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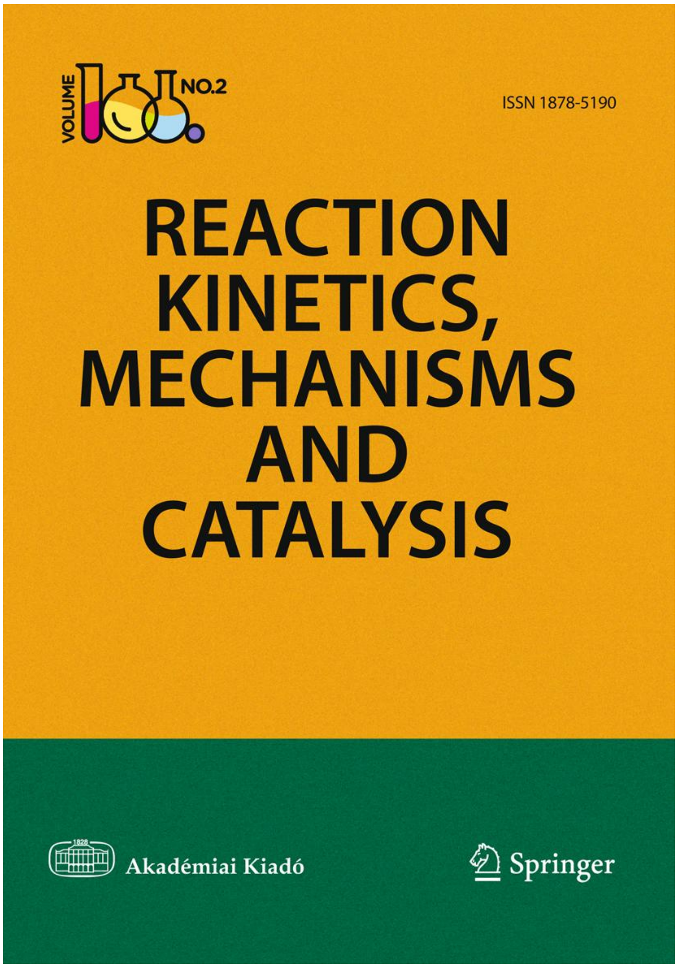

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Montmorillonite KSF as catalyst for degradation of acetaminophen with heterogeneous Fenton reactions

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Abstract The degradation of acetaminophen (APAP) in aqueous solutions with heterogeneous Fenton reactions was investigated with montmorillonite KSF as catalyst. The influencing factors of the initial APAP concentration, initial pH value, initial KSF dosage and H_2O_2 dosage were studied. The results showed that APAP could be effectively degraded under the conditions of pH 4.0, KSF 0.2 g/L and H_2O_2 0.5 mM, and the degradation efficiency of 0.5 mg/L APAP reached 93.5% after reaction for 30 min. The degradation kinetics of APAP followed the pseudo first-order rate law.

Keywords Acetaminophen · Heterogeneous Fenton · Montmorillonite KSF

Introduction

Pharmaceuticals and Personal Care Products (PPCPs), which have been recognized as emerging environmental pollutants, have received much concern in recent years [1, 2]. Traditional treatments cannot effectively remove PPCPs in the water environment, and a lot of researchers have found many kinds of drugs and their metabolites even in drinking water [3–5]. Acetaminophen (or *N*-acetyl-*p*-aminophenol, or 4-acetamidophenol, or *N*-acetyl-4-aminophenol, further APAP, Scheme 1) is a PPCP which has been widely used for antipyretic analgesics in cold medicine. China is the second largest APAP manufacturing country and one of the

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largest consumption countries because of huge population. Thus, environmental issues related with APAP should be paid enough attention [6].

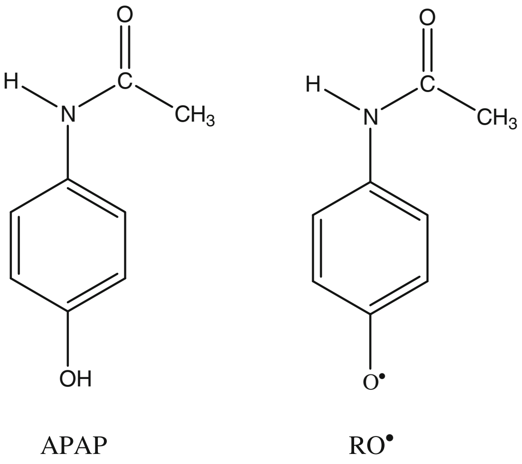
Some research on the oxidation of APAP has already been reported. Zhang et al. reported that APAP could be effectively photodegraded with the catalysis of TiO_2 [6] and the degradation efficiency could reach 59%. Li et al. studied the photocatalytic degradation of APAP in Fe(III)/oxalate system [7], and found that the degradation efficiency could reach 96.6% under optimal experimental conditions. Based on HPLC, 2D ^1H, ^{13}C, ^{15}N NMR and GC/MS analysis, Vogna et al. found the main degradation pathways for APAP were derived from three different hydroxylation steps [8]. Andreozzi et al. found APAP could be mineralized up to 30 and 40% while using ozonation and H_2O_2 photolysis, respectively [9].

