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Simulation of degradation of organic contaminants comprising ethylene glycol and phenol by iron nanoparticle using kinetic Monte Carlo method

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We applied the kinetic Monte Carlo simulation to study kinetics and degradation mechanism of organic pollutants including ethylene glycol and phenol by iron (III) nanoparticle and hydrogen peroxide as a catalytic system. The values of the rate constant for each step of the reaction mechanisms are obtained as adjustable parameters. In both degradation process complex of [Fe^{II}•OOH] is formed. This complex can be oxidized phenol. But, [Fe^{II}•OOH] complex produced hydroxyl radical in separate kinetic step for destruction of ethylene glycol. Ethylene glycol is oxidized by hydroxyl radical. In this research the kinetic Monte Carlo simulation results represents agree qualitatively with the available experimental data for destruction process of ethylene glycol and phenol.

1. Introduction

Organic contaminants often exist in drinking water, groundwater, domestic and industrial wastewaters. The chemical degradation of organic pollutants by advanced oxidation processes (AOPs) is a developing method for the treatment of industrial wastewater and purifying of drinking water and groundwater.[1-4] The oxidation by AOPs has been applied using Fenton's reagent ($Fe^{+2}/Fe^{+3}/H_2O_2$) as a promising and attractive treatment method for the effective destruction of a wide range of organic compounds.[5-9] The Fenton process is a catalytic reaction for the generation of very reactive free hydroxyl radicals ($^{\bullet}$OH) and it is based on an electron transfer between hydrogen peroxide (H_2O_2) and iron ions as the homogeneous catalysts. The hydroxyl radical is highly reactive, non-selective oxidizing agent and able to degrade a large number of organic compounds under ambient conditions.[10-12] This catalytic system is used for cleaning industrial water based on AOPs. [13,14] In order to oxygenation of organic contaminants such as ethylene glycol and phenol, Zelmanov and his coworker reported the applicability of iron oxide nanoparticle in Fenton system.[15]
We tried to study of kinetic parameter and mechanism of the degradation of organic pollutants using computational modelling. Kinetic Monte Carlo method demonstrated a significant level of performance as a powerful tool in simulation of various chemical reactions.[16–18] In the present work we employed an efficient method for identification and comparison of destruction kinetic mechanisms of phenol and ethylene glycol by iron oxide nanoparticle using kinetic Monte Carlo simulation. The rate constant of each step was determined by simulation. Also it is obtained the concentration curves versus time for oxidation process of phenol and ethylene glycol (EG) by simulation.

2. Kinetic Monte Carlo method

In order to simulation of the experimental data for degradation of organic pollutants by iron oxide nanoparticle, we used the kinetic Monte Carlo method developed by Gillespie.[19] Kinetic simulations were performed by the help of the Chemical Kinetic Simulator software, version 1.01.[20] In the algorithm of this simulation the reaction mechanism possess a series of several reactions:

$$nN + mM + \ldots \rightarrow products \tag{2.1}$$

The input data for the simulation are the steps, the rate constants of each step (k_i), temperature (T) and number of molecules (C_i). The algorithm of this simulation is based on the reaction probability density function ($P(\tau,i)$) which is obtained by Master equation:

$$P(\tau,i) = k_i C_i exp\{-\Sigma k_i C_i \tau\} \tag{2.2}$$

In fact the reaction probability density function is a two-variable probability density function that can be written as the product of two one-variable probability density functions:

$$P(\tau,i) = P(\tau).P(i) \tag{2.3}$$

Here $P\tau\ (d\tau)$ is the probability of occurrences of the next reaction between times $t+\tau$ and $t+\tau+d\tau$, irrespective of which reaction it could be and $P(i)$ shows the probability that the next reaction may be an Ri reaction that happens at time $t+\tau$.

