



DEGRADATION OF NITROBENZENE BY ADVANCED OXIDATION PROCESS

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abstract: The work deals with the degradation of nitrobenzene by advanced catalytic oxidation reagent generated in the system $\text{Fe}^{(0)}$ -EDTA- O_2 - H_2O . The obtained results demonstrated that this oxidation process was suitable to degrade nitrobenzene to CO_2 , H_2O and other compounds like low molecular acids. The nitrobenzene degradation was expressed by

$$D = \frac{[\text{COD}]_0 - [\text{COD}]}{[\text{COD}]_0} 100.$$

The effects of initial concentrations of nitrobenzene, EDTA, iron mass and temperature on advanced oxidation process have been studied. In solution of 0.1mM nitrobenzene, 0.1mM EDTA, 10g –iron mass, oxygen from air, the nitrobenzene conversion at 20°C to CO_2 , H_2O and others substances achieved 94%. The D conversion of nitrobenzene in the studied system depends on the ratio of EDTA/iron mass. An expression of reaction rate law based on the decrease of COD has been evaluated. By experimental data, the expression of reaction rate law let's calculate kinetic parameters.

key words: degradation of nitrobenzene; advanced oxidation; nitrobenzene; oxygen activation

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1. Introduction

The degradation of nitro aromatic compounds, especially nitrobenzene is of interest because they are common environmental contaminants resulting from munition, insecticides, herbicides, pharmaceuticals and dyes manufacturing. They also may be formed in the environment from aromatic contaminants found in atmospheric waters. Degradation of nitrobenzene has been implemented by many methods such as its reduction to aniline by zero-valent iron, photo-oxidation, phytoremediation and advanced oxidative methods. In this study was investigated the advanced oxidation of nitrobenzene by iron metal in batch system containing ethylenediamine tetraacetic acid and atmospheric oxygen to (i) assess the potential utility of $\text{Fe}^{(0)}$ -EDTA- O_2 oxidative system to degrade nitrobenzene in groundwater remediation, (ii) further understanding of role of $\text{Fe}^{(0)}$, EDTA and O_2 in aqueous medium. The obtained results indicate that nitrobenzene degradation by $\text{Fe}^{(0)}$ -EDTA- O_2 advanced

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oxidation system may reduce the COD values faster than its reduction only by $\text{Fe}^{(0)}$ alone. This is due to the formation of strong oxidative reagent by conversion of atmospheric oxygen by $\text{Fe}^{(0)}$ -EDTA- H_2O system.

2. Experimental section

Chemicals

Nitrobenzene compound was obtained in high purity from Merck Company. 2mM stock solutions of nitrobenzene were prepared in distilled water. Iron powder (99.9% purity), with grain size (mostly > 45 mesh) and EDTA (99% purity) were purchased from China. The trace impurities of iron powder are 0.02% C, 0.008% S, 0.003% Si, 0.002% P, 0.002% Mn. 2mM stock solutions of EDTA were prepared in distilled water.

Iron pretreatment

Prior to use, the $\text{Fe}^{(0)}$ grains were treated in 10% HCl (v/v) for 10 min to remove surface oxides or other contaminants. The cleaned metal was washed four times with distilled water to remove residual acidity or chloride remaining after the acid treatment.

Model reaction systems

Individual degradation experiments were performed in aerobic (opened) batch systems prepared in 250 –ml bottles containing 50ml of nitrobenzene solution 2mM and 50ml of EDTA 2mM, 10g of dry iron powder. The bottle was placed on a magnetic stirrer set to 600 rpm to start the reaction. The 3.5 pH of experiments was set up by H_2SO_4 acid 0.01M. Liquid samples were withdrawn at 30, 60, 90, 120, 150, 180, 240, 300 min to analyze nitrobenzene concentrations and COD values.

Analytical methods

Samples of 10ml were taken by a 25ml syringe from experimental bottle. The nitrobenzene concentration in solution was analyzed after acidified by H_2SO_4 , 0.1 M. The total nitrobenzene concentration and its intermediate products in solution were expressed in COD values analyzed by $\text{K}_2\text{Cr}_2\text{O}_7$ method in H_2SO_4 . The nitrobenzene conversion grade expressed by COD versus reaction time has been calculated by the expression:

$$D = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \cdot 100.$$

Here $[\text{COD}]_0$, $[\text{COD}]_t$ are corresponding to their initial and t -time values.