Oxidation with Fenton's reagent (Fe^{2+}/H_2O_2) has been proven as an effective technology for destruction of a large number of organic pollutants by hydroxyl radicals generated in the system [10, 11]. Advantages of Fenton's reagent over other oxidation methods mainly include high efficiency, simplicity and flexibility [12].

However, it should be pointed out that the traditional homogeneous Fenton process has the significant disadvantage of losing catalyst iron. Moreover, homogeneously catalyzed reactions need up to 50–80 ppm of iron ions in solution, which is much higher than the discharge standard requirement (2 ppm) of the European Union [13]. In addition, the removal of the iron from wastewater by flocculation and sedimentation produces much sludge containing iron ions, which makes secondary pollution and needs more money in the solid waste treatment [14].

However, heterogeneous Fenton process can overcome the disadvantage cited above by reducing the loss of iron [15]. Various iron-containing solids like oxides and clays have been considered as the catalysts for heterogenous Fenton processes. Clays, both natural and chemically modified, are attractive catalysts for the Fenton process [16–22].

Montmorillonite KSF is an acid modified montmorillonite [23] and contains a higher content of iron than ordinary montmorillonite. These two properties of KSF could be used in heterogenous Fenton system which has higher oxidation potential



Scheme 1 Acetaminophen (APAP) and *N*-acetyl-4-aminophenoxyl radical ($RO^\bullet$)

in the presence of high concentration iron at acidic pH. In this work, the kinetics of the degradation processes of APAP in aqueous solution and influence factors in the heterogeneous Fenton system with KSF as catalyst were investigated to confirm the possibility and potential of the catalytic activity of KSF.

Experimental

Reagents

Acetaminophen (98%) was purchased from Alfa Aesar (Alfa Aesar, Britain) and was used without further purification. Methanol was HPLC grade (LEDA, USA). Montmorillonite KSF was purchased from Alfa Aesar. The size of the particles was 20–25 μm. The surface area of montmorillonite KSF was 20–40 m^2/g. Other reagents were all AR grade. Hydrochloric acid and sodium hydroxide were used to adjust the pH of the solutions.

Oxidation reaction

500 ml ultra-pure water was put into a cylindrical glass reactor. The KSF powder of certain weight was put into the reactor and the KSF suspension was stirred thoroughly for 5 min on a magnetic stirrer. The initial pH of KSF suspension was adjusted to the desired value with hydrochloric acid or sodium hydroxide. After that, the appropriate amount of acetaminophen was put into the KSF suspension which was continuously stirred by an electric mixer at the rate of about 300 rpm for 5 min before starting the reaction. At this stage, only adsorption of APAP on KSF occurred. The desired amount of H_2O_2 was then added into the aqueous suspension to initiate the Fenton reaction. The reaction was carried out under stirring at the above mentioned rate. At different time intervals, 5 mL suspension was sampled and the remaining APAP was detected by HPLC.

Analysis

The sample of KSF suspension containing APAP was filtered through 0.22 μm membrane filters, and then the 20 μL filtrate was injected into HPLC (Shimadzu LC-10A, Japan) to analyze the concentration of APAP. The reversed phase Kromasil C18 column (4.6 × 250 mm, 5 μm) was used for APAP analysis at a flow rate of 1.0 mL min^{-1} and wavelength of UV absorbance detection was 243 nm. The mobile phase was CH_3OH/H_2O mixture (30/70, v/v). The retention time of APAP was 3.5 min. The standard curve equation was $\text{Area} = 75{,}211 \times C + 1{,}189$ ($R^2 = 0.9993$, C ranged from 0.2 to 2 mg/L). Measurements were carried out in triplicate, and the relative error was <5%.