By the addition theory for probabilities, $P\tau\ (d\tau)$ is achieved by summation of $P(\tau,\ i)\ d\tau$ overall i-values:

$$P(\tau) = \sum_{i=1}^{M} P(\tau,i) \tag{2.4}$$

That $P(i)$ is obtained by substituting of equation (2.4) in equation (2.3) as:

$$P(i) = P(\tau,i)/\sum_{i=1}^{M} P(\tau,i) \tag{2.5}$$

These two equations clearly express the two one-variable density functions in equation (2.3) that give two-variable density function $P(\tau,\ i)$. By substitution of equation (2.2) in equations (2.4) and (2.5) $P(\tau)$ and $P(i)$ are obtained as:

$$P(\tau) = a\,exp(-a\,\tau) \qquad 0 \le \tau < \infty \tag{2.6}$$

$$P(i) = \frac{a_i}{a} \qquad (i = 1,2\ldots,M) \tag{2.7}$$

Where we have in summary:

$$a_i = k_iC_i \qquad (i=1,2,\ldots,M) \tag{2.8}$$

$$a = \sum_{i=1}^{M} a_i = \sum_{i=1}^{M} k_iC_i \tag{2.9}$$

In this special case, $P(i)$ is independent of τ. It is also noted that, both of these one-variable density functions are correctly standardized over their respective explanation:

$$\int_0^\infty P(\tau)d\tau = \int_0^\infty a\exp(-a\tau)\,d\tau = 1\,, \qquad \sum_{i=1}^{M} P(i) = \sum_{i=1}^{M} \frac{a_\mathrm{i}}{a} = 1$$

The idea of this method is creating a random value of τ according to $P(\tau)$ in equation (2.6), then produce a random integer i according to $P(i)$ in equation (2.7). The result of random pair (τ,i) can be distributed according to $P(\tau,i)$.

A random value τ can be generated according to $P(\tau)$ in equation (2.6) by obviously drawing a random number r_1, from the uniform distribution in the unit interval and calculating

$$\tau = \left[\frac{1}{a}\right] ln\left[\frac{1}{r_1}\right] \tag{2.10}$$

Then, a random integer i may be created according to $P(i)$ in equation (2.7) by drawing another random number r_2 from the uniform distribution in the unit interval by taking i to be that integer for which,

$$\sum_{\nu=1}^{i-1} a_\nu < r_2a \le \sum_{\nu=1}^{i} a_\nu \tag{2.11}$$

In this method, two random numbers r_1 and r_2 are created and τ and i are calculated by equation (2.10) and equation (2.11), respectively.

The simulation was extended by continually selecting at random among the probability weighted steps in the mechanism and updating the reactants and products populations according to stoicheiometry of the selected step, system state variables and reaction rates. The results were obtained as concentration versus time curves. This stochastic numerical simulation method has been used to simulate several chemical reactions.[16–18] In this project kinetic Monte Carlo simulation has been used to kinetic study of degradation of organic compounds by Fenton reagent via iron nanoparticles.

3. Results and discussion

In this research it was investigated kinetics and mechanism of an experimental destruction of organic contaminant by Fenton reaction.[15] Zelmanov and his coworker[15] have studied the degradation of ethylene glycol and phenol using iron oxide nanoparticle and hydrogen peroxide as catalytic system. The concentration of this organic compound versus time curves was obtained for various concentration of Fe(III) nanoparticles. In the present work the kinetics modelling of the degradation of ethylene glycol and phenol was performed using kinetic Monte Carlo simulation.

3.1. Simulation of ethylene glycol degradation by iron (III) nanoparticles and H_2O_2

In order to simulation of ethylene glycol oxygenation, the input data are temperature (298 K), initial concentrations of ethylene glycol ($[EG]_\circ$= 25.78×10^{-2} M), initial concentrations of hydrogen peroxide ($[H_2O_2]_\circ$= 1.83 M), initial concentrations of iron oxide nanoparticles ($[Fe\ NPs]_\circ$= 98.2×10^{-4} M)[15], the steps of mechanism and rate constants of each step. The values of rate constants were adjusted until a reasonable fitting of the calculated data with experimental kinetic data was afforded. Different mechanisms have been examined for the degradation of ethylene glycol using Monte Carlo simulation. The mechanism which is obtained by kinetic Monte Carlo simulation and has a good fitting with experimental results can be written as:

$$\mathrm{Fe\ (III)_{nano}} + \mathrm{H_2O_2} \xrightarrow{k_1} \mathrm{[Fe^{II}{\bullet}OOH]_{nano}} + \mathrm{H^{\bullet}} \tag{3.1.1}$$

$$\mathrm{[Fe^{II}{\bullet}OOH]_{nano}} \underset{k_3}{\overset{k_2}{\rightleftarrows}} \mathrm{FeO_{nano}} + \mathrm{{}^{\bullet}OH} \tag{3.1.2}$$

$$\mathrm{HOCH_2CH_2OH+2{\bullet}OH} \overset{k_4}{\rightarrow} \mathrm{HOCH_2CHO} + \mathrm{2H_2O} \tag{3.1.3}$$

