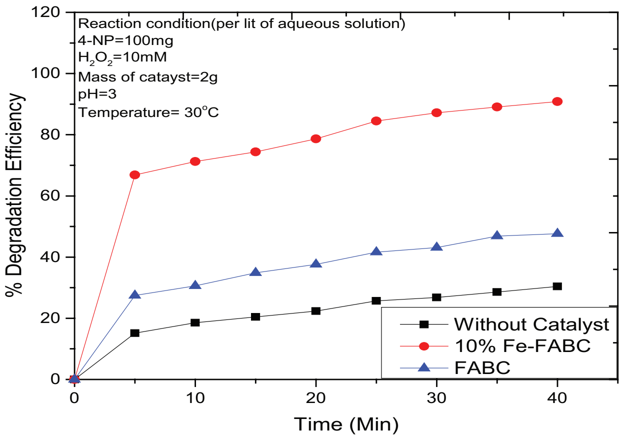


Fig. 14. Comparative study for degradation of 4-NP with different conditions.

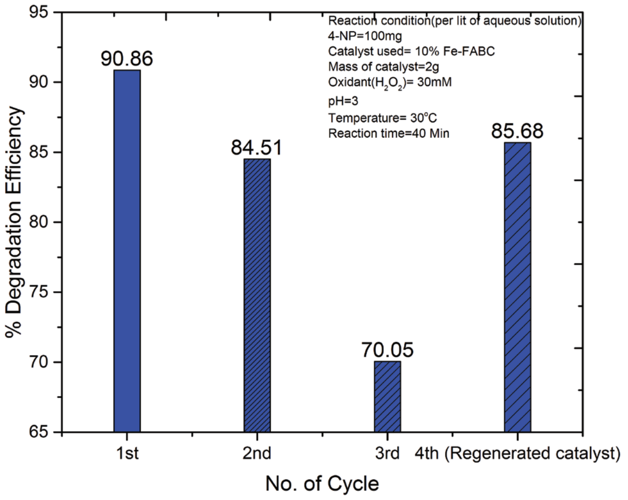


Fig. 15. Effect of recycle number of the catalyst (10% Fe-FABC) on the degradation of 4-NP, with or without regeneration.

Table 2
Values of rate constant obtained in degradation of 4-NP catalyzed by Fe-FABC as a function of different wt% of Fe

$k_{1,3\%Fe\text{-}FABC}$	0.01277 min^{-1} (minimum)
$k_{2,5\%Fe\text{-}FABC}$	0.02246 min^{-1}
$k_{3,10\%Fe\text{-}FABC}$	0.0284 min^{-1} (maximum)
$k_{4,15\%Fe\text{-}FABC}$	0.02554 min^{-1}

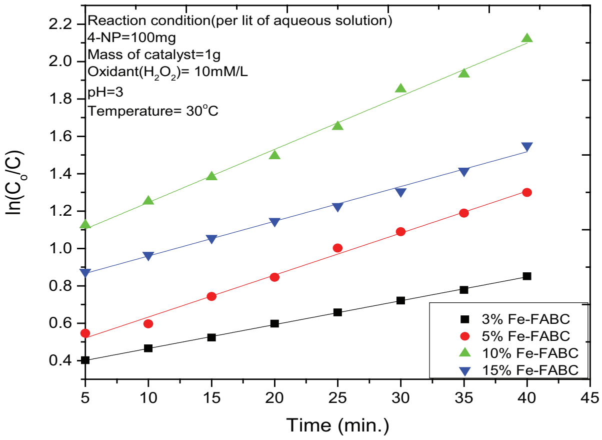


Fig. 16. Kinetics of 4-nitropheol degradation catalyzed by Fe-FABC as a function different wt% of Fe.

The principal intermediates are most likely hydroquinone and 4-nitrocatechol. The intermediates might be distinguished by HPLC or LC/MS. As depicted in such a large number of literary works, hydroxyl radicals are receptive species in H_2O_2 process, reaction of hydroxyl radicals with aromatic groups occurs by means of electrophilic expansion. Within the site of 4-NP, hydroxyl radicals may enter in the ortho position to shape 4-nitrocatechol (4-NC). Based on data, the reaction pathway appeared in Plan 2 has been proposed for the photo-oxidative degradation of 4-NP. 4-NC will react with hydroxyl radical to shape 1,2,4-benzenetriol (1,2,4-BT) [49]. Reaction of the essential intermediates with hydroxyl radicals prompt ring opening and development of oxygenated aliphatic compounds, short-chain carboxylic acids such as fumaric acid, oxalic acid and formic acids, and so on [50]. Besides this, the complete degradation of 4-NP can be clarified by the arrangement of short-chain carboxylic acids that are finally oxidized by •OH to CO_2 and H_2O as mineralization products. Direct attack of the hydroxyl radicals to nitro group position can cause to arrangement of hydroquinone (HQ). HQ similar to 4-NC responds with hydroxyl radical to shape 1,2,4-BT. The degradation of 4-NP to shape 4-NC and HQ which furthermore encourage response with hydroxyl radical to frame 1,2,4-BT is the same as the degradation pathway proposed for the photo-catalytic degradation of 4-NP in UV/TiO_2 [4].

6. Conclusions

The effectiveness of the Fe-FABC/H_2O_2 for the degradation of 4-nitrophenol in aqueous solutions was investigated. The results ratify that Fe-FABC can be used as a heterogeneous catalyst for the activation of H_2O_2 in the process. The results show that a Fenton reagent in the presence of Fe-FABC is cost-effective (since the FABC is used as a support matrix); and easy to operate. Based on the results obtained, the best operation parameters for the Fenton oxidation of 4-NP were 10 wt% of iron-loaded catalyst, 2.0 g/L of catalyst dosage and 30 mM/L of H_2O_2 oxidant dosages for 100 ppm aqueous solution of 4-NP at an initial pH 3, room temperature of 30°C. Under these conditions, 92% degradation efficiency of 4-NP in aqueous solution was achieved within 40 min of reaction time.

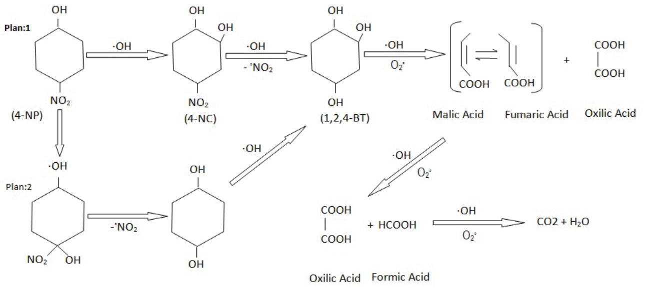


Fig.17. Degradation mechanism for 4-NP.

Acknowledgments

This work was supported by Department of Science and Technology – Science and Engineering Research Board (File No. YSS/2014/000996), India.

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