3. Results and discussion

The oxidation of nitrobenzene in the $\text{Fe}^{(0)}$ -EDTA- O_2 system has been demonstrated by the decrease of COD versus reaction time (see Fig. 1). This indicated that in the oxidation process, nitrobenzene was converted into CO_2 , H_2O and others compounds like low

molecular acids. The nitrobenzene is a reluctant compound to oxidation. This conversion of nitrobenzene is certainly due to the presence of the advanced activated oxygen reagent formed in $\text{Fe}^{(0)}$ -EDTA- O_2 system. This is similar to experiments indicated in the works [1].

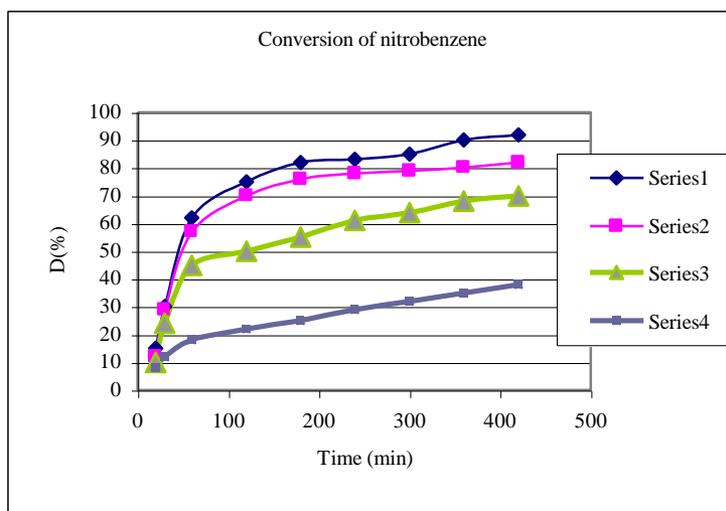


Fig. 1 Conversion of nitrobenzene ($D\%$) versus time for different initial nitrobenzene concentrations (NB) Series 1: NB = 0.1mM, Series 2: NB=0.3 mM, Series 3: NB = 0.5 mM, Series 4: NB = 1mM. $[\text{EDTA}]_0 = 0.1\text{mM}$, $\text{Fe}^{(0)} = 10\text{g}$, $[\text{O}_2] = 8\text{mg/l}$

3.1. Effect of nitrobenzene initial concentration on COD conversion grade (D)

The effect of initial nitrobenzene concentration on the conversion was investigated by the change of D values versus time. Fig. 1 shows the nitrobenzene conversion for four initial nitrobenzene concentrations. All the curves revealed a similar trend. The higher was the initial concentration of nitrobenzene, the lower was the conversion. After 400 min, the achieved nitrobenzene conversions were 94%, 83%, 68% and 37%, for nitrobenzene concentrations: 0.1, 0.3, 0.5 and 1mM, respectively. The decrease of nitrobenzene conversion D versus the increase of the initial concentration of nitrobenzene may be explained by the adsorption of nitrobenzene and its intermediate products on iron surface. Blanks without EDTA or atmospheric oxygen showed there was not or very low conversion in the system. An experiment with air bubbling was also done to evaluate oxygen influence on the oxidation process of nitrobenzene. The operating conditions were an initial concentration of nitrobenzene of 0.1mM, iron mass of 10g and EDTA concentration of 0.1mM. In this case, the nitrobenzene conversion achieved 98 % compared with 94% obtained without air bubbling. It means that the amount of initially oxygen dissolved from atmosphere during the reaction is sufficient to convert the system into advanced oxidation reagent.

3.2. Effect of temperature on D values

Fig. 2 illustrates the variation of D values versus reaction temperature in the range of 20-40°C.

