



Benzoic Acid Degradation by Highly Active Heterogeneous Fenton-like Process using Fe^{3+} - Al_2O_3 Catalyst

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This work examines oxidative degradation of benzoic acid in an aqueous solution using an eco-friendly advanced oxidation (heterogeneous Fenton) process. The degradation of benzoic acid ($1,000 \text{ mgL}^{-1}$) with H_2O_2 was performed using Fe^{3+} immobilized within an Al_2O_3 matrix as a heterogeneous Fenton catalyst and the efficiency of the system was compared to that of the homogeneous $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system. The influence of various operational conditions like catalyst dosage, H_2O_2 concentration, Fe^{3+} concentration, pH of the solution and initial substrate concentration on % degradation for both the processes has been studied to find out the best operating conditions for these processes. The experimental results show that the optimum conditions for homogeneous $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ process are $[\text{Fe}^{3+}] = 1,250 \text{ mgL}^{-1}$, $[\text{H}_2\text{O}_2] = 2,000 \text{ mgL}^{-1}$, initial pH = 3 and 87.5 % degradation was obtained within 35 min. In the case of heterogeneous catalyst, degradation improved to 91.7% using 12.5 gL^{-1} catalyst for the same duration keeping other operating conditions the same. The use of iron immobilized in alumina matrix as heterogeneous Fenton catalyst is an alternative approach for degrading organic contaminants.

Keywords: Advanced oxidation technologies (AOTs), Catalyst characterization, Environmental remediation, Heterogeneous supported catalyst, Hydroxyl radicals

Introduction

The growing concern about the problem of wastewater decontamination from organic pollutants has led to research for further human or industrial use. In recent years, among Advanced Oxidation Processes (AOPs), Fenton and Fenton-like oxidations, have been actively employed to treat industrial effluents.¹⁻⁵ Advanced oxidation processes produce reactive radicals, primarily hydroxyl radicals ($\text{HO}\cdot$), which are extremely oxidative, with the ability to degrade a variety of organic contaminants. A notable shortcoming of the homogeneous Fenton process is the production of sludge that contains iron caused by the settling of ferric hydroxide complexes. The separation and discard of a large amount of sludge is a serious concern, the application of conventional Fenton and Fenton-like process is restricted to industrial wastewater treatment processes.^{6,7}

In this context, heterogeneous solid catalysts can provide an effective technological solution in treating different kinds of wastewater. Fenton-like reactions can be facilitated by these catalysts throughout a wide

pH range. This is attributed to Fe^{3+} ions in the catalysts being "immobilized" inside the structure and pore/interlayer of the catalyst. Consequently, the catalyst's capacity to produce $\cdot\text{OH}$ from H_2O_2 is maintained, and iron hydroxide precipitation is avoided. Other advantages of heterogeneous catalyst include: limited leaching of iron ions, reuse of catalyst for successive operations.⁸

Benzoic Acid (BA) is an important precursor for the synthesis of many organic substances and also used in petrochemical and chemical processes. It is introduced into the environment by a variety of industrial and natural sources. High concentration of benzoic acid is known to affect liver and kidney. This aromatic organic compound is very toxic to lungs, nervous systems and it is widely used as a food preservative and in pharmaceutical industrial effluents.

One study focused on the degradation of benzoic acid through heterogeneous photo-Fenton process by utilizing $\text{Fe}_2\text{O}_3/\text{SBA-15}$ as a catalyst.⁹ Another study revealed details of the photodegradation of benzoic acid in water with Degussa P-25 TiO_2 suspensions.¹⁰

Some researchers have looked into the catalytic wet oxidation (CWO) of aqueous benzoic acid (BA)

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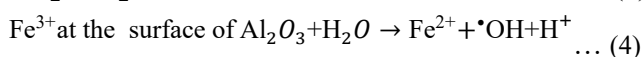
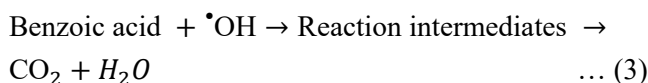
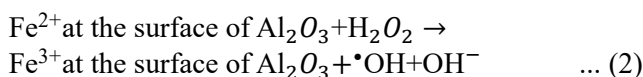
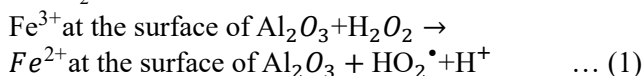
solutions utilizing a variety of copper and iron-based catalysts.¹¹ There have been no work reported so far on the degradation of BA by heterogeneous iron supported or incorporated Fe³⁺ on Al₂O₃ in presence of H₂O₂.

