

Effect of Operating Parameters, Reaction Kinetics and Comparative Assessment of Fluidized-Bed Fenton Oxidation of 4-Nitrophenol

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ABSTRACT: *The oxidation of 4-Nitrophenol (4-NP) has been studied using recirculating fluidized-bed Fenton process. The effect of various parameters such as pH, the concentration of hydrogen peroxide, concentration of ferrous ions, various type of carriers, and dosage of carrier were investigated on the oxidation of 4-NP. Al₂O₃ and SiO₂ were used as two different carriers for the oxidation of 4-NP. The experimental results are reported in terms of degradation percentage of 4-NP, Chemical Oxygen Demand (COD), and Total Organic Carbon (TOC). The results showed that the degradation and COD removal of 4-NP in the presence of Al₂O₃ carrier was higher as compared to SiO₂ carrier. The degradation of 96% was achieved under the optimal operating conditions of pH 3, 0.2 mM Fe²⁺, 4 mM H₂O₂, and 5g/L of Al₂O₃ as a carrier. The TOC and COD removals were 70% and 55%, respectively after 1 h of reaction time. The presence of Fe-O bond onto Al₂O₃ carrier after the reaction was confirmed by the FT-IR studies. The total iron remained in the solution after reaction using fluidized-bed Fenton process was lower (8.5%) than homogeneous Fenton process (17%). Fluidized bed Fenton process also showed higher TOC and COD removal as compared to homogeneous Fenton process.*

KEYWORDS: *4-Nitrophenol; Fluidized-bed Fenton process; Carrier; Crystallization; Total organic carbon; Total iron.*

INTRODUCTION

4-NP is an important derivative of phenol and a significant intermediate in insecticides, pesticides, pharmaceuticals, dyes, oil refineries, and other organic chemicals manufacturing industries [1]. Wastewater containing 4-NP must be treated before discharging it to main water bodies. Many traditional technologies such as physical adsorption and absorption, biological treatment, chemical oxidation have been adopted to remove 4-NP from wastewater [2].

These traditional methods do not assure complete oxidation of 4-NP and are often accompanied by by-products, high operating costs, and low efficiency due to high stability and solubility in wastewater [3]. Thus, continuous research has been carried out to devise an efficient and environmentally benign technique for the complete oxidation of 4-NP.

Advanced oxidation processes (AOPs) have already been used extensively for the treatment of many

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recalcitrant organic pollutants from wastewater [4, 5]. Fenton process is one of the most popular technologies for wastewater treatment under the broad definition of AOPs. The Fenton process generates hydroxyl radicals ($\text{HO}\cdot$) from hydrogen peroxide (H_2O_2) catalyzed by ferrous ions (Fe^{2+} ions) in acidic medium [6, 7].

But, the main disadvantage of Fenton process was the production of large amount of sludge that needed further treatment and disposal [8-10]. The recirculating type fluidized bed (R-FBR) Fenton process is an alternate process that could avoid/reduce the ferric hydroxide ($\text{Fe}(\text{OH})_3$) sludge formation by crystallizing the iron sludge onto carrier's surface [11-14].

The fluidized-bed Fenton process involves four processes that add to the improvement and better performance in comparison to homogeneous Fenton process: firstly, the degradation of 4-NP by homogeneous Fenton's reaction that generated $\cdot\text{OH}$ radicals [7]. The second process involved the crystallization of iron sludge on the carriers' surface reducing the amount of sludge and improves Fenton process applicability. Thirdly, the precipitation of iron oxides onto the carrier surface led to the formation of fluidized iron oxides particles that could act as heterogeneous Fenton catalyst, an extra source of $\cdot\text{OH}$ radicals. Lastly, the fluidization of iron oxides elevated the oxide reductive dissolution of Fe^{2+} that regenerates the Fenton homogeneous catalyst and enhanced the Fenton's reaction [15, 16]. Thus, fluidized-bed reactors could improve considerably not only the homogeneous and heterogeneous Fenton process but also allow interactive combination of both processes [17, 18]. The application of fluidized-bed reactor for the oxidation of 4-NP from wastewater has not been reported earlier.

Therefore, the present study showed the degradation of 4-NP using recirculating type fluidized bed Fenton process. The effect of various operating parameters such as effect of carriers, pH, concentration of H_2O_2 , concentration of Fe^{2+} and dosage of carrier on the oxidation of 4-NP in terms of degradation (%), TOC and COD removal (%) have been evaluated. Fluidized-bed Fenton process performance has also been compared with homogeneous Fenton process in terms of % degradation, TOC and COD removal efficiency of 4-NP.

EXPERIMENTAL SECTION

Materials

4-NP (w/w, 98% purity), ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (w/w, purity >99%), silica dioxide (SiO_2 ,

diameter of particles range from 0.105 mm to 0.420 mm), alumina oxide (Al_2O_3 , diameter of particles range from 0.099 mm to 0.2 mm), 1-10 phenanthroline (purity 99.5%) and HCl (35%) were obtained from Loba Chemie Pvt. Ltd. (Mumbai, India). Hydrogen peroxide (30% w/w) was purchased from Ranbaxy Fine Chemicals Limited (Gujarat, India). All other chemicals used were of reagent grade and were obtained from s.d. fine Chemical Limited (Mumbai, India). All the solutions were prepared using double distilled water.