In the above mechanism, ethylene glycol degraded by hydroxyl radical ($^{\bullet}$OH). According to this mechanism complex of [$Fe^{II\bullet}$OOH] is formed by reaction between nano Fe(III) and hydrogen peroxide (reaction (3.1.1)). The rate constant of this step is k_1. Hydroxyl radical is created from this complex by an equilibrium reaction (reaction (3.1.2)). The rate constants of forward and reverse reactions are k_2 and k_3, respectively. Finally, ethylene glycol is destroyed by $^{\bullet}$OH in reaction and formed glycoaldehyde (3.1.3) (rate constant= k_4).

The rate constants of each step at the proposed mechanism were gained as adjustable parameters by kinetic Monte Carlo simulation. The obtained mechanism has been employed to simulation of this reaction with different initial concentration of iron (III) nanoparticles ($[Fe\ NPs]_\circ$= 17.86×10^{-3}, 26.79×10^{-3}, 44.64×10^{-3} M). The rate constants values for degradation of ethylene glycol by various concentration of Fe (III) nanoparticles are listed in Table 1. It is shown in this table that the third step (reaction (3.1.3)) is the rate-determining step. Therefore, k_4 is more important than other rate constants in the destruction process. Also k_1, k_2 and k_3 are constant for this reaction at different concentration of nano Fe(III) but k_4 increase with increasing of nanoparticles concentration.

<Table 1>

Concentrations of ethylene glycol versus time curves have been obtained to different concentration of Fe(III) nanoparticles by simulation and results were shown in Fig. 1. As seen in this figure, there is good agreement between simulated and experimental data.[15] This agreement demonstrates that proposed mechanism can be suitable for study kinetics of degradation of ethylene glycol.

<Fig. 1>

A possible mechanism for oxidation of ethylene glycol by hydroxyl radical has been shown in Scheme 1.[21] Glycoaldehyde is formed by $^{\bullet}OH$ reaction with ethylene glycol. At the end of this pathway formic acid is created by sequential $^{\bullet}OH$ attacks and it produces carbon dioxide and water.

<Scheme 1>

3.2. Simulation of phenol destruction by iron(III) nanoparticles and H_2O_2

The input data for the simulation of phenol degradation are temperature (298K), initial concentrations of phenol ($[PhOH]_{\circ}= 1.45\times10^{-2}$ M), initial concentrations of iron oxide nanoparticles ($[Fe\ NPs]_{\circ}= 2.68\times10^{-4}$ M), initial concentrations of hydrogen peroxide ($[H_2O_2]_{\circ}= 2.13\times10^{-1}$ M),[15] the steps of proposed mechanism and rate constants of each step. The values of rate constants were adjusted until a reasonable fitting of the calculated data with experimental results was obtained. Various mechanisms have been examined for the oxygenation of phenol by Monte Carlo simulation. The mechanism which has been afforded by kinetic Monte Carlo simulation can be shown as:

$$\text{Fe (III)}_{\text{nano}} + \text{H}_2\text{O}_2 \xrightarrow{k_1} [\text{Fe}^{\text{II}\bullet}\text{OOH}]_{\text{nano}} + \text{H}^{\bullet} \qquad (3.2.1)$$

$$[\text{Fe}^{\text{II}\bullet}\text{OOH}]_{\text{nano}} + \text{PhOH} \xrightarrow{k_2} \text{FeO}_{\text{nano}} + \text{Hydroquinone} + \text{H2O} \qquad (3.2.2)$$

In this mechanism Fe(III) nanoparticles reacts with hydrogen peroxide and the $[Fe^{II\bullet}OOH]$ complex is created at the first step (reaction (3.2.1), the rate constant of this step is k_1. Then this complex reacts with phenol and produced hydroquinone by reaction (3.2.2) (rate constant= k_2).