Benzoic acid is the parent element of various phenolic compounds present in agro-industrial effluents like gallic, vanillic, syringic, veratric, and hydroxybenzoic acids, thus BA was chosen as a target organic pollutant for this study. Also, it is refractory and resistant to biodegradation.¹²

The present work deals with the BA degradation by Fenton-like process with Fe impregnated in Alumina catalyst and H₂O₂. To compare with homogeneous process some experiments were also carried out with Fe³⁺/H₂O₂ system. The operational factors such as Fe³⁺ concentration, catalyst dose, H₂O₂ concentration, pH of the solution, and initial BA concentration were changed to identify the best conditions for higher degradation with prepared catalyst and homogeneous process.

Benzoic acid Degradation Mechanism by Immobilized Fe

In the heterogeneous Fenton process, the Fe³⁺ is reduced to Fe²⁺ further at the surface of Al₂O₃ that Fe²⁺ reacts with H₂O₂ based on the following mechanism. This is in line with the work of authors who dealt with a similar system for destruction of dye molecules as shown in Eqs (1) – (4).⁽¹³⁾ The reactions start when Fe³⁺ present on [Fe³⁺-Al₂O₃] surface is reduced to Fe²⁺ by H₂O₂. Afterwards, the Fe²⁺ further reacts with H₂O₂ and produces ·OH radicals. Fe³⁺ on the surface of Al₂O₃ may also react with H₂O to produce ·OH radicals. These ·OH radicals reacting with BA lead to production of reaction intermediates. Those intermediates are eventually converted to CO₂ and H₂O.



Materials and Methods

Reagents

Merck, India, supplied hydrogen peroxide (50%, v/v), benzoic acid, and ferric nitrate. H₂SO₄ and NaOH were utilized to adjust the pH of the

solution. Aluminum oxide (Al₂O₃) was supplied by Merck, India. Ethanol was obtained from Chang Yang Chemical Corporation, China. Distilled water was utilized throughout to prepare synthetic solution.

Catalyst Preparation and Characterization

Selection of Matrix to Prepare Catalyst

The catalyst prepared for the degradation of above contaminants was Fe³⁺ immobilized in aluminum oxide using ferric nitrate salt, Fe(NO₃)₃ · 9H₂O. The nitrate salt was chosen for high solubility, low cost, and easy availability. The method of preparation and characterization of the catalyst is discussed below. Aluminum oxide (alumina, Al₂O₃) is a valuable oxide ceramic, since it has many engineering applications like coatings, heat-resistant materials and advanced ceramics and also acts as a matrix on which active species can be immobilized. This is owing to alumina's unique physico-chemical characteristics such as hardness, well resistance to acids and bases, very good performance at high temperatures and high wear resistance. Apart from that, alumina can be very effectively used as a support material for heterogeneous catalyst as it is thermally stable and its high surface area enables the distribution of active phases on it.

Preparation of Catalyst

There are various methods to prepare heterogeneous catalysts, however, in this study hydrothermal method of synthesis was used to prepare alumina/iron heterogeneous catalysts. In this method, 100 mL mixture of ethanol and water (60:40 v/v) was taken to prepare different catalysts. In a beaker 5 gm of aluminum oxide (Al₂O₃) was mixed with four different amounts of ferric nitrate (15, 20, 25 and 30 gm) to prepare the catalyst with four different iron wt.%. Each sample was vigorously stirred for around 3 hours at room temperature. Followed by this, the aqueous mixture was passed through Whatman 42 filter paper and then, the Fe³⁺ impregnated alumina was collected. After that, this catalyst was kept in a hot air oven for 12 hrs at 105°C to dry and remove any moisture in the prepared heterogeneous iron-aluminum catalyst.

