





Simulation study of phenol degradation by Fenton process using ASPEN-Plus

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Present study deals with the simulation of the Fenton's process for the removal of phenol using ASPEN-Plus. The effect of phenol concentration, catalyst loading, mole ratio of H_2O_2 to iron ion, and temperature on the phenol degradation rate has been studied using the developed process flow diagram. The result shows higher flow rate of hydrogen peroxide (4.2 kmol/h) favours phenol degradation (98%) since the hydroxyl radical availability rises. Increase in catalyst loading (186 g) and rise in mole ratio of hydrogen peroxide to iron ion (~1) improves the removal of phenol (~97%) from wastewater since the hydroxyl radical formation improves and thus affect the mechanism and chemical kinetics of Fenton reaction. Increase in temperature improves the degradation, however high temperature above optimum condition (32.5°C) does not favour the degradation of phenol.

Keywords: Advanced Oxidation Process, ASPEN Plus, Fenton's process, Hydrogen peroxide, Phenolic compounds, Phenol degradation

The wastewater pollution due to industrial effluents has become a very serious issue and requires attention everywhere. Among the variety of pollutants released from different industries, phenol/phenolic compounds are generally regarded as one of the most toxic organic pollutants^{1,2}. Teratogenic and carcinogenic effect of phenol and phenolic compound demands the immediate treatment prior to discharge³. Wastewater containing phenol and phenolic compounds are discharged without further treatment into the waterbodies by industries like oil and gas industries, coal industries, petrochemical industries, smelting and metallurgical operations, polymer industries, paint and dye industries, fiberglass plants, and pharmaceutical industries^{4,5}. Phenol being a critical intermediate in various industrial products, many researchers have carried out study of its removal from wastewater. In the last two decades, removal of phenolic compounds from wastewater has received global attention because of their endocrine disrupting properties and toxicity effects⁶⁻⁸.

A number of processes are studied to remove phenol and phenolic compounds from wastewater. Existing methods for the removal of these compounds from wastewater include adsorption, chemical oxidation, solvent extraction, and biological degradation ⁹⁻¹¹. Biological/microbial degradation is often the most

economical and environmentally friendly method. Still their application is restricted at high concentrations of phenol since microorganisms get deactivated. Further interaction of phenol compounds with microorganism, organic and inorganic compound produces substituted compounds or moieties that are also toxic. Generally, microbial degradation requires a large land area and longer time; it is therefore considered as less flexible in design and operation¹².

Conventional wastewater treatment methods are effective but they only transfer the contaminants from one medium to another. They are not suitable for wastewater with higher concentrations of the organic contaminants and results in operational difficulties^{13,14}. Over the years, Advanced Oxidation Process (AOP) have shown better results for the wastewater treatment, since the process involves generation of hydroxyl radicals¹⁵. Generally, hydroxyl radicals are strong oxidants because of their high oxidation potential, and thus they can oxidize and mineralize organic molecules in pollutants into less toxic inorganic ions and CO₂. Hydroxyl radicals are capable of oxidizing and mineralizing harmful organic pollutants into less harmful CO₂ and inorganic ions⁸.

Photocatalysis is an AOP, where light absorption on a semiconductor material generates strong oxidation and reductants in valence and conduction band, respectively. Examples for heterogeneous photocatalyst includes, TiO₂, CuO, ZnS, ZnO, CdS, MOF¹⁶, Z-scheme based hybrids¹⁷, metal free graphite carbon nitride¹⁸, bismuth oxyhalide¹⁹, and also Fe₃O₄¹⁶. Similarly, Fenton process is widely used Advanced Oxidation Process (AOP) having extensive application in industries for organic pollutant degradation at moderate concentrations, shows high performance and simple to adopt with oxidation of organics by reduction of H₂O₂ with Fe²⁺ and produce environmentally safe species like H₂O and O₂. Fenton process is adopted to treat pharmaceutical effluents, textile effluents and effluent containing phenols. Heterogeneous catalyst usage can overcome the drawbacks of the reaction such as small pH range, higher H₂O₂ consumption and ferric sludge accumulation that affects the efficiency of the process^{20,21}. During the Fenton process, reactive hydroxyl radicals *OH are generated through interaction of iron ions (Fe²⁺/Fe³⁺) with hydrogen peroxide. The Fenton reaction in the presence of Fe²⁺/H₂O₂ is shown below in Eq. $(1) - (3)^{22}$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + ^*OH + OH^-$$
 ...(1)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + O_2H^* + H^*$$
 ...(2)

$$Fe^{3+} + O_2H^* \rightarrow Fe^{2+} + O_2 + H^+$$
 ...(3)