The rate constants k_1 and k_2 were obtained as adjustable parameters by kinetic Monte Carlo simulation. The proposed mechanism was applied to simulation of this reaction in various initial concentrations of Fe(III) nanoparticles ($[Fe\ NPs]_{\circ}= 5.36\times10^{-4}$, 1.07×10^{-3} M). Table 2 shows the values of the rate constants for phenol degradation by different initial concentrations of nanoparticles (entries 1-3). As seen in this table the rate-determining step is production of $[Fe^{II\bullet}OOH]$ complex (reaction (3.2.4)). Thus k_1 is more important than k_2 in the oxidation of phenol. Also k_1 and k_2 are almost constant for this reaction at different concentration of iron nanoparticle and the rate of phenol destruction depends on concentration of Fe(III) nanoparticles.

<Table 2>

The curves of phenol concentrations versus time have been gained for different concentration of iron nanoparticle using kinetic Monte Carlo simulation and the results were illustrated by Fig. 2(a). As represented in this figure, there is perfect agreement between simulated and existing experimental destruction data.[15]

<Fig. 2>

Also this proposed mechanism was used to simulation of degradation of phenol by different condition ($[PhOH]_{\circ}=5.45\times10^{-2}$ M, $[H_2O_2]_{\circ}= 1.07$ M, $[Fe\ NPs]_{\circ}= 2.14\times10^{-3}$, 3.57×10^{-3}, 4.28×10^{-3} M).

The amounts of the rate constants demonstrate the rate-determining step is production of $[Fe^{II\bullet}OOH]$ complex for simulation of phenol degradation with aforementioned condition (Table 2, entries 4-6).

As a result of these simulations k_1 and k_2 are almost constant for this reaction at different initial concentrations of phenol, Fe(III) NPs and H_2O_2.

Fig. 2(b) shows concentration of phenol versus time curves for aforementioned condition using kinetic Monte Carlo simulation. As can be seen, simulated data have well agreement with experimental data.[15] According to these results, proposed mechanism will be appropriate to study kinetics of degradation of phenol.

A probable pathway for the degradation of phenol by $[Fe^{II\bullet}OOH]$ complex was presented in scheme 2. As shown in this scheme phenol is chelated to Fe in $[Fe^{II\bullet}OOH]$ complex followed by the reductive elimination reaction to produce of hydroquinone. Organic acid is formed by sequential oxidation of hydroquinone by $^{\bullet}OH$ and finally carbon dioxide and water is created.[22-24]

<Scheme 2>

The results are shown in this section, the mechanisms of oxygenation to phenol and ethylene glycol are different. $[Fe^{II\bullet}OOH]$ complex converts to hydroxyl radical in degradation of ethylene glycol. Ethylene glycol is oxidized by $^{\bullet}OH$, But in the destruction of phenol, it is directly oxidized by the $[Fe^{II\bullet}OOH]$ complex. The reasons may be attributed to the degradation pathways of phenol and ethylene glycol (Schemes 1 and 2). In the pathway for phenol oxidation, $^{\bullet}OH$ is substituted on the aromatic ring which needs to metal assisted for the transfer. This transfer is performed on the nanoparticle surface. Therefore the $[Fe^{II\bullet}OOH]$ complex reacts with phenol.

4. Conclusions

We used kinetic Monte Carlo simulation to predict and study the kinetics and mechanism of organic pollutant (ethylene glycol and phenol) degradation by iron oxide Fe(III) nanoparticles and hydrogen peroxide as a catalytic system. The kinetic Monte Carlo simulated results show good agreements with existing experimental results for ethylene glycol degradation. The obtained mechanism has been applied for simulation of experimental data at different initial concentration of iron (III) nanoparticles. Also our model predictions well agree with destruction experimental results of phenol oxidation in variety initial concentration of reactants and Fe(III) nanoparticles. Therefore these proposed mechanisms can be suitable for the study of degradation reactions. Our results were shown $[Fe^{II\bullet}OOH]$ complex is formed in both oxidation processes. It converts to hydroxyl radical in degradation of ethylene glycol and hydroxyl radical oxidize Ethylene glycol. But, the $[Fe^{II\bullet}OOH]$ complex can be oxidized directly phenol in the destruction of phenol.