Characterization of Catalyst

The prepared catalyst was characterized. The Scanning Electron Microscope (SEM) images of only Al₂O₃ and prepared catalyst of 28 weight percentage of iron are shown in Fig. 1. The image for untreated aluminum oxide is displayed in Fig. 1(a) and the iron

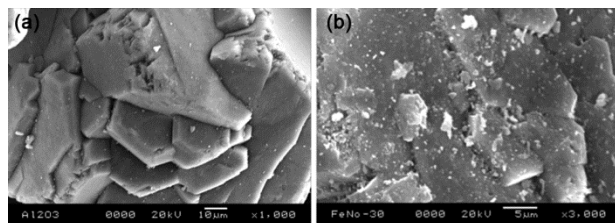


Fig. 1 — (a) SEM image of untreated Al_2O_3 , (b) SEM image for Fe^{3+} - Al_2O_3 catalyst of 28% iron

crystallites covering the alumina matrix are shown in Fig. 1(b). The composites morphologies of the prepared four catalyst samples were observed. But, only optimized one is shown in figures. The amount of iron incorporated in aluminum is increased as weight percentage of iron is increased. The dispersion of iron on the aluminum matrix was confirmed in Fig. 1(b). The SEM image reveals that the particles are evenly dispersed and linked to each other via the grain boundary, forming agglomerated particles. A scanning electron microscope (Model no: JEOL JSM6301-F) combined with Energy dispersive X-ray (EDX) spectroscopy was used to analyze the sample. The EDX spectrum of catalyst specifying the iron percentage is displayed in Fig. 2. The amount of iron content in prepared catalyst was determined by EDX and the catalyst was labeled by % of iron present in it. For example, 28 wt % Fe^{3+} - Al_2O_3 consists of 28 wt % of Fe in the final catalyst as per EDX analysis.

The solid catalyst was also characterized by X-ray diffraction (XRD) and the pattern was recorded by a Siemens D-500 diffractometer at 40 kV and 30 mA using filtered $\text{Cu K}\alpha$ radiation. The X-ray diffraction pattern of the alumina/iron heterogeneous catalyst prepared by hydrothermal synthesis is shown in Fig. 3. The XRD study confirmed the crystal structures and various phases of the alumina. X-ray diffraction patterns of 22 wt % Fe^{3+} - Al_2O_3 , 28 wt % Fe^{3+} - Al_2O_3 and 32 wt % Fe^{3+} - Al_2O_3 composites were obtained. X-ray diffraction peaks were observed at values of 36.52, 39.66, 42.75, 45.71 and 64.37. The peaks at 36.52, 39.66, and 45.71 indicate the presence of a rhombohedral structured Fe_2O_3 (JCPDS FILE NO-(79-1741)) while the peaks at 42.75 and 64.37 relating to the existence of orthorhombic structured $\text{AlO}(\text{OH})$. Hydrothermally synthesized composite oxide consists of a blend of $\text{d-Fe}_2\text{O}_3$ along with $\text{AlO}(\text{OH})$ phases (JCPDS FILE NO-(81-0464))

Experimental Procedure

Experiments were conducted in batch mode in a 1,000 ml beaker containing 300 ml of BA solution for