Out of these reactions, Eq. (2) is the rate limiting step with the lowest rate constant (9.1 \times 10⁻⁷ L/mol.s) in comparison with other two steps. Thus, the overall rate of the reaction is determined by Eq. (2) that necessitates a large amount of H_2O_2 and catalyst in order to generate sufficient quantities of OH^{*23} . The objective of this work is to simulate the phenol degradation reaction by Fenton reaction using ASPEN plus and understand the influence of different parameters on the degradation efficiency.

Experimental Section

Simulation Set-up

The simulation setup for the phenol degradation in ASPEN Plus is shown in Fig. 1. The input stream

consists of wastewater (WASTEH₂O) stream containing phenol to be removed and hydrogen peroxide (H₂O₂). Both the input streams are sent to MIXER, and then they are sent (as a single stream) to the packed bed reactor (PBR). PUMP is used (for lifting the fluid) after the reaction from packed bed reactor. VALVE-1, VALVE-2 and VALVE-3 are the valves that are used to maintain the flow rates of all the input and output streams. The final PRODUCT stream, after the VALVE-3 is the product stream contains CO₂ and H₂O.

Selection of components

In this process, the wastewater contains the toxic pollutant phenol. For degradation of phenol, iron ion is used as a catalyst (heterogeneous catalyst). Thus, in ASPEN, for component selection it has been selected as a solid component. All the other components involved in the process like H₂O, H₂O₂, C₆H₅OH (phenol), and CO₂, are the conventional components of the ASPEN data book.

Chemical kinetics

The specific chemistry used to understand the behaviour of packed bed reactor and demonstrate the use of Aspen Plus is the reaction of Phenol (P) with Hydrogen peroxide (H) to form the product treated water (W) and carbon dioxide (CD). The reactions in the liquid and gas phase are assumed to be irreversible. Eq. (4) shows the phenol degradation reaction²⁴.

$$C_6H_6O + 14H_2O_2 \rightarrow 17H_2O + 6CO_2$$
 ...(4)

According to the literature, the Fenton reaction is irreversible and elementary, thus, the apparent order of the reaction is taken as second-order^{25,26}. As the main reaction for the process is the Fenton reaction, the values of rate constant and activation energy has been taken accordingly from the literature. The rate constant of the Fenton reaction is 0.01 M⁻¹s^{-1 19} and the apparent activation energy is 79.5 kJ/mol²⁷. The reactions involving the peroxyl and oxyl radicals have

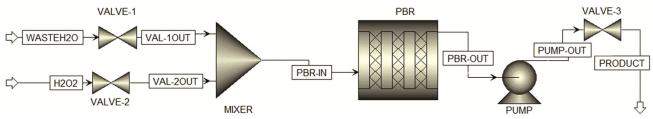


Fig. 1 — Schematic representation of the packed bed reactor

highest rate constants whereas the oxidation-reduction reactions of iron and organic compounds involved lower rate constants values.

Results and Discussion

Simulation study was carried out for a number of parameters like molar flow rate of hydrogen peroxide, mole fraction of components in product stream, temperature, catalyst loading, mole ratio of hydrogen peroxide to iron and degradation efficiency. Percentage degradation of phenol has been chosen as the parameter for evaluation in the present study. The effect of abovementioned parameters on the percentage degradation of phenol was investigated. The initial values of the parameters related to the study are given in Table 1²⁸.

Effect of hydrogen peroxide (H2O2)

Effect of molar flow rate of H_2O_2 (feed) on molar flow rate of phenol, H_2O_2 , CO_2 and H_2O (product)

The effect of molar flow of hydrogen peroxide in the feed stream on the molar flow of unreacted phenol, hydrogen peroxide, carbon dioxide and water in the product stream was studied (Fig. 2). The initial molar flow of phenol was kept constant at 0.026 kmol/h. The molar flow of phenol in the product stream decreases continuously upon increasing the molar flow rate of hydrogen peroxide and reaches almost zero at 4.62 kmol/h flow rate of H₂O₂. Similar observation of decrease in amount of phenol at higher