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Table 1. Rate constants of simulated mechanism for degradation of ethylene glycol by different concentration of Fe(III) nanoparticles

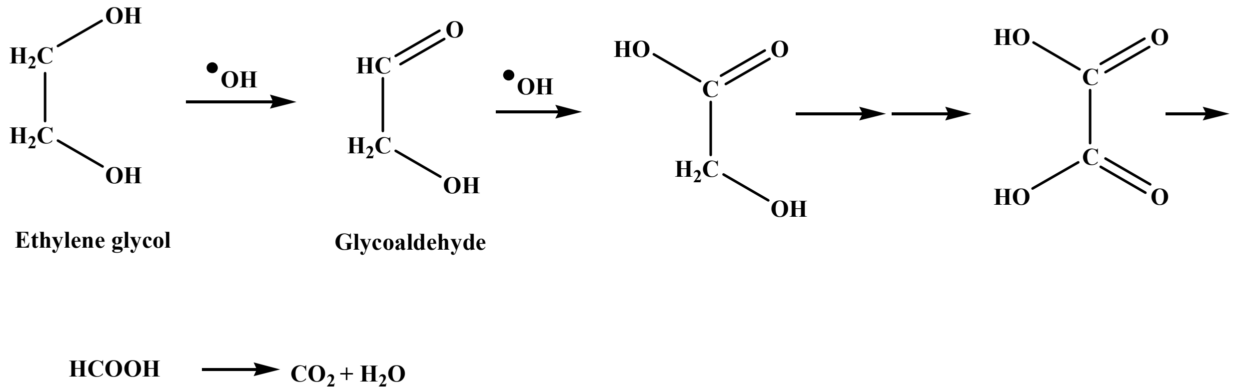
[Fe NPs]$_\circ$ (M)	k_1(min^{-1})	k_2(min^{-1})	k_3(min^{-1})	k_4(min^{-1})
98.2×10^{-4}	1.0	0.5	1.0×10^{-2}	7.3×10^{-3}
17.86×10^{-3}	1.0	0.5	1.0×10^{-2}	2.2×10^{-2}
26.79×10^{-3}	1.0	0.5	1.0×10^{-2}	4.4×10^{-2}
44.64×10^{-3}	1.0	0.5	1.0×10^{-2}	1.4×10^{-1}