Fluidized bed reactor

Recirculating type fluidized bed reactor is a batch reactor consisting of a cylindrical glass vessel with conical bottom, inlet, outlet and a recirculation pump. It has a capacity of 0.5 L and has dimensions of 60 mm diameter and 176.8 mm height (Fig. 1). The reactor was equipped with a perforated plate at the bottom to support glass beads of diameter ranging from 1-3 mm. pH probe was installed at the top and sampling port was located below the recirculation point. Above the glass beads, carrier was loaded. Studies have been made using two different type of carrier i.e. Al_2O_3 and SiO_2 . The particle's size of Al_2O_3 carrier was ranged between 0.099 mm to 0.2 mm and for SiO_2 carrier it was 0.105 mm to 0.420 mm. The carrier was fluidized and the bed expansion was kept at 50% by controlling the recirculation flow rate.

Experimental procedure

A cylindrical glass R-FBR was used for all experiments. 0.5 L of 100 mg/L (0.72 mM) 4-NP solution was poured into the reactor containing glass beads (1-3 mm diameter) and 5 g Al_2O_3 carrier [19]. The pump was turned on to mix the solution and to suspend the Al_2O_3 carriers. The pH of the solution was adjusted by adding 0.1 M H_2SO_4 and 0.1 M NaOH solution. After the stabilization of pH, 0.1 mM $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution was added. The reaction was started by adding 1 mM of H_2O_2 solution. Samples were extracted from the sampling port at selected interval of time in test tubes containing 1-2 drops of 0.1 M NaOH to stop the Fenton reaction. The samples were then filtered using filter paper (pore size 11 μm) and analyzed for degradation, TOC and COD removal. The experiments were repeated by varying the concentration of Fe^{2+} ion from 0.1 mM to 0.5 mM, concentration of H_2O_2 from 1 mM to 5 mM, dosage of carrier from 5 g to 15 g.

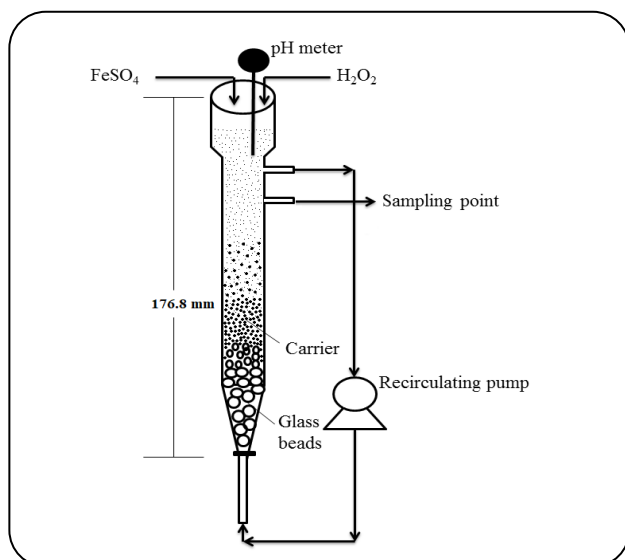


Fig. 1: Recirculating type fluidized bed Fenton reactor.

Experiments were also performed using SiO_2 carrier. All the experiments were conducted at room temperature. All the experiments were repeated three times to get reproducibility of $\pm 5\%$.

Analytical methods

The concentrations of 4-NP were analyzed for degradation (%) using UV/Vis spectrophotometer (Shimadzu double beam spectrophotometer, model: UV-2600, Shimadzu, Japan) at λ_{max} 318 nm. TOC analysis before and after the reaction, were performed using the total organic carbon analyzer by a non-dispersive infrared method (model: ASI-V and TOC-V CPN, Shimadzu, Japan). Chemical Oxygen Demand (COD) measurements were made as per APHA method using a MAC COD digester (Model: COD-439, Karnal, India). The concentration of total iron was examined using light absorbance measurements with UV/VIS spectrophotometer at λ_{max} 510 nm after forming complex with 1-10 phenanthroline following standard APHA method [20]. FT-IR spectra of Al_2O_3 carrier before and after the reaction were obtained with an FT-IR instrument (Perkin Elmer, Model RX-I, Tokyo, Japan) with a resolution of 1 cm^{-1} and scan range of 4000 cm^{-1} to 400 cm^{-1} .

RESULTS AND DISCUSSION

Effect of carriers

Carriers were used as inert solid particles for providing the surface area for the crystallization of iron sludge onto

carrier surface and reducing the sludge formation during the Fenton reaction in Fluidized-Bed Fenton (FBF) reactor. The degradation studies of 4-NP (100 mg/L) were carried out using Al_2O_3 and SiO_2 carriers independently. During the reaction, the concentration of Fe^{2+} was 0.2 mM, pH was 5.7 and H_2O_2 concentration was varied from 3 to 5 mM. Results showed that the degradation of 4-NP increased with increase in time up to 40 min, after that it remained almost constant (Fig. 2). The degradation and COD removal of 4-NP using Al_2O_3 and SiO_2 carriers were observed maximum at H_2O_2 concentration of 4 mM. After the reaction, the color of the Al_2O_3 carrier has changed from white to light brown and color of SiO_2 carrier has changed from white to light bluish (Fig. 3).

The total iron content remaining in the solution after the completion of reaction were also analyzed for both the carriers at H_2O_2 concentration of 4 mM. The degradation of 4-NP using Al_2O_3 carrier showed lower iron content (0.04264 mg/L) in the solution after the reaction than SiO_2 carrier (0.07158 mg/L) which meant that the crystallization of iron sludge was higher on the surface of Al_2O_3 carrier as compared to SiO_2 carrier (Table 1). Therefore, the Al_2O_3 carrier is further used to explore the degradation and mineralization efficiency of 4-NP in the fluidized bed Fenton process to study the effects of other parameters.

Effect of pH

In Fenton's reaction, pH of the solution has great impact on the degradation as it influences the generation of $\text{HO}\cdot$ radicals. Fenton process is more predominant in acidic medium, thus the present studies have been made on pH variation from 1 to 5 at 4 mM of H_2O_2 and 0.2 mM Fe^{2+} for 1 h reaction time. Fig. 4 showed the effect of pH on removal percentage of 4-NP in FBF reactor.