Table 1 — Parameters for phenol before simulation ²⁸	
Parameter	Value
Overall volume of solution (L)	3
Temperature (°C)	30
pH	3.0
Initial concentration of phenol (mol L ⁻¹)	12.1×10 ⁻³
Initial concentration of H_2O_2 (mol L ⁻¹)	6

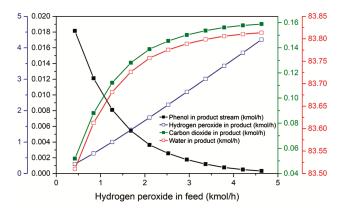


Fig. 2 — Effect of molar flow rate of hydrogen peroxide in the feed with the molar flow rate of phenol, hydrogen peroxide, carbon dioxide and water in the product

hydrogen peroxide was reported in the literature⁵. It indicates that hydroxyl radicals ('OH) are in sufficient amount to degrade phenol at tested conditions of simulations. Continuous decrease of phenol in the product stream with the addition of H₂O₂ indicates the effect of the Fenton reaction and its degradation in the treated water.

As evident in the graph, the molar flow of hydrogen peroxide in the product kept on increasing when hydrogen peroxide in the feed was increased. This is due to the small and constant molar flow rate of phenol in the feed (0.026 kmol/h) as some of the hydrogen peroxide is utilized for the oxidation of phenol. Because the amount of hydrogen peroxide in the feed is increasing, some unutilized amount of hydrogen peroxide will come out in the product stream. A higher initial concentration means a higher amount of residuals of hydrogen peroxide which needs to be removed prior to final discharge²⁹.

The molar flow of carbon dioxide is changing within a very small range as seen in Fig. 2. As the molar flow of phenol is constant, availability of phenol for the chemical reaction with hydrogen peroxide is also small. Thus, molar flow of carbon dioxide was observed as smaller in the product stream even when the hydrogen peroxide was increased. The variation in molar flow of water in the product stream is also varying under certain range (Fig.2). As the formation of water is also dependent on chemical reaction of phenol and hydrogen peroxide and because phenol molar flow is constant, similar effect was observed in case of carbon dioxide. The initial values of molar flow rates were selected for simulation study after model validation.

Effect of molar flow of hydrogen peroxide on the percentage degradation of phenol

The effect of molar flow of hydrogen peroxide on the percentage degradation of phenol was studied. As the molar flow of hydrogen peroxide was increased, continuous increase in percentage degradation was observed (Fig. 3). Initially, when hydrogen peroxide is present in small amount, no degradation in phenol was observed. At 1 kmol/h of hydrogen peroxide, about 60% degradation was reported. Upon further increase in hydrogen peroxide (slightly greater than 4 kmol/h) percentage degradation kept increasing continuously. Almost 98% of phenol degradation is obtained with the hydrogen peroxide flow rate in the feed is around 4.2 kmol/h. According to the research reported in the literature, the increase in hydrogen

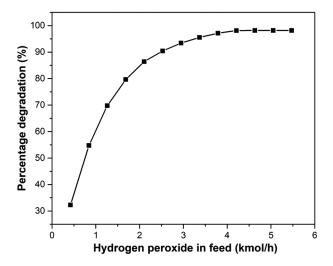


Fig. 3 — Effect of molar flow rate of hydrogen peroxide with the percentage degradation

peroxide results in increase in removal rate of phenol⁵.

When hydrogen peroxide was increased further, above 4.2 kmol/h not much change in percentage degradation could be reported. It indicates that percentage degradation can't be improved above this point. This is due to the fact that when hydrogen peroxide is present in excess amount, it starts to react with hydroxyl radicals. This reaction generates HO₂* (hydro peroxy) radicals, which are less reactive than initially present hydroxyl radicals. Thus, percentage degradation was not affected significantly. Similar results were obtained during the degradation study of phenol using Fenton-like process³⁰. HO₂* is a weak oxidant and the electrode potential of the HO₂* is less than that of OH* thus, less percentage degradation was reported at higher hydrogen peroxide concentration^{31,32}. No change in percentage degradation was observed at higher flow rate. Thus, a molar flow of 4.2 kmol/h hydrogen peroxide can be suggested as an optimum molar flow for phenol degradation based on the conditions used in the simulation study.