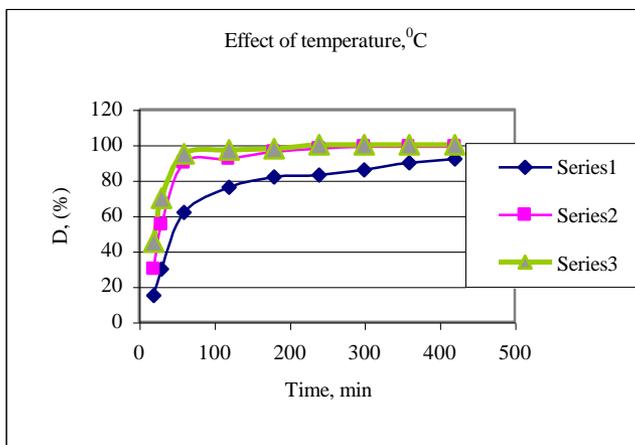


Fig. 2 Conversion of nitrobenzene versus time for different temperature,

Series 1: 20°C, Series 2: 30°C, Series 3: 40°C. (NB) = 0.1mM, [EDTA]₀ = 0.1mM, Fe⁽⁰⁾ = 10g, [O₂] = 8mg/l.

The nitrobenzene conversion by oxidation in the system at low temperature (20°C) achieved 90% after 360 min. As expected, the increase of the temperature led to an augment of the reaction rate, reaching at 30°C or 40°C, the same conversion of nitrobenzene of 90% after only 80 and 60 min respectively. This effect is similar with the phenol conversion in a similar oxidative system [1,2].

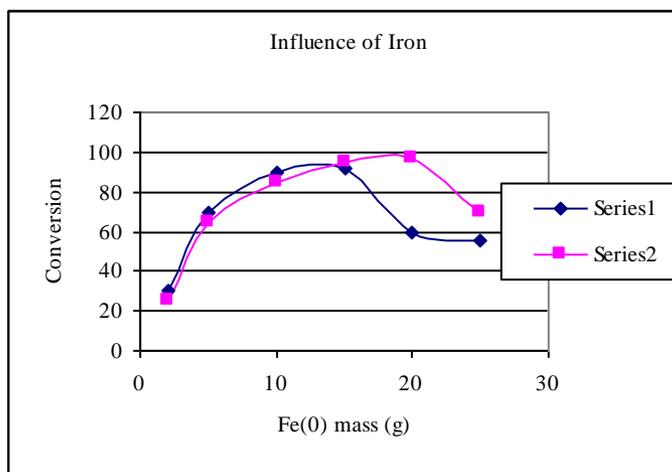


Fig. 3 Conversion of nitrobenzene versus mass of iron,

Series 1: EDTA 0.1 mM, Series 2: EDTA 0.3 mM.

3.3. Effect of catalyst concentration on D values

The influence of the EDTA initial concentration and iron mass was investigated separately at 30°C. The influence of increasing amount of both initial iron and EDTA was studied at varied Fe⁽⁰⁾/EDTA ratio. The experimental conditions are: Fe⁽⁰⁾ mass varied from 2.5, 5, 10,

15, 20 to 25 g at constant nitrobenzene (0.1mM) concentration and of EDTA were 0.1mM (series 1) and 0.3mM (series 2), (see Fig. 3).

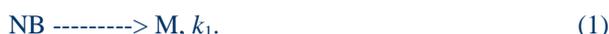
Fig. 3 illustrates that the D conversion depends on the relative ratio between iron and EDTA ranged from 12g Fe/ 0.1mM EDTA to 18 gFe/0.3 mM EDTA. This has demonstrated that the Fe⁽⁰⁾/EDTA ratio plays important role for the nitrobenzene conversion. The interaction between Fe⁽⁰⁾- EDTA may produce a catalyst that converts atmospheric oxygen to an advanced oxidation reagent. This prediction is in good agreement with other authors [3].

3.4. The predicted reaction law on the nitrobenzene oxidation (conversion) by advanced activated oxygen process

When nitrobenzene is added in a system consisting of Fe⁽⁰⁾-H₂O-EDTA-O₂, first it is observed its reduction by Fe⁽⁰⁾ to aniline like [4] as follows:



The reaction may be simplified by the expression as follows:



The system consisting of Fe⁽⁰⁾- H₂O – EDTA- O₂, may produce free radical OH , that causes the aniline oxidation process to form the low molecular acids, CO₂, H₂O and other compounds which reduce the COD of samples. This is in accordance with [3]. The oxidation reaction of intermediates with k₂ reaction rate constant may be written:



When there is free radical OH (a strong oxidative reagent in solution) a direct oxidation of nitrobenzene compound would be happened with k₃ reaction rate constant to form F final product. Here is:



According to this prediction the rate of nitrobenzene reduced reaction is as follows:

$$\frac{d \text{ NB}}{d t} = -(k_1 + k_2) \cdot [\text{NB}] \text{ or } [\text{NB}] = [\text{NB}]_0 e^{-(k_1+k_2)t} \tag{1}$$

Here [NB] is nitrobenzene concentration at t – time; [NB]₀ is nitrobenzene concentration at initial time.