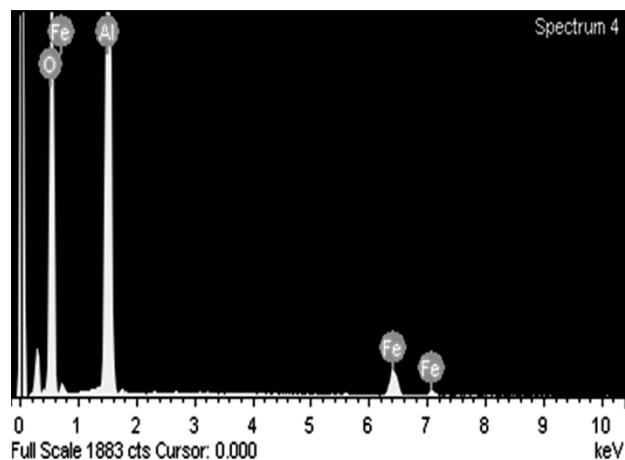


Fig. 2 — EDX spectrum of Fe^{3+} - Al_2O_3 catalyst with 28% iron

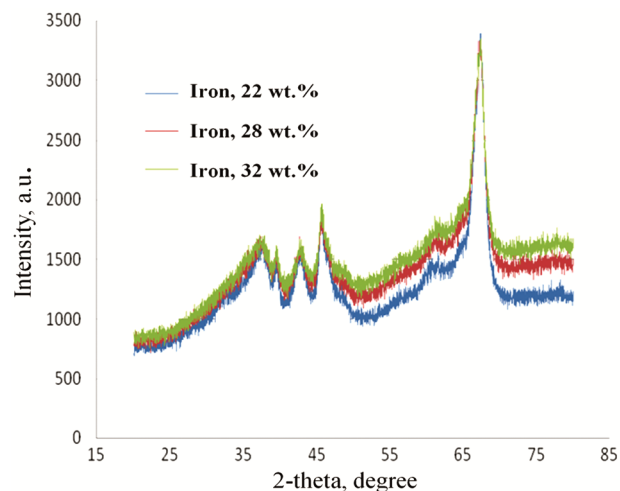


Fig. 3 — XRD pattern of the heterogeneous iron alumina catalyst

its degradation purpose with immobilized Fe^{3+} catalyst and homogeneous Fenton-like process. To maintain the required pH, 3N H_2SO_4 or NaOH solution was used. Ferric nitrate solution was prepared and part of this solution was injected into the beaker to achieve the required Fe^{3+} initial concentration for the Fenton-like homogeneous process of $\text{Fe}^{3+}/\text{H}_2\text{O}_2$. A required quantity of H_2O_2 was poured into that solution to initiate the oxidation reaction. For well mixing of the whole solution, a magnetic stirrer was used constantly throughout all the experiments. The catalyst was added in the beaker instead of ferric nitrate solution for conduction of experiments with immobilized Fe^{3+} catalyst.

Samples were taken from the beaker time to time by a pipette during the reaction time. Further reaction was prevented by using 3N NaOH. After filtering through Whatman filter paper (No. 42) the BA

concentration was determined using High-performance Liquid Chromatography (HPLC).

Analytical Methods

The BA concentration was determined by HPLC (Perkin Elmer Series 200). A reverse-phase C-18 column (4.6 mm i.d × 250 mm length) was used. Organic Acid was used as a stationary phase. The mobile phases were eluted using 60% deionized water and 40% acetonitrile. The injection volume was 20 µL, with a fixed flow rate of 1 mL/min. A digital pH meter from Toshcon Industries Pvt Ltd. with model number CL 46+ was used to check the sample pH. The EDX combined with SEM (Model No: JEOL JSM5800) measured the amount of Fe immobilized in the alumina matrix.

Results and Discussion

In the present study, the operating variables (initial pH of the solution, concentration of H₂O₂, dosage of Fe³⁺, dose of catalyst, initial substrate concentration) have been optimized for maximizing concentration reduction. The influence of Fe³⁺ impregnated on to the surface of alumina was also studied in this work.

Influence of Fe³⁺ Impregnation on Alumina Matrix for Benzoic acid Degradation

Experiments for the removal of BA were carried out with 16, 22, 28 & 32 % Fe on the prepared catalyst. The BA degradation results for different percentages of iron loading on catalysts are displayed below in Fig. 4. The BA degradation got improved from 82.1 % to 91.7 %, when the loading was increased from 16 to 28 %. More than 28 % iron

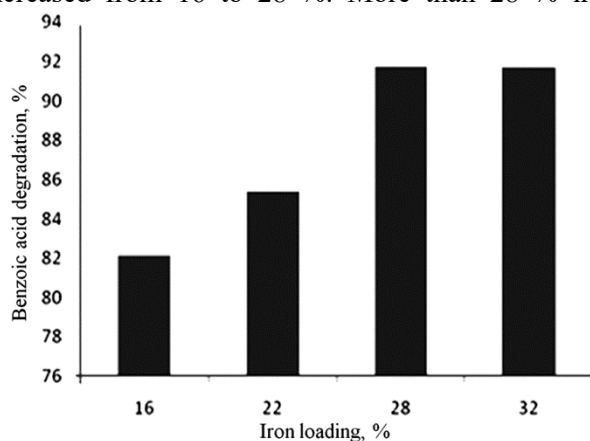


Fig. 4 — Influence of iron loading on Al₂O₃ for BA degradation, % with Catalyst concentration = 12.5 gL⁻¹, initial BA = 1,000 mgL⁻¹, H₂O₂ concentration = 2,500 mgL⁻¹, initial pH = 3, Time = 35 minutes

loading, % degradation improvement was not significant. Increasing iron loading in the catalyst may lead to leached iron into the solution. Iron loading of 28 wt% onto the alumina surface was found to be optimal as there was no significant improvement in degradation after that. So, consecutive experiments were carried out with catalyst of 28 wt% Fe.