It has been observed that the degradation of 4-NP increased from 40% to 96% by increasing the pH from 1 to 3. But, with further increase in pH from 4 to 5, the degradation of 4-NP decreased from 96% to 78%. The maximum degradation of 4-NP was 96% at pH 3. The COD removal (%) and TOC removal (%) of 4-NP also increased with increase in pH from 1 to 3 and then decreased with increase in pH from 4 to 5 in the reactor. The maximum COD removal and TOC removal were 55% and 70% respectively at pH 3. At lower pH value (below 3), due to scavenging effect of H^+ , H_2O_2 could capture this proton to form oxonium ion (H_3O_2^+) [21] (Eq. (1)).

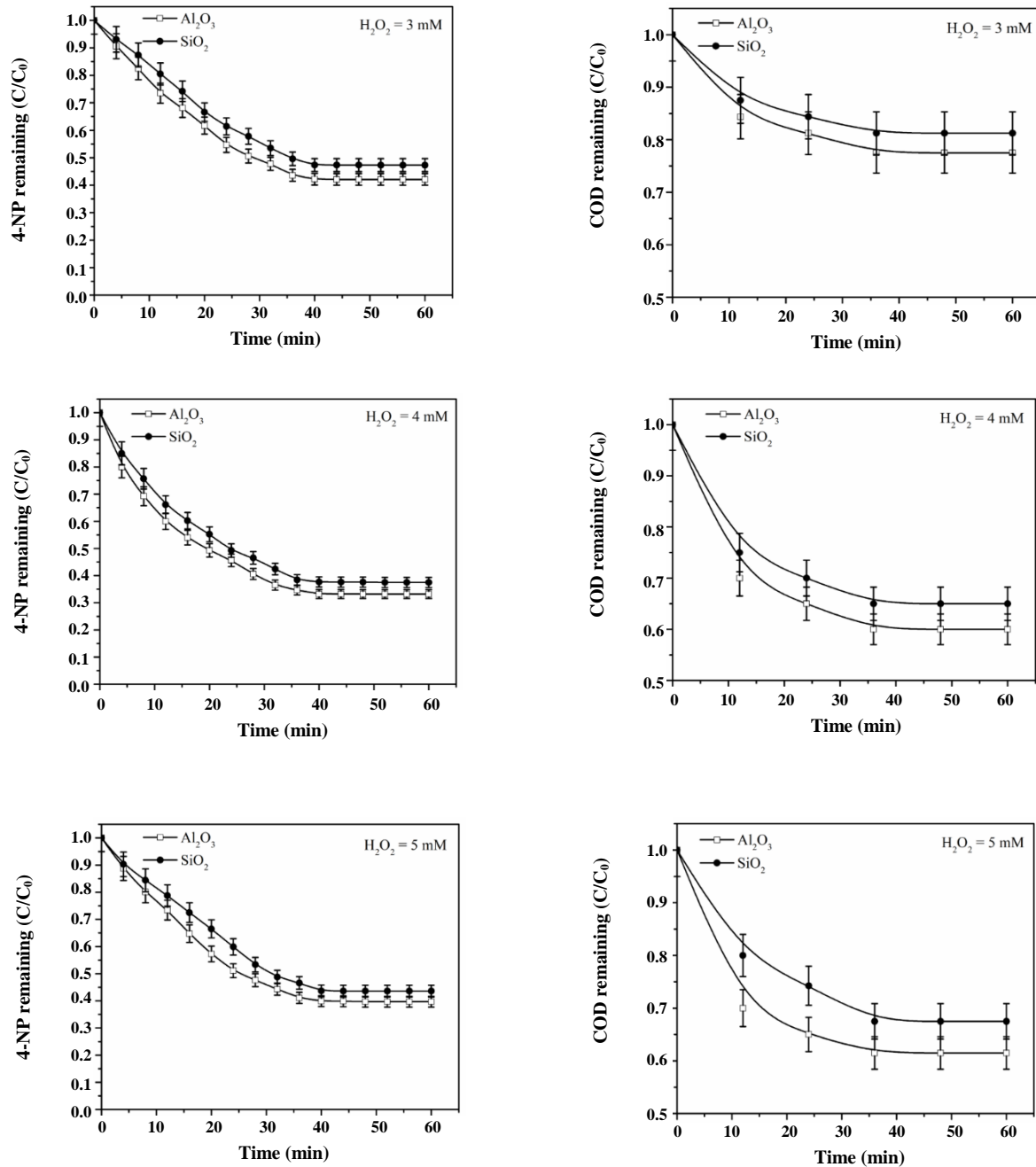


Fig. 2: Effect of Al_2O_3 and SiO_2 carriers on degradation and COD removal of 4-NP at 0.2 mM concentration of Fe^{2+} , pH 5.7 with 2.5 g/L carrier dosage.

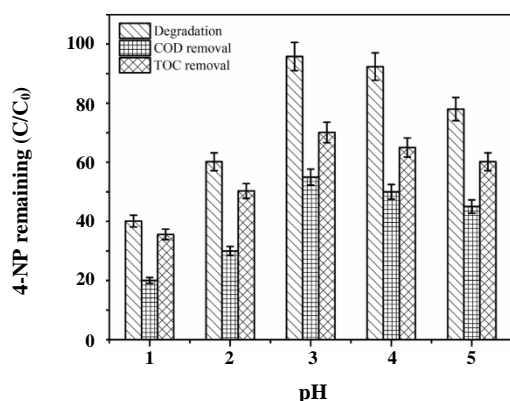


The formed oxonium ion made H_2O_2 electrophilic and enhanced its stability that reduced the reactivity of H_2O_2 with Fe^{2+} ions [22]. At pH higher than 3, the regeneration of Fe^{2+} ions from Fe^{3+} becomes lower and Fe^{3+} ions

precipitates as iron hydroxide due to the insolubility of Fe^{3+} ions in higher pH solution, ceasing the Fenton's chain reaction [15, 24]. At pH 3, the generation of HO^\bullet radicals was favored due to decomposition of H_2O_2 and resulted in higher oxidation of 4-NP. The results of maximum

Table 1: Effect of SiO₂ and Al₂O₃ carriers on degradation (%) and COD removal of 4-NP.