Table 2. Rate constants of simulated mechanism for degradation of phenol

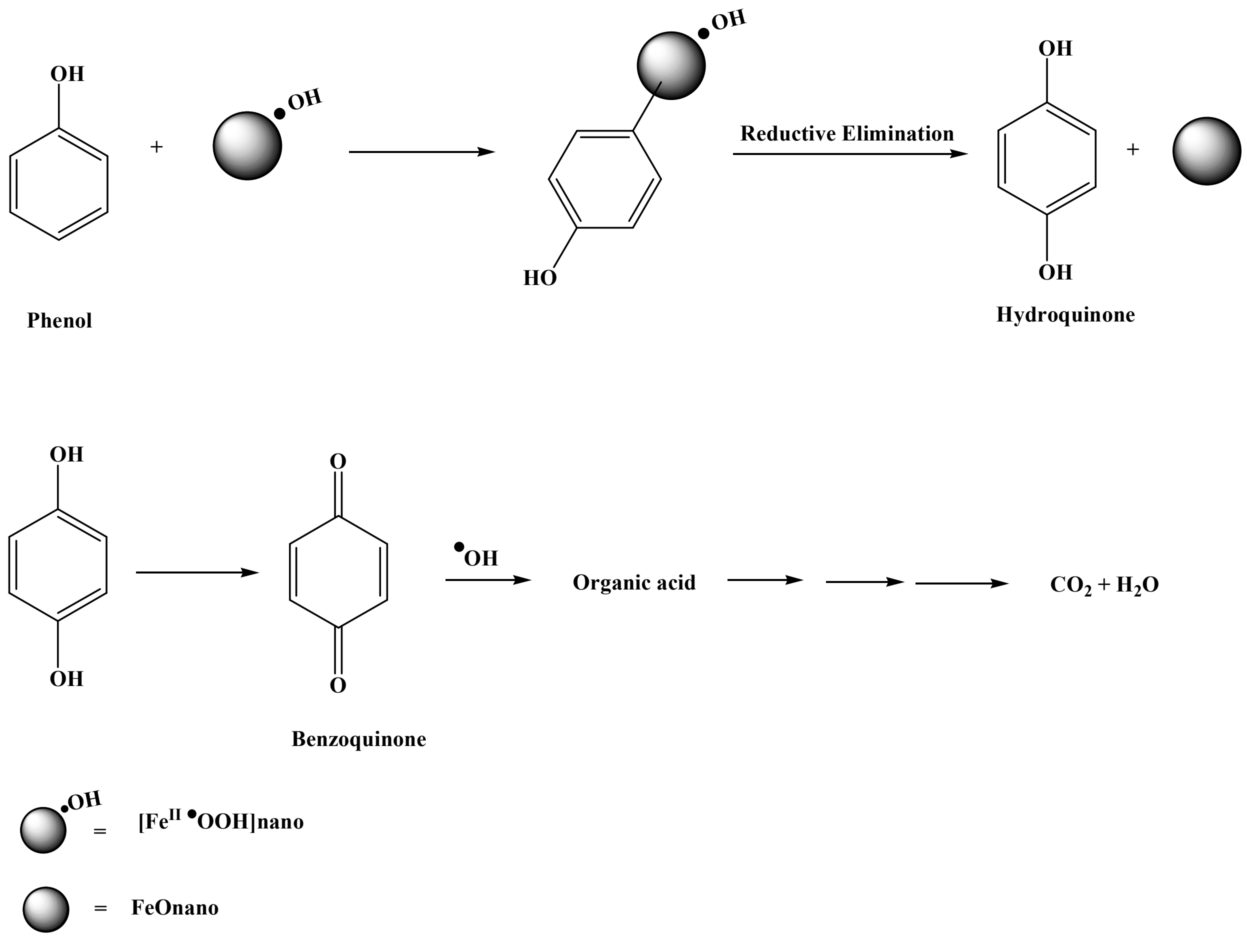
Entry	[Fe NPs]$_\circ$ (M)	k$_1$(min^{-1})	k$_2$(min^{-1})
1[a]	2.68×10^{-4}	1.00	6.48×10^{1}
2[a]	5.36×10^{-4}	1.00	6.50×10^{1}
3[a]	1.07×10^{-3}	1.00	6.50×10^{1}
4[b]	2.14×10^{-3}	1.00	6.53×10^{1}
5[b]	3.57×10^{-3}	1.00	6.55×10^{1}
6[b]	4.28×10^{-3}	1.00	6.56×10^{1}

[a] Simulation conditions: $[PhOH]_\circ = 1.45\times10^{-2}$ M, $[H_2O_2]_\circ = 2.13\times10^{-1}$ M

[b] Simulation conditions: $[PhOH]_\circ = 5.45\times10^{-2}$ M, $[H_2O_2]_\circ = 1.07$ M



Sheme 1. The possible pathway for degradation of ethylene glycol by hydroxyl radical.



Scheme 2. The probable mechanism for degradation of phenol by $[\mathrm{Fe}^{\mathrm{II}\bullet}\mathrm{OOH}]_{\mathrm{nano}}$.