Influence of Fe³⁺ Concentration on Benzoic acid Degradation

In the homogeneous system, the concentration of Fe³⁺ was varied from 750 mgL⁻¹ to 1,500 mgL⁻¹ with ferric nitrate solution as displayed in Fig. 5(a). The Fe³⁺ content in Fe-impregnated catalysts was altered by increasing the dose of catalyst from 7.5 gL⁻¹ to 15 gL⁻¹ as demonstrated in Fig. 5(b). The other operating process parameters (H₂O₂, pH, substrate conc.) were kept unchanged. Catalyst with 28wt% Fe was used in this experiment. Since, Fe³⁺ dosage is a vital parameter in determining the optimum degradation efficiency, it is essential to optimize its concentration during the treatment. Degradation of the BA initially rises up to certain concentration with Fe³⁺ dosage increment as there is an enhancement of •OH radical concentration as depicted in Fig 5. But, the further increase in concentration did not lead to higher degradation. This indicates that an oxidant dose higher than an optimum dose can't produce satisfactory results. A progressive fall in the concentration of the pollutant was observed. It can be seen that the degradation reaches a peak as the concentration of Fe increases from a small value and then falls again. Maximum degradation of BA is 86.1% at 1,250 mgL⁻¹ by using ferric nitrate and maximum degradation of 87.2% is at 12.5 gL⁻¹ by using immobilized Fe, after which it starts falling. The % decrease in degradation was observed which

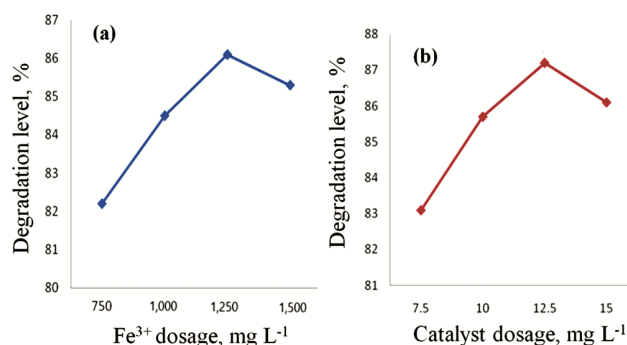


Fig. 5 — Influence of Fe³⁺ concentration on degradation of BA (1,000 mgL⁻¹) using (a) ferric nitrate and (b) Fe impregnated at room temperature (at pH = 3 with H₂O₂ = 1,000 mgL⁻¹ under 35 min)

possibly signifies the scavenging action by hydroxyl radical with excess Fe^{2+} as shown in Eq. (5).⁽¹⁴⁾



Alumina is a Lewis acid and it plays a crucial role for maximum degradation. The addition of Lewis acid to iron helps in the reduction of Fe^{3+} via hydrogen peroxide by seeking additional electron from the iron center, lowering the Fe^{3+} promptly.¹⁵ It is very obvious that the reaction between Fe^{2+} and H_2O_2 is faster compared to reaction between Fe^{3+} and H_2O_2 . This may be the actual reason behind the better performance of the immobilized catalyst than homogeneous catalytic process.

Influence of H_2O_2 Concentration on Benzoic acid Degradation

H_2O_2 being the source of $\cdot\text{OH}$ radicals, the formation of $\cdot\text{OH}$ radicals depends on the concentration of H_2O_2 . Addition of excess H_2O_2 beyond the optimized amount does not produce satisfactory results. Thus, optimization of the H_2O_2 dose is very essential to avert scavenging of $\cdot\text{OH}$ radicals. Experiments were carried out with varying initial H_2O_2 concentrations while keeping the other parameters constant. The concentration of H_2O_2 was varied from $1,000 \text{ mgL}^{-1}$ to $3,000 \text{ mgL}^{-1}$ to observe the change in degradation % with different oxidant concentration. In the homogeneous Fenton-like process ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$), the Fe^{3+} concentration was set at $1,250 \text{ mgL}^{-1}$, and the amount of Fe impregnation was fixed at 12.5 gL^{-1} in the synthesized catalyst. The % degradation of BA at different initial H_2O_2 concentrations is shown in Fig. 6 (a) & (b). A rise in hydrogen peroxide concentration than this optimum level has a negative impact on the process, and percent degradation starts to decrease. A minor increase in % degradation was found at the lower