Pollutant	H ₂ O ₂ (mM)	Fe ²⁺ (mM)	Degradation (%)		COD removal (%)		Total iron after reaction (mg/L)	
			Al ₂ O ₃	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃	SiO ₂
4-NP	3	0.2	58.00	52.65	36.00	30.00	-	-
	4	0.2	67.00	63.50	40.00	35.00	0.04264	0.07158
	5	0.2	60.25	56.40	38.00	32.25	-	-

**Fig. 3: The physical change (color) onto the carriers before and after the experimental run, (a) SiO₂ before experiment, (b) SiO₂ after 1st experimental run, (c) Al₂O₃ before experiment and (d) Al₂O₃ after 1st experimental run.****Fig. 4: Effect of pH on the degradation (%), COD removal (%) and TOC removal (%) of 4-NP at Fe²⁺: 0.2 mM, H₂O₂: 4 mM, Al₂O₃ carrier: 5g/L and time: 60 min.**

degradation at pH 3 are consistent with the previous studies by Zhou *et al.* (2012) [11] and Muangthai *et al.* (2010) [25]. Thus, pH 3 is the found to be optimum for the degradation of 4-NP.

Effect of H₂O₂ concentration

H₂O₂ is an essential element of Fenton's reagent and acts as a strong oxidizing agent. Thus it is important to study the effect of H₂O₂ dosage on the degradation (%)

of 4-NP in FBF reactor. The concentration of H₂O₂ was varied from 1 mM to 5 mM and other parameters were kept constant (0.2 mM of Fe²⁺ concentration and pH 3). Results indicated that the degradation of 4-NP, COD removal (%) and TOC removal (%) were increased by increasing the H₂O₂ concentration up to 4 mM, afterwards it decreased (Fig. 5). The maximum degradation of 4-NP, COD removal (%) and TOC removal (%) were observed at 4 mM of H₂O₂ concentration. The degradation of 4-NP was increased from 41% to 96% with the increase in H₂O₂ concentration from 1 mM to 4 mM for 1 h reaction time. Similarly, COD removal increased from 25% to 55% and TOC removal was increased from 38% to 70%. The degradation of 4-NP was increased by increasing the concentration of H₂O₂ due to the increase in HO• radicals [26].

The degradation, COD removal and TOC removal of 4-NP decreased above 4 mM of H₂O₂ concentration due to HO• radicals scavenging effect of H₂O₂ (Eq. (2)) [27, 28]. For further experiments, 4 mM concentration of H₂O₂ was used.

$$\text{H}_2\text{O}_2 + \text{HO}^\bullet \rightarrow \text{H}_2\text{O} + \text{HO}_2^\bullet \quad (2)$$

Effect of Fe²⁺ ions concentration

The Fe²⁺ ions concentration was varied from 0.05 mM to 0.5 mM while keeping other parameters constant and

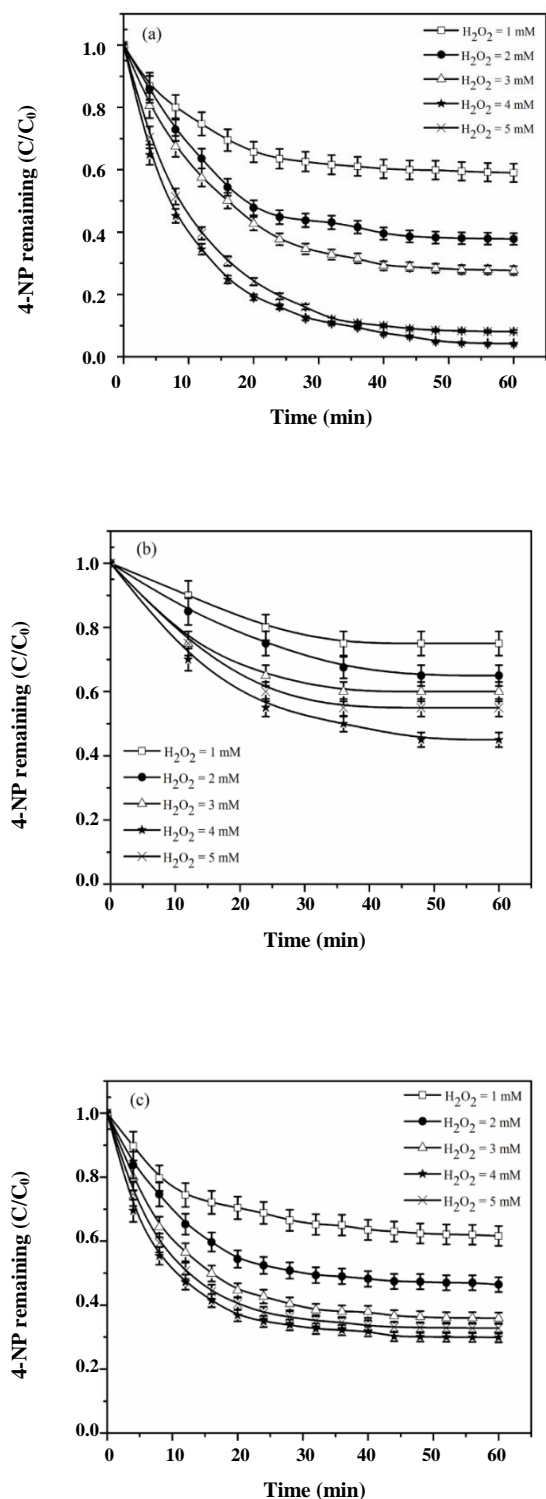
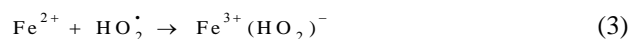