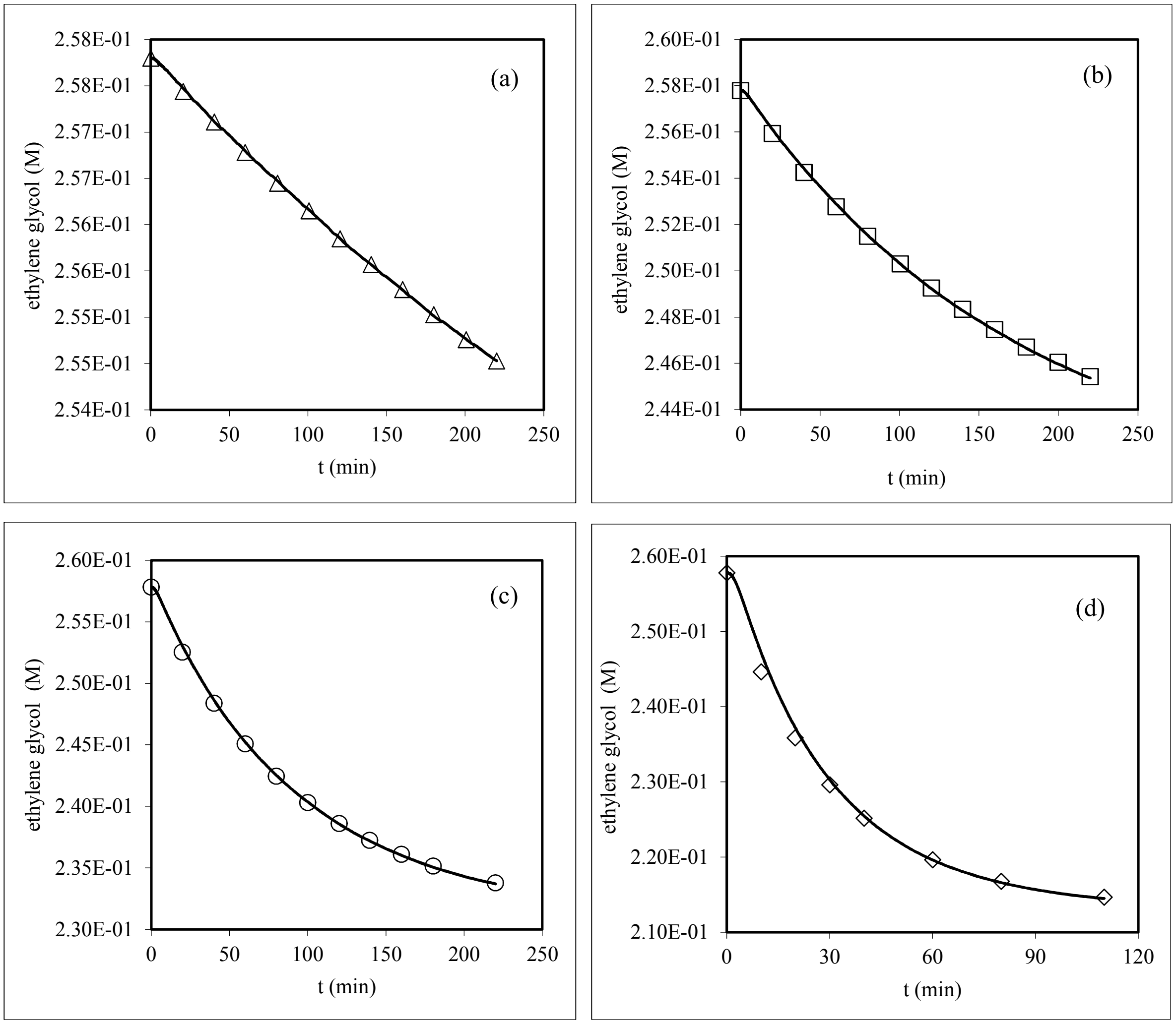


Fig. 1. Kinetic data for Degradation of ethylene glycol in the Fenton-like process at different concentrations of Fe(III) nanoparticles: (a) 98.2×10^{-4} (b) 17.86×10^{-3}, (c) 26.79×10^{-3} and (d) 44.64×10^{-3} M, experimental data (open circles) and theoretical data (solid line).