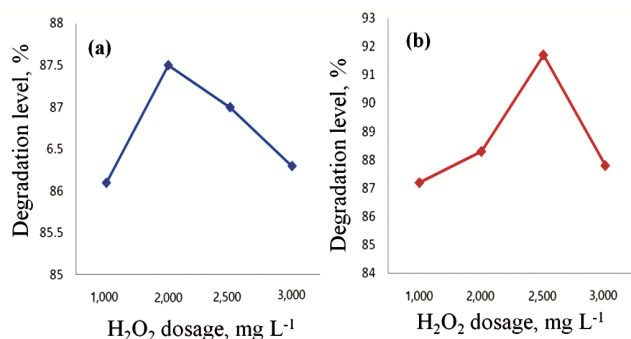
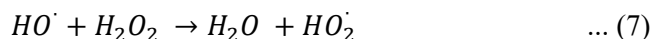


Fig. 6 — Effect of H_2O_2 concentration on decomposition of BA ($1,000 \text{ mgL}^{-1}$) using (a) ferric nitrate and (b) Fe impregnated at room temperature and $\text{pH} = 3$, $\text{Fe}^{3+} = 1,250 \text{ mgL}^{-1}$, $\text{Fe(III)-Al}_2\text{O}_3 = 12.5 \text{ gL}^{-1}$, time = 35 minutes

initial concentration of H_2O_2 , as H_2O_2 produces more hydroxyl radical with rise in H_2O_2 concentration. It is primarily due to an increase in hydroxyl radicals generated by extra H_2O_2 . Scavenging of $\cdot\text{OH}$ by H_2O_2 becomes prominent above the critical concentration, along with the formation of hydroperoxy radicals (HO_2^\cdot), which can also be explained in terms of H_2O_2 critical concentration.^{16,17} The following scavenging reactions are shown by Eqs (6) & (7).



Maximum degradation of BA was 87.5% and 91.7% at $2,000 \text{ mgL}^{-1}$ and $2,500 \text{ mgL}^{-1}$ of H_2O_2 , respectively for ferric nitrate case and immobilized iron-alumina case.

Influence of Initial pH on BA Degradation

The Fenton based reactions highly depend on pH. Formation of hydroxyl radicals ($\cdot\text{OH}$) are controlled by reaction pH. For all the experiments, the initial BA concentration was $1,000 \text{ mgL}^{-1}$ and the initial pH values of the solution were adjusted to 2, 3, 4 and 5 by addition of H_2SO_4 and NaOH , as and when required.

Experiments were carried out with various initial pH levels of the solution while keeping all other reaction conditions constant. The pH variation was 2 to 5 in different experiments with reaction duration of 35 minutes. In the case of ferric nitrate, the concentration of Fe^{3+} and H_2O_2 i.e. $1,250 \text{ mgL}^{-1}$ and $2,000 \text{ mgL}^{-1}$, respectively were maintained, while for impregnated Fe, the amount of $\text{Fe(III)-Al}_2\text{O}_3$ catalyst was fixed at 12.5 gL^{-1} and the concentration of H_2O_2 was $2,500 \text{ mgL}^{-1}$. The results are depicted in Fig. 7 (a) & (b) to evaluate the impact of starting pH on BA degradation.

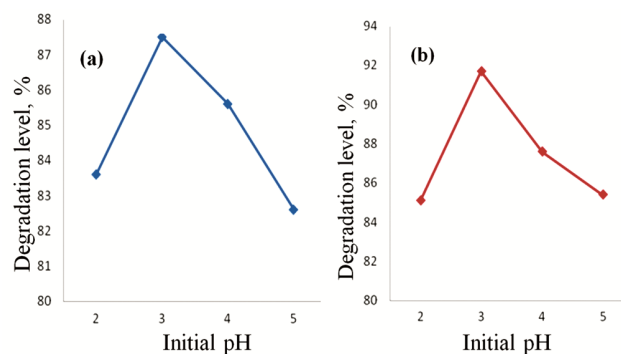


Fig. 7 — Influence of pH on degradation of BA ($1,000 \text{ mgL}^{-1}$) using (a) ferric nitrate and, (b) immobilized Fe at room temperature and $\text{Fe}^{3+} = 1,250 \text{ mgL}^{-1}$, $\text{Fe(III)-Al}_2\text{O}_3 = 12.5 \text{ gL}^{-1}$, time = 35 minutes