Fig. 5: Effect of H₂O₂ concentration on (a) 4NP remaining, (b) COD remaining, (c) TOC remaining after oxidation reaction of 4-NP at 0.2 mM Fe²⁺ concentration, pH 3, Al₂O₃ carrier = 5g/L and time 60 min.

the results are presented in Fig. 6. It was observed that the degradation of 4-NP increased by increasing the Fe²⁺ ions concentration from 0.05 mM to 0.2 mM in FBF reactor (Fig. 6a). The mineralization efficiency i.e. the COD removal and TOC removal was also increased by increasing the concentration of Fe²⁺ ions from 0.05 mM to 0.2 mM (Fig. 6b and c). On further increase in the concentration of Fe²⁺ ions, the degradation and mineralization efficiency (TOC removal and COD removal) decreased. The maximum degradation of 4-NP was 96% at 0.2 mM of Fe²⁺ ions concentration. With increase in Fe²⁺ ions concentration from 0.05 mM to 0.2 mM, the COD removal was increased from 45% to 55% and TOC removal was increased from 58% to 70%.

The increase in degradation, COD removal and TOC removal were due to the reason that Fe²⁺ ions catalyze the decomposition of H₂O₂ to generate HO• radicals which is a main oxidizing agent for the oxidation of 4-NP [25]. At very low concentration of Fe²⁺ ions (0.05 mM), the catalytic effect of Fe²⁺ ions were limited and resulted in lesser decomposition of H₂O₂ to form HO• radicals. When the concentration of Fe²⁺ ions was increased from 0.05 mM to 0.2 mM, the production of HO• increased and resulted in enhanced degradation. When Fe²⁺ ions are in excess, then there is inhibition effect as there is competition between excess Fe²⁺ ions and pollutants molecules for HO• radicals (Eq. 3- 5) [29]. Also, due to excess Fe²⁺ ions, superoxide (O₂^{•-}) radicals were generated which reacted with Fe²⁺ ions leading to undesirable reaction (Eq. 5) [29, 30].



Excess loading of Fe²⁺ ions may scavenge HO• radicals and will lead to unutilized quantity of iron salts (Eqs. (3) and (5)) which further increase the total dissolved solids and the sludge formation in the solution [22, 31].

Effect of carrier dose

To study the effect of carrier dose, the dose of Al₂O₃ was varied from 5 g to 15 g for 500 mL of 4-NP solution at the optimized conditions of 4 mM of H₂O₂, 0.2 mM of Fe²⁺ and pH 3 in FBF reactor. Results tabulated in Table 2 indicated that as the dose of carrier was increased

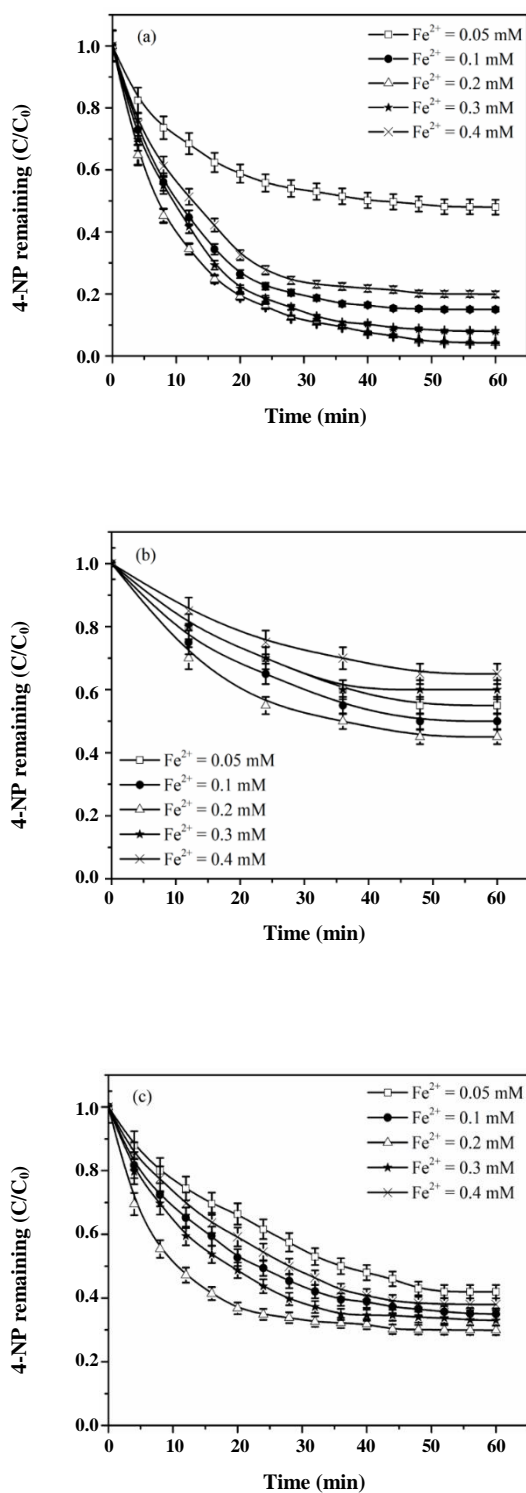


Fig. 6: Effect of Fe^{2+} ions concentration on (a) 4-NP remaining, (b) COD remaining and (c) TOC remaining after oxidation reaction at 4 mM of H_2O_2 concentration, pH 3, Al_2O_3 carrier = 5g/L and time = 60 min..

from 5 g to 15 g, the degradation of 4-NP increased from 92% to 96%. Further, the total iron content remained in the solution after the completion of reaction decreased with increase in carrier dose.