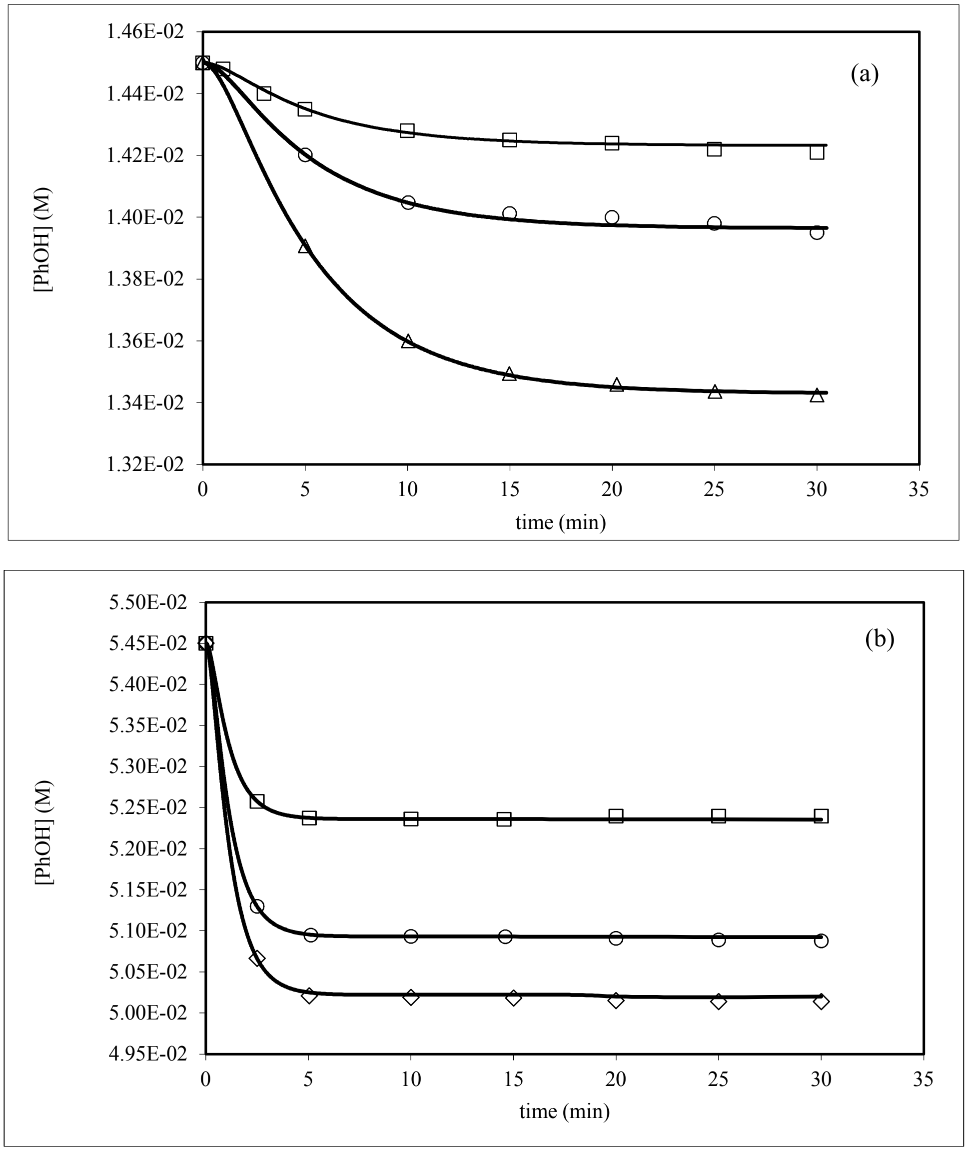


Fig. 2. Kinetic data for Degradation of phenol in the Fenton-like process (a) $[PhOH]_\circ = 1.45\times10^{-2}$ M, $[H_2O_2]_\circ = 2.13\times10^{-1}$ M at different concentrations of Fe(III) nanoparticles, M: (□) 2.68×10^{-4}, (○) 5.36×10^{-4}, (Δ) 1.07×10^{-3}. (b) $[PhOH]_\circ = 5.45\times10^{-2}$ M, $[H_2O_2]_\circ = 1.07$ M, concentrations of Fe(III) nanoparticles, M: (□)2.14×10^{-3}, (○)3.57×10^{-3}, (◊) 4.28×10^{-3}. Experimental data (open circles) and theoretical data (solid line).

Graphical Abstract