Maximum degradation of 87.5 % and 91.7 % was observed at pH 3 in case of Fe³⁺/H₂O₂ and immobilized Fe based process, respectively. At higher pH, ferrous ion gets easily converted to ferric ions,¹⁸ which has more inclination towards the formation of ferric-hydroxo complexes with hydrogen peroxide¹⁹ and as a result back generation of Fe²⁺ is prevented. So, it reduces the generation of hydroxyl radical which is very much essential for BA degradation. At higher pH, Fe³⁺ also precipitates as Fe(OH)₃, arrests the reaction between Fe³⁺ and H₂O₂. Fe²⁺ ions are more efficient compared to Fe³⁺ ions as only Fe²⁺ ions are able to directly generate [•]OH.^{20,21} The H₂O₂ decomposes faster to molecular O₂ and water rather than formation of significant amount of [•]OH radicals.²² This is also an additional reason. The scavenging impact of [•]OH radicals by H⁺ becomes more significant at pH level below 3.^(23,24) At lower pH, the hydroxyl radical is scavenged by H⁺ ions, resulting in a decreased BA degradation as shown in Eq. (8)⁽²⁵⁾:



The Impact of the Initial Concentration of BA on Degradation

Experiments were conducted with different concentrations of BA keeping other processes variables constant for 35 minutes. The BA initial concentrations for the different experiments were 1,000 mgL⁻¹ and 1,250 mgL⁻¹ and 1,500 mgL⁻¹ at pH 3. The starting concentration of H₂O₂ was 2,500 mgL⁻¹ and 12.5 gmL⁻¹ for immobilized catalyst and for Fe³⁺/H₂O₂ system, initial H₂O₂ concentration was 2000 mgL⁻¹ and Fe³⁺ concentration was 1,250 mgL⁻¹. The results are shown in Fig. 8 (a) & (b). It was found that percentage degradation wanes with the escalation of initial concentration.

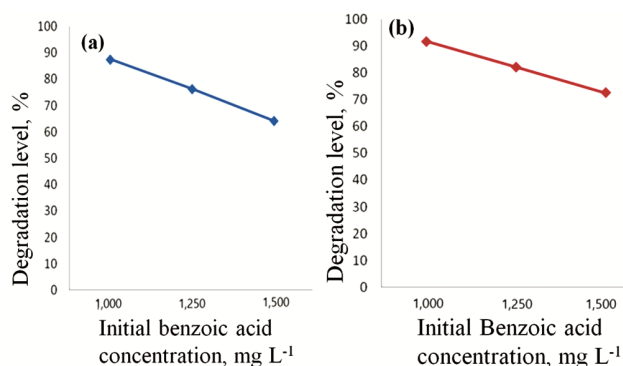


Fig. 8 — The impact of the starting concentration of BA on degradation by using (a) Ferric Nitrate, (b) Iron-alumina catalyst

This is due to the unavailability of the proportional amount of oxidizing agent. As the amount of H₂O₂ is constant, [•]OH radicals generation also remains unchanged.

Using optimum conditions, BA degradation of 87.5% degradation in Fenton's like process and 91.7% in case of immobilized Fe (Fe(III)-Al₂O₃ catalyst) was achieved within 35 minutes. All experiments have been performed at room temperature.

Conclusions

It can be concluded from the studies that process parameters like Fe³⁺ concentration, dose of catalyst, hydrogen peroxide concentration, pH, and initial pollutant concentration have a major impact in determining the overall process efficiency. The prepared heterogeneous iron-alumina catalyst (Fe (III)-Al₂O₃) can degrade Benzoic acid effectively. The degradation pattern of benzoic acid will be very useful for designing a treatment facility for pre-treatment / treatment of wastes containing impurities. More than 90% degradation can be achieved in 35 minutes of time at room temperature. Iron immobilized in alumina matrix can be effectively used as heterogeneous Fenton catalyst in wastewater treatment. To make the process of wastewater treatment environmentally sustainable iron-free system, a solid heterogeneous insoluble catalyst, can be a better choice for the degradation of organic pollutants.

References

- Bautista P, Mohedano A F, Casas J A, Zazo J A & Rodriguez J J, An overview of the application of Fenton oxidation to industrial wastewaters treatment, *J Chem Technol Biotechnol*, **83** (2008) 1323–1338.
- Pignatello J J, Oliveros E & MacKay A, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, *Crit Rev Environ Sci Technol*, **36** (2006) 1–84.
- Neyens E & Baeyens J, A review of classic Fenton's peroxidation as an advanced oxidation technique, *J Hazard Mater*, **98** (2003) 33–50.
- Chakinala A G, Bremner D H, Burgess A E & Namkung K C, A modified advanced Fenton process for industrial wastewater treatment, *Water Sci Technol*, **55** (2007) 59–65.
- Mijangos F, Varona F & Villota N, Changes in solution color during phenol oxidation by Fenton reagent, *Environ Sci Technol*, **40** (2006) 5538–5543.
- Benatti C T, da Costa A C & Tavares C R, Characterization of solids originating from the Fenton's process, *J Hazard Mater*, **163** (2009) 1246–53.