The change in the color of the carrier was also observed before and after the reaction in FBF reactor (Fig. 7). It was observed that as the dose increased the white crystal color of Al_2O_3 changed from light brown to dark brown. This indicated that the crystallization of iron has been taken place onto the surface to Al_2O_3 carrier and hence resulted in decrease in ferric hydroxide sludge in the solution.

FTIR spectra of Al_2O_3 carrier

The FTIR spectra of the Al_2O_3 carrier (5g/L) before and after the reaction was observed to analyse the crystallization of iron onto the surface of carrier and are shown in Fig. 8. It was observed that after the reaction of 60 min in FBF reactor, the additional peaks at 588.23 cm^{-1} and 447.51 cm^{-1} in the spectra of Al_2O_3 carrier appeared due to the presence of Fe-O bond [32] (Fig. 8b). The FT-IR spectra indicated that the $\text{Fe}(\text{OH})_3$ sludge is precipitated onto the surface of Al_2O_3 carrier.

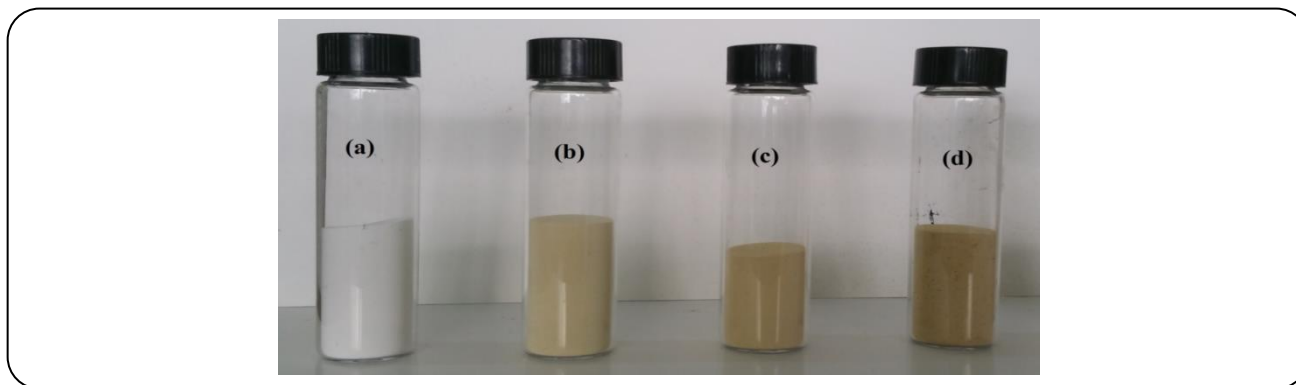
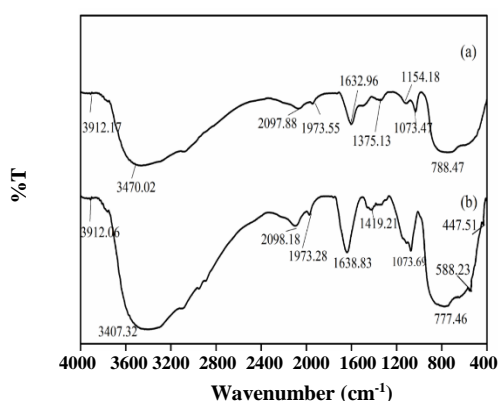
Advantage of fluidized bed Fenton process over homogeneous Fenton process

The oxidation of 4-NP has been carried out for homogeneous Fenton process at the optimum reactions conditions of 0.2 mM Fe^{2+} concentration, 4 mM of H_2O_2 concentration and pH 3. The results of homogeneous Fenton process are compared with fluidized-bed Fenton process under similar conditions using 5g/L of Al_2O_3 carrier. The oxidation results for both homogeneous Fenton process and fluidized-bed Fenton process are presented in Fig. 9. It was observed that initially the rate of degradation of 4-NP was higher in homogeneous Fenton process as compared to fluidized-bed Fenton process but after 35 min of reaction time the degradation rate of 4-NP decreased in homogeneous Fenton process. The degradation of 4-NP was 96% in fluidized-bed Fenton process whereas it was 94% in homogeneous Fenton process after 60 min of reaction time. The COD and TOC removal of 4-NP in fluidized-bed Fenton process were higher than homogeneous Fenton process (Fig. 9b and c).

The initial degradation rate of in homogeneous Fenton process was higher as during the initial reaction time,

Table 2: Effect of carrier dose (Al_2O_3) on degradation (%) and total iron content in solution after the completion of reaction.

Pollutant	Carrier	Dose of carrier/500 mL 4-NP (g)	Degradation (%)	Total iron content (mg/L)
4-NP	Al_2O_3	5	92.00	0.01204
		10	95.80	0.00795
		15	96.10	0.00743

**Fig. 7: Effect of Al_2O_3 carrier dose on the degradation of 4-NP, (a) Fresh Al_2O_3 , (b) 5 g Al_2O_3 , (c) 10 g Al_2O_3 and (d) 15 g Al_2O_3 at 4 mM H_2O_2 , 0.2 mM of Fe^{2+} and pH 3.****Fig. 8: FTIR spectra of Al_2O_3 carrier in Fluidized-bed Fenton process (a) before reaction and (b) after reaction.**

$\text{Fe}^{2+}/\text{H}_2\text{O}_2$ was the dominant mechanism and the other mechanism $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ caused slower oxidation. In fluidized-bed Fenton oxidation, crystallization of $\text{Fe}(\text{OH})_3$ and reductive dissolution of iron oxides occurred other than homogeneous oxidation (Fig. 10) [27]. The increased degradation rate, COD and TOC removal of 4-NP from aqueous solution in fluidized-bed Fenton process was due to crystallization of $\text{Fe}(\text{OH})_3$ onto carriers. In fluidized-bed Fenton process, the 4-NP was degraded to CO_2 , H_2O and some unconverted products formed with the release of inorganic N-species like NO_x and NO_3^- [33].