Sequential degradation experiment

To test the stability and recycling of the catalyst, a sequential degradation experiment was performed. This experiment included four kinetic runs. Three-first runs lasted 0.5 h, and the fourth run lasted 3 h. The initial amounts of reagents for the first run were 0.5 mg/L of APAP, 0.5 mM of H_2O_2 and 0.2 g/L of KSF. After the end of each run, the appropriate amounts of APAP and H_2O_2 were added to the reactor to make their initial concentrations to be the same as in the beginning of the first run.

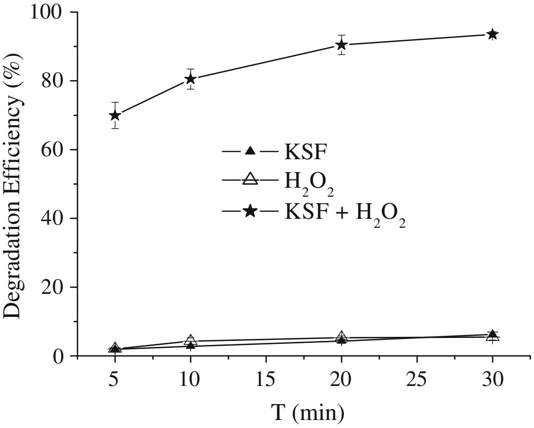
Results and discussion

Control experiment

Fig. 1 shows APAP removal percentage variations versus time with an initial concentration of 0.5 mg/L under different conditions. The degradation efficiency for APAP with KSF and H_2O_2 was higher than degradation with KSF or H_2O_2 alone. After 30 min, the removal efficiency was only 6.2% with KSF alone by adsorption and 5.5% with H_2O_2 oxidation alone; however, the degradation rate could reach 93.5% in presence of both KSF and H_2O_2.

Iron is a relatively abundant component in KSF (4.8%) [23], so if iron eluted from KSF completely, the concentration would be 170 μM when the KSF dosage was 0.2 g/L. Both Fe(II) and Fe(III) ions are removed from KSF under mildly acidic conditions, and Fe(II) is leached preferentially with respect to Fe(III) [24]. About 8% of the total amount of iron leaches from KSF at pH 3–4, and the Fe(III) to Fe(II) ratio is ca. 3:4 [23]. Accordingly, the dissolved total iron in 0.2 g/L KSF suspension at pH 3 was estimated to be about 9.8 μM (including 5.6 μM Fe(II) and 4.2 μM Fe(III)). Therefore, KSF provided enough free iron ions to make up Fenton reagent together with H_2O_2 at concentration of 0.5 mM which was about 100 times as that of the ferrous ion.

Fig. 1 Degradation rate changes of APAP in control experiments (H_2O_2 0.5 mM, APAP 0.5 mg/L, KSF 0.2 g/L, pH = 4.0)



It should be noted that the mentioned amount of total iron is ca. 0.56 mg/L. This is much less than the typical wastewater discharge limits (e.g., the U.S. Environmental Protection Agency discharge limit for total iron is 100 mg/L [25]). Moreover, according to the World Health Organization recommendations [26], the total amount of iron in drinking water should not exceed 0.3 mg/L, which is close enough to the value used in this work.

Effect of pH on the degradation of APAP

It is well established that the pH shows significant effect on the hydroxyl radical oxidation in various AOTs involving the Fenton reagent [27]. Therefore, the effect of initial pH on the degradation of APAP was also investigated in this work. As shown in Fig. 2, rapid degradation of APAP was observed at initial pH 3.0 and 4.0. The degradation efficiency was 60% at 30 min with the initial pH 4.0, however, there was no obvious degradation at the initial pH from 5.0 to 8.0.

Recently, Gil et al. reported that pH 3.0 was an optimal value for the photo-Fenton process catalyzed by Fe-treated laponite [22]. Guo et al. reported the stability of H_2O_2 is independent of having a homogeneous or heterogeneous process, it is affected by the pH, the lower degree of decomposition was observed at pH values between 3.0 and 4.0 [28]. Then above pH 4.0, the rapid H_2O_2 decomposition produces molecular oxygen without formation of appreciable amounts of hydroxyl radicals, which may decrease the degradation of APAP. Another reason for the decrease in the catalytic activity at pH >4 is the precipitation of iron(III) from the solution bulk. Moreover, acidic pH facilitates the elution of iron species from KSF solid [23], and then the production of hydroxyl radical will be more efficient. To avoid performing reaction at such lower pH value, pH 4.0 was chosen as the initial solution pH for further experiments so that the detailed influence of other factors could be investigated.