The change of M intermediate concentration is:

$$\frac{d \text{ M}}{d t} = k_1 [\text{NB}] - k_3 [\text{M}], \tag{2}$$

At the time t = 0, we have [M] = [M]₀ = 0. When t > 0, we have:

$$[\text{M}] = [\text{M}]_0 e^{-k_3 t} + \frac{k_2 \text{ NB}}{k_1 + k_2 - k_3} \left[e^{-k_3 t} - e^{-k_1+k_2 t} \right] \tag{3}$$

The combination between (1) and (3) gives the following form:

$$\frac{NB + M}{NB + M}_t = \frac{k_2}{k_1 + k_2 - k_3} e^{-k_3 t} + \frac{k_1 - k_3}{k_1 + k_2 - k_3} e^{-k_1 + k_2 t} \quad (4)$$

Here, $([NB] + [M])_t$ are the total organic compound concentrations existing into solution at t – time. $([NB] + [M])_0$ are the initial NB concentrations M_0 being zero. In the case, the conversion of nitrobenzene exhibited by $[COD]/[COD]_0$ we have:

$$COD/ COD_0 = ([NB] + [M])/([NB] + [M])_0$$

$$\text{or: } \frac{COD}{COD}_0 = \frac{k_2}{k_1 + k_2 - k_3} e^{-k_3 t} + \frac{k_1 - k_3}{k_1 + k_2 - k_3} e^{-k_1 + k_2 t} \quad (5)$$

$$\text{or } [COD] = [COD]_0 \left[\frac{k_2}{k_1 + k_2 - k_3} e^{-k_3 t} + \frac{k_1 - k_3}{k_1 + k_2 - k_3} e^{-k_1 + k_2 t} \right]. \quad (6)$$

The expression (6) is an integrated form of reaction law of nitrobenzene oxidation by advanced activated oxygen in the system consisted of $Fe^{(0)}$ - EDTA- O_2 - H_2O . This equation is in accordance with the experimental data and similar to [5]. When $k_1 > k_3$ and $k_1 + k_2 \gg k_3$, the expression (6) becomes:

$$[COD] = [COD]_0 \left[\frac{k_2}{k_1 + k_2} e^{-k_3 t} + \frac{k_1}{k_1 + k_2} e^{-k_1 + k_2 t} \right] \quad (7)$$

$$\text{or } \frac{[COD]}{[COD]_0} = \frac{k_2}{k_1 + k_2} e^{-k_3 t} + \frac{k_1}{k_1 + k_2} e^{-k_1 + k_2 t} = \frac{k_2 e^{-k_3} + k_1 e^{-(k_1 + k_2)t}}{k_1 + k_2},$$

$$\frac{[COD]_0 - [COD]}{[COD]_0} = \frac{k_1 + k_2 - k_2 e^{-k_3} + k_1 e^{-(k_1 + k_2)t}}{k_1 + k_2} \quad (8)$$

By the experimental data from Figs. 1 and 2, the values of k_1 , k_2 , k_3 and other reaction constants may be determined but this aspects constitutes the subject of a next paper.

Conclusion

An experimental investigation was carried out to evaluate the feasibility of degradation of nitrobenzene by advanced catalytic activated oxygen in system consisting of $Fe^{(0)}$ - EDTA- H_2O - O_2 . The obtained results demonstrated that this oxidation process was suitable to degrade nitrobenzene. The nitrobenzene degradation into CO_2 , H_2O and other compounds like low molecular acids was expressed by the conversion $D = \frac{[COD]_0 - [COD]}{[COD]_0} 100$. The

effects of initial concentration of nitrobenzene, EDTA, iron mass and temperature influenced the advanced oxidation process. The D conversion of nitrobenzene in the studied system depends on the ratio of EDTA/iron mass. An expression of reaction rate law based on the decrease of COD has been evaluated. By experimental data, the expression of reaction rate law let's calculate kinetic parameters.

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