The total Fe remained in the solution at consequent times during the reaction is also analyzed and results are presented in Fig. 9d. Results showed that the amount of Fe remained in solution for homogeneous Fenton and fluidized bed Fenton process increased with time. However, total Fe remained in solution in fluidized bed Fenton process was much lower as compared to homogeneous Fenton process. The total Fe remained in the solution after completion of homogeneous Fenton oxidation in 60 min of reaction time was 17% whereas it was only 8.5% in fluidized-bed Fenton process. In fluidized-bed Fenton process the crystallization of $\text{Fe}(\text{OH})_3$ sludge onto the surface of Al_2O_3 carriers has been occurred and resulted in lowering of iron sludge in solution which increased the COD and TOC removal efficiencies. Thus the use of carrier (Al_2O_3) in fluidized-bed Fenton process by crystallization of $\text{Fe}(\text{OH})_3$ onto its surface has an added advantage over homogeneous Fenton process.

COMPARATIVE ANALYSIS

Comparison of the homogeneous Fenton oxidation process and fluidized-bed Fenton oxidation process

The performance of the two processes i.e. homogeneous oxidation Fenton process and fluidized-bed Fenton oxidation process in terms of percentage

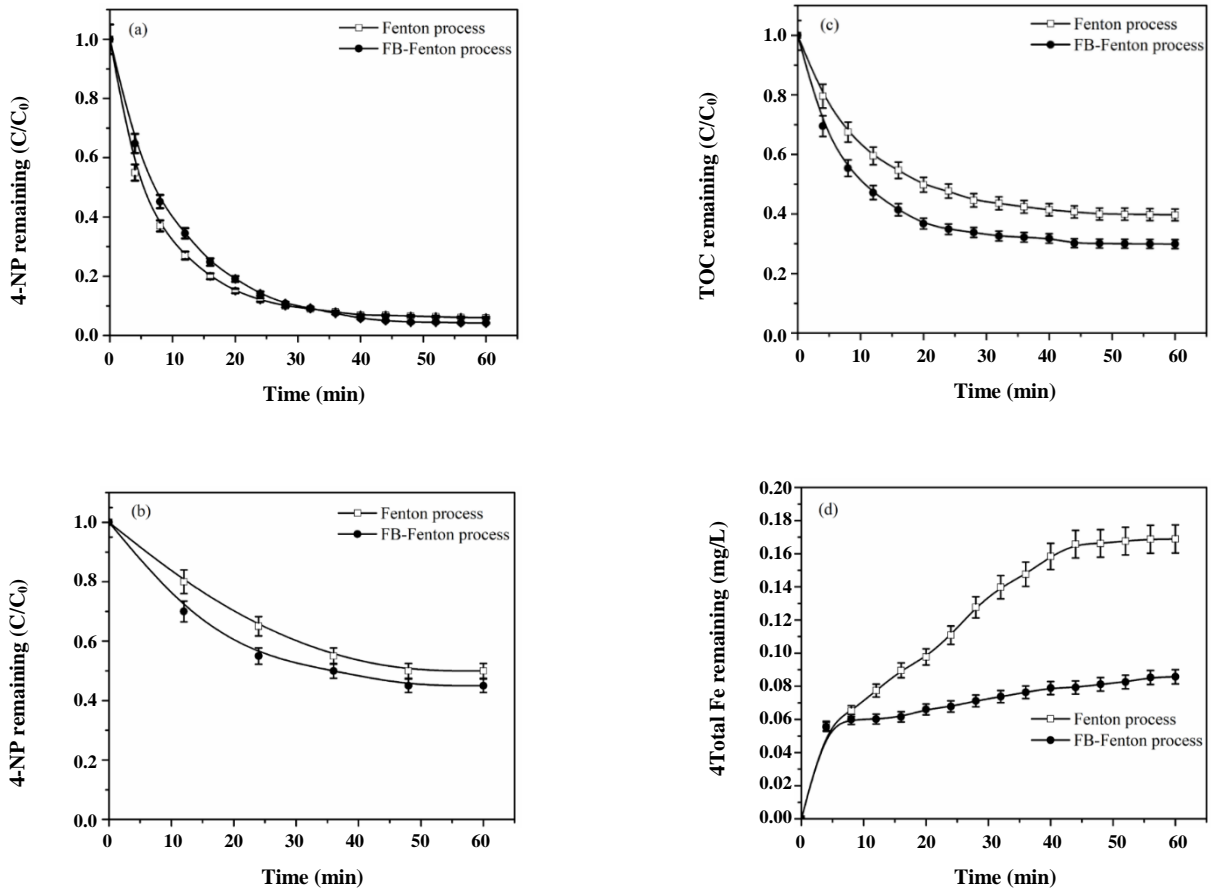


Fig. 2: Effect of Al₂O₃ and SiO₂ carriers on degradation and COD removal of 4-NP at 0.2 mM concentration of Fe²⁺, pH 5.7 with 2.5 g/L carrier dosage.