Effect of Phenol

Effect of molar flow rate of phenol on the molar flow rate of H_2O_2 & CO_2 (product)

The simulation study was carried out to assess the effect of molar flow of phenol in feed on the molar flow of hydrogen peroxide and carbon dioxide in product. Initially, at low molar flow rate of phenol, sudden decrease in molar flow of hydrogen peroxide in the product stream was noticed. As the amount of hydrogen peroxide was kept constant and phenol flow rate was varied, the behaviour is drastically changed

and very small amount of hydrogen peroxide is found in the product stream than what was observed initially. It is due to the fact that when molar flow of phenol is smaller, the hydrogen peroxide and hence the hydroxyl radicals are available in excess for oxidation of trace amount of phenol. Therefore, some amount of hydrogen peroxide could be utilized for the degradation of small amount of phenol and large amount of hydrogen peroxide was found in the product stream. As the molar flow of phenol (> 0.2 kmol/h) was increased in feed, it could utilize more amount of hydrogen peroxide; consequently, most of the hydrogen peroxide is used for the oxidation of phenol. Hence, small quantity of hydrogen peroxide was left in the product stream

Since phenol is the only component responsible for the conversion of carbon into carbon dioxide in the wastewater, formation of carbon dioxide varies with respect to the amount of phenol. The curve representing molar flow of carbon dioxide shows opposite behaviour than the molar flow of phenol. In the initial zone of graph, at low molar flow rate of phenol, sudden increase in the molar flow of carbon dioxide can be seen. At phenol molar flow rate (> 0.2) kmol/h), molar flow of carbon dioxide was observed to increase gradually. At higher molar flow rate of phenol, the change in molar flow of carbon dioxide is smaller than earlier. As the reaction between phenol and hydrogen peroxide forms carbon dioxide, it can be said that more amount of phenol in feed results in more formation of carbon oxide depending upon the availability of hydroxyl radicals.

Effect of molar flow rate of phenol on the mole fraction of H_2O_2 , CO_2 and H_2O (product)

The simulation study was carried out to assess the effect of molar flow of phenol in feed on the mole fraction of hydrogen peroxide and carbon dioxide in the product. Molar flow of hydrogen peroxide in feed was kept constant (4.32kmol/h). The simulation, using mole fraction was carried out to analyze the components in the product stream. The behaviour of curves in Fig. 4 can be explained in the same way as explained in the preceding section. The molar flow rate behaviour of hydrogen peroxide and carbon dioxide are repeated for mole fraction behaviour.

As seen in Fig.4, mole fraction of water in the product stream is increasing up to 0.4 kmol/h of phenol in feed. Above this molar flow, the increase in mole fraction of water is very small. At higher mole flow of phenol, it starts to decrease first then becomes

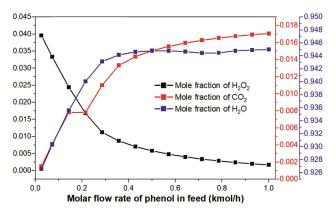


Fig. 4 — Effect of molar flow rate of phenol (feed) with the mole fraction of H_2O_2 and CO_2 and H_2O_2

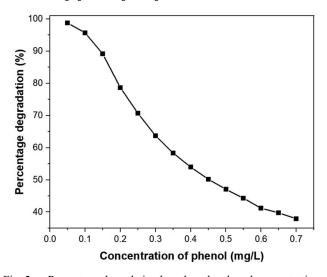


Fig. 5 — Percentage degradation based on the phenol concentration

constant near 1 kmol/h of phenol. Literature study suggests that higher the moles of carbon dioxide and water in product stream, larger the degree of mineralization³³.

Effect of concentration of phenol on the percentage degradation

Initial contaminant (phenol) concentration in wastewater is important to study the effect of treatment on the percentage degradation of the pollutants. Thus, effect of initial phenol concentration was studied in simulation to determine the degree of degradation of phenol in the treated water. The study of Fig. 5 suggests that increase in initial phenol concentration results in decrease in percentage degradation. Initially, at very low concentration of phenol, very high degradation was observed. Later, when the concentration of phenol was increased, the percentage degradation was observed to decrease up to about 0.7 mg L⁻¹ of phenol. Similar behaviour in experiment was reported during the degradation study of phenol and chlorinated phenols