- 7 Hsueh C L, Huang Y H, Wang C C & Chen C Y, Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system, *Chemosphere*, **58** (2005) 1409–1414.
- 8 Ghosh P, Kumar C, Samanta A N & Ray S, Comparison of a new immobilized Fe³⁺ catalyst with homogeneous Fe³⁺-H₂O₂ system for degradation of 2, 4-dinitrophenol, *J Chem Technol Biotechnol*, **87** (2012) 914–923.
- 9 Velegraki T & Mantzavinos D, Conversion of benzoic acid during TiO₂-mediated photocatalytic degradation in water, *Chem Eng J*, **140** (2008) 15–21.
- 10 Velegraki T, Nouli E, Katsoni A, Yentekakis I V & Mantzavinos D, Wet oxidation of benzoic acid catalyzed by cupric ions: Key parameters affecting induction period and conversion, *Appl Catal B*, **101** (2011) 479–485.
- 11 Gernjak W, Maldonado M I, Malato S, Cáceres J, Krutzler T, Glaser A & Bauer R, Wet oxidation of benzoic acid catalyzed by cupric ions: Key parameters affecting induction period and conversion, *Sol Energy*, **77** (2004) 567.
- 12 Muthukumari B, Selvam K, Muthuvel I & Swaminathan M, Photoassisted hetero-Fenton mineralisation of azo dyes by Fe (II)-Al₂O₃ catalyst, *Chem Eng J*, **153** (2009) 9–15.
- 13 Yang M, Hu J & Ito K, Characteristics of Fe²⁺/H₂O₂/UV oxidization process, *Environ Technol*, **19** (1998) 183–191.
- 14 Lim H, Lee J, Jin S, Kim J, Yoon J & Hyeon T, Highly active heterogeneous Fenton catalyst using iron oxide nanoparticles immobilized in alumina coated mesoporous silica, *Chem Commun*, **4** (2006) 463–465.
- 15 Critenden J C, Hu S, Hand W D & Creen A S, A kinetic model for H₂O₂/UV process in a completely mixed batch reactor, *Water Res*, **33** (1999) 2315–2328.
- 16 Buxton G V, Greenstock C L, Helman W P & Ross A B, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH[•]/O[•]) in aqueous solutions, *J Phys Chem Ref Data*, **17** (1988) 513–886.
- 17 Kwon B G, Lee D S, Kang N & Yoon J, Characteristics of p-chlorophenol oxidation by Fenton's reagent, *Water Res*, **39** (1999) 2110–2118.
- 18 Kang Y W & Hwang K Y, Effects of reaction conditions on the oxidation efficiency in the Fenton process, *Water Res*, **34** (2000) 2786–2790.
- 19 Ntampeglitis K, Riga A, Karayannis V, Bontozoglou V & Papapolymerou G, Decolorization kinetics of Procion H-ex dyes from textile dyeing using Fenton-like reactions, *J Hazard Mater*, **136** (2006) 75–84.
- 20 Lunar L, Sicilia D, Rubio S, Pérez-Bendito D & Nickel U, Identification of metal degradation products under Fenton's reagent treatment using liquid chromatography-mass spectrometry, *Water Res*, **34** (2000) 3400–3412.
- 21 Ramirez J H, Costa C A, Madeira L M, Mata G, Vicente M A, Rojas-Cervantes M L, Lopez-Peinado A J & Martin-Aranda R M, Fenton-like oxidation of Orange II solutions using heterogeneous catalysts based on saponite clay, *Appl Catal B*, **71** (2007) 44.
- 22 Feng J, Hu X, Yue P L, Zhu H Y & Lu G Q, Degradation of azo-dye orange II by a photoassisted Fenton reaction using a novel composite of iron oxide and silicate nanoparticles as a catalyst, *Ind Eng Chem Res*, **42** (2003) 2058–2066.
- 23 Muruganandham M & Swaminathan M, Decolourisation of Reactive Orange 4 by Fenton and photo-Fenton oxidation technology, *Dyes Pigment*, **63** (2004) 315–321.
- 24 Lucas M S & Peres J A, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, *Dyes Pigment*, **71** (2006) 236–244.