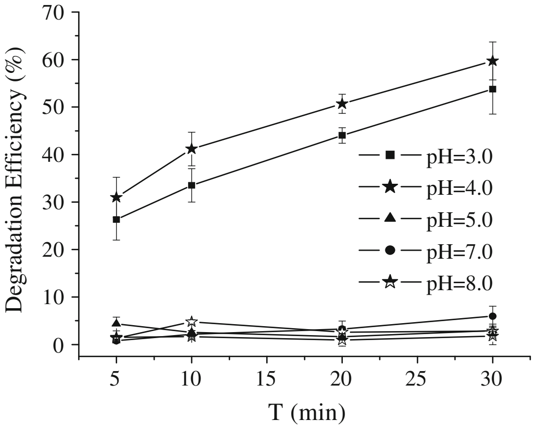


Fig. 2 Effect of pH on the degradation of APAP (H_2O_2 2 mM, APAP 0.5 mg/L, KSF 0.1 g/L)

Effect of montmorillonite KSF dosage on the degradation of APAP

The influence of KSF dosage on the degradation rate of APAP was examined with adding montmorillonite KSF dosages 0.1, 0.2 and 0.4 g/L. As shown in Fig. 3, the degradation efficiency increased with increasing the dosage of KSF in solution, which suggested that the participation of KSF could accelerate the degradation of APAP. And the degradation efficiency was about 95% at the dosage 0.2 g/L which was nearly the same as that at the dosage 0.4 g/L after reaction for 20 min. So the optimal dosage of KSF was 0.2 g/L in the range of 0.1–0.4 g/L.

Effect of H_2O_2 dosage on the degradation of APAP

In a Fenton reaction, generally, the degradation rate of organic compounds increases as the H_2O_2 concentration increases until a critical H_2O_2 concentration is achieved [29]. The degradation of APAP aqueous solutions with various H_2O_2 concentrations is shown in Fig. 4. Apparently, the degradation efficiency of APAP increased when the concentration of H_2O_2 increased from 0.05 to 2.0 mM. After 30 min of reaction, about 93.5% of APAP decomposed in the aqueous solution with 0.5 mM H_2O_2, while only 52% of APAP was degraded with 0.05 mM H_2O_2. Increase of the H_2O_2 concentration beyond 0.5 mM did not change apparent degradation of APAP compared with that of 0.5 mM H_2O_2. Therefore, in this work, the optimal concentration of H_2O_2 was 0.5 mM.

Effect of initial APAP concentration

The effect of the initial APAP concentration on the reaction rate was estimated. Fig. 5 shows the initial parts of the kinetic curves of APAP degradation at different APAP concentrations. From the kinetic data in the first 10 min presented in Fig. 5, the initial reaction rates r_0 were estimated as derivatives of the kinetic curves. As

Fig. 3 Effect of montmorillonite KSF dosage on the degradation of APAP (H_2O_2 2 mM, APAP 0.5 mg/L, pH = 4.0)

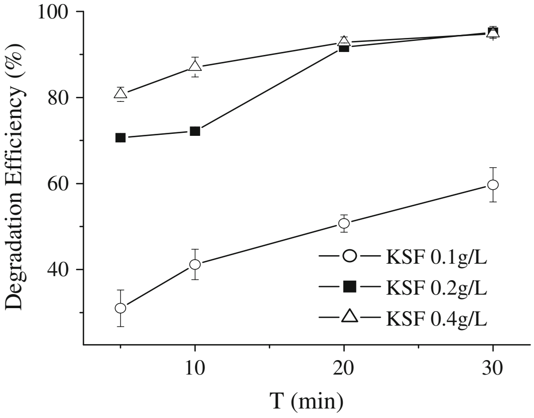
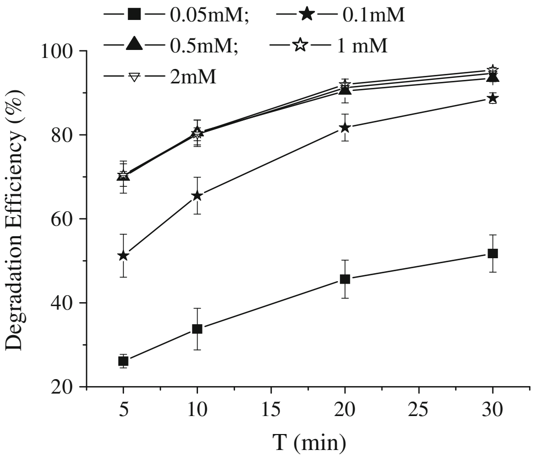


Fig. 4 Effect of H_2O_2 dosage on the degradation of APAP (APAP 0.5 mg/L, KSF 0.2 g/L, pH = 4.0)