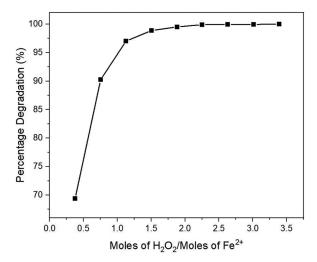


Fig. 6 — Percentage degradation based on the mole ratio of ${\rm H_2O_2}$ and ${\rm Fe^{2^+}}$

using Fenton's reagent³⁴. When the initial concentration of phenol was higher in the wastewater, smaller percentage degradation was achieved. This may be due to the fact that with the increase in initial concentration of phenol/phenolic compound, the number of molecules of phenol/phenolic compound per unit volume also increases. Thus, lower removal rate is observed. Degradation study of the phenolic compound bisphenol by the Fenton advanced oxidation process reports that when the initial concentration of phenolic compound (bisphenol) is increased, relatively low removal rate of bisphenol is obtained³⁵. Higher concentration of pollutants (phenol) initially in the wastewater results in smaller pollutant degradation.

Effect of mole ratio (hydrogen peroxide/iron ion) on the percentage degradation

The effect of mole ratio of H₂O₂/Fe²⁺ion affects the degradation of pollutants in wastewater containing phenol, thus simulation study was carried out for the same and shown in Fig. 6. The literature study suggests that at low concentration of ferrous ion, if the OH* radical concentration is low; the chemical reaction does not proceed significantly. Therefore, at very low mole ratio, low percentage degradation of phenol was observed.

Literature study suggests that the mole ratio of hydrogen peroxide to iron ion affects the removal of phenol from wastewater according to the mechanism and chemical kinetics of Fenton reaction. Therefore, simulation study was carried out to determine the effect of mole ratio of hydrogen peroxide to iron ion on the degradation efficiency of phenol. Refer to the Fig. 6, at initial mole ratio of about 0.375, nearly 69%

degradation of phenol was observed. Above mole ratio of 1.0, a sudden improvement in degradation efficiency was observed (about 97%). Further increase in mole ratio from 1.13 to 1.88 resulted in gradual increase in percentage degradation and reached a constant value after a mole ratio of about 1.88.

On the other hand, when high amount of catalyst is used, hydroxyl radicals are generated in larger amount at the start of reaction; consequently, side reactions are initiated. Subsequently, these reactions result in decrease of removal of phenol as compared to earlier. Thus, constant removal efficiency was observed in the later part of the graph (Fig.6) at higher mole ratios⁷. Above mole ratios of 1.88, increase in percentage degradation is not appreciable. Thus, a mole ratio of 1.88 can be suggested as an optimum value for maximum degradation of 99.5%.

Effect of catalyst weight on the percentage degradation

The simulation study was carried out to assess the effect of catalyst weight or catalyst loading on percentage degradation of phenol. The effect of iron content on the catalyst activity by varying doses of iron in the packed bed reactor was studied in simulation. The study was performed using the iron catalyst within the weight range of 15-250 g. It can be seen that when small amount of catalyst (about 16 g) was used, approximately 25% degradation of phenol was reported (Fig. 7). A continuous increase was observed up to about 186 g of catalyst weight that can be correlated to the increase in hydroxyl radical formation that leads to better phenol degradation. Upon further increasing the catalyst load (above 186 g), percentage degradation was nearly constant.

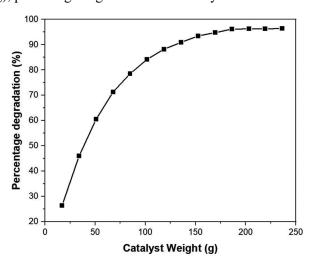


Fig. 7 — Percentage degradation based on the weight of catalyst

The amount of catalyst determines the active sites available for the reaction. With respect to increase in the catalyst amount, the hydroxyl radicals are generated more that results in better phenol degradation. Once the optimum catalyst loading is reached, further phenol degradation need not be achieved. This may be due to the increase in catalyst surface area with the increase in catalyst load. According to the literature, higher surface area promotes the generation of reactive radicals which in turn improves the percentage degradation³⁶. These observations can be supported by the research in which it was suggested that the increase in catalyst loading results in acceleration of phenol degradation²⁴. Similar results of increase in percentage degradation of phenol and its intermediates were observed during the study of heterogeneous Fenton process²⁴. They observed improved rate of degradation in case of higher catalyst loading. At a higher catalyst load (above 200 g), nearly constant percentage degradation was observed. No change in degradation at higher catalyst load may be due to the availability of excessive iron ion which results in the formation of iron complexes³⁴. As per an experimental finding, iron complexes consume some OH*, which results in lower or unchanged degradation³².