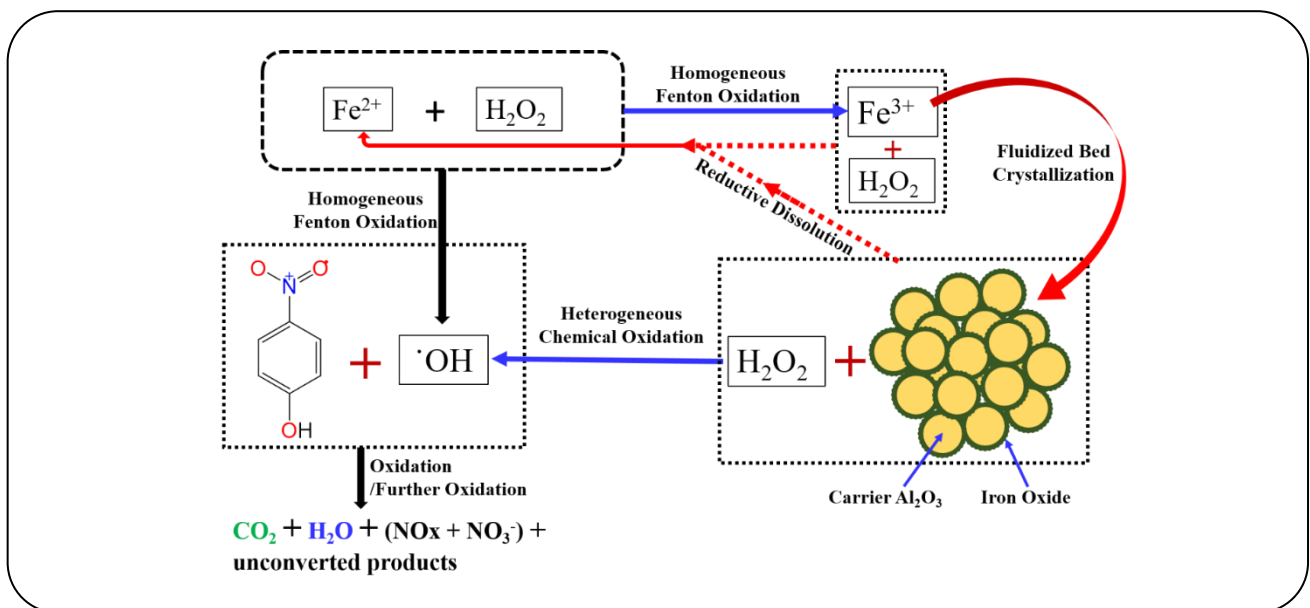


Fig. 10: Scheme of processes involved in fluidized-bed Fenton process.

Table 3: Comparison of homogeneous, heterogeneous and fluidized Fenton process.

Process	Catalyst	Reaction conditions	Degradation (%)	COD removal (%)	TOC removal (%)	Drawbacks/advantages
Homogeneous Fenton process	-	[4-NP] ₀ = 100 mg/L, [Fe ²⁺] = 0.2 mM, pH = 3, [H ₂ O ₂] = 4 mM, T = 30°C and t = 40 min	93.6	50	60.3	Sludge formation is high
Fluidized-bed Fenton process	-	[4-NP] ₀ = 100 mg/L, [Fe ²⁺] = 0.2 mM, pH = 3, [H ₂ O ₂] = 4 mM, T = 30°C and t = 60 min, Al ₂ O ₃ carrier = 5 g/L	96	55	70	Formation of sludge is low

degradation, COD removal (%), and TOC removal (%) of 4-NP are reported in Table 3. The result indicated that both the methods have proved to be efficient in the degradation of 4-NP. But, the fluidized-bed Fenton oxidation process showed higher COD and TOC removal efficiency of 4-NP as compared to the homogeneous Fenton process. The COD removal (%) and TOC removal (%) in the fluidized-bed Fenton oxidation process was increased by 5% and 10% in fluidized-bed Fenton process. The sludge formation was reduced in fluidized-bed Fenton process as compared to homogeneous Fenton process.

CONCLUSIONS

The oxidation of 4-NP was carried out using the Fluidized-bed Fenton process and the effect of various parameters such as pH, the concentration of H₂O₂, concentration of Fe²⁺ carrier type, and dosage were investigated.

1- The oxidation of 4-NP using Al₂O₃ carrier showed higher degradation and COD removal (67% and 40%) as compared to SiO₂ carrier (63% and 35%) at 0.2mM Fe²⁺, 2.5 g/L of carrier dosage at 5.7 pH. Total iron remained in the solution after the reaction using Al₂O₃ carrier (0.0426 mg/L) was lower than SiO₂ carrier (0.0716 mg/L).

2- The maximum degradation of 4-NP was 96%, TOC and COD removal efficiencies of 70% and 55%, respectively were achieved under the optimal operating conditions of pH 3, the molar ratio of [H₂O₂]: [Fe²⁺] = 20 and 5g/L of Al₂O₃ as a carrier.

3- FTIR studies showed the presence of Fe-O bond on the Al₂O₃ carrier and hence resulted in crystallization of iron onto the surface of Al₂O₃ in the Fluidized-bed Fenton process

4- For fluidized-bed Fenton oxidation the total iron remained in the solution after completion was 8.5% whereas it was only 17% in homogeneous Fenton oxidation. The crystallization of Fe(OH)₃ sludge onto the surface of Al₂O₃ carriers resulted in the lowering of

sludge in the Fluidized-bed Fenton oxidation process.

5- Fluidized-bed Fenton process also showed higher COD and TOC removal efficiencies as compared to homogeneous Fenton oxidation

6- Comparison of homogeneous Fenton oxidation process and fluidized-bed Fenton oxidation showed that the mineralization efficiency was higher in the fluidized-bed Fenton process.

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