No significant change in percentage degradation of phenol was observed above 186 g of catalyst load. Thus, based on the conditions used in the simulation study, it can be suggested that 186 g catalyst load can be suggested as an optimum value for maximum degradation of 96%.

Effect of temperature on percentage degradation

The temperature of chemical reaction is an important parameter kinetically as it affects the rate constant and eventually the rate of reaction. The variation in phenol degradation with the change in reaction temperature is given in Fig. 8. In Fenton oxidation system, temperature of the reaction medium is one of the most significant factors which affect the degradation efficiency³⁷. Therefore, simulation study was carried out to assess the effect of temperature on the removal of phenol from wastewater. Generally, the rate of reaction with Fenton's reagent increases with increase in temperature. As per the Arrhenius theory for rate constant, the increase in temperature should lead to higher hydroxyl radical formation. However, at higher temperature conversion of hydrogen peroxide into water and oxygen declines the availability of reactant in Fenton reaction³⁶.

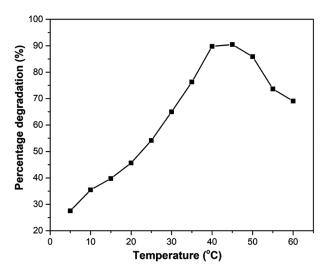


Fig. 8 — Percentage degradation based on the temperature of reactor

At temperature below 30°C, linear increase in percentage degradation of phenol was observed. Above the temperature the degradation was observed to improve at a lower rate than earlier. Above 32.5°C temperature a decrease in percentage degradation was observed and no further increase thereafter. This decline in degradation of phenol may be due to either the low availability of hydrogen peroxide or because of incomplete utilization. This decrease in degradation also suggests that at temperature above 32.5°C decomposition of hydrogen peroxide would have accelerated into oxygen and water and thus, significant mineralization was not reported. Also, high temperature leads to the decomposition of hydrogen peroxide and increase the loss of iron ion which does not favour the degradation of phenol^{32,35}.

Moreover, in case of complex reactions, temperature not only accelerates the main reaction but also favours the side reactions. It can be suggested that in this case, increase in temperature is initially helpful to activate the radicals. High temperature results in decomposition of H_2O_2 as follows⁷.

$$H_2O_2 \rightarrow H_2O + 0.5O_2$$

It can also be said that because reaction is exothermic, increase in temperature is not favourable for degradation or conversion of original components or pollutants initially present in the wastewater³⁸. The maximum degradation was observed at 45°C temperature, after this value decline in percentage degradation can be seen in the graph. This temperature (32.5°C) can be suggested as an optimum value for maximum degradation of phenol (90%) under the conditions used in simulation study.

Conclusion

Influence of various parameters including phenol concentration, hydrogen peroxide concentration, and catalyst loading on the product concentration and degradation efficiency is analyzed using simulation of the Fenton process in Aspen Plus. With the increase in H₂O₂ concentration in the feed, reactant phenol concentration is observed to decrease and products CO₂, H₂O concentration is increased along with increase in phenol degradation. Phenol degradation is improved due to the availability of hydroxyl radical concentration with the rise in hydrogen peroxide flow. Similarly, increase in phenol flow rate in the feed results in increase in the product, CO₂ and H₂O, flow rate due to improvement in mineralization of phenol and decrease in phenol degradation. Higher pollutant concentration lowers the degradation efficiency. Improvement in phenol degradation is observed with the H₂O₂/Fe²⁺ ion and catalyst loading due to better generation of OH* radical essential for Fenton reaction. Degradation rate improved with the rise in temperature that correlates with the Arrhenius law and further increase in temperature after optimum value lowers the degradation due to lowering of mineralization. The optimum percentage degradation of phenol was attained at around 4.2 kmol/h of H₂O₂ in the feed, catalyst loading of 186 g, 1.88 mole ratio of H₂O₂/Fe²⁺, and 32.5°C temperature. It can be concluded that the key parameters that influence the phenol degradation in Fenton reactions are, H₂O₂ concentration in the feed, catalyst loading, H_2O_2/Fe^{2+} and temperature of the reaction.

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Conflicts of interest

The authors declare no conflict of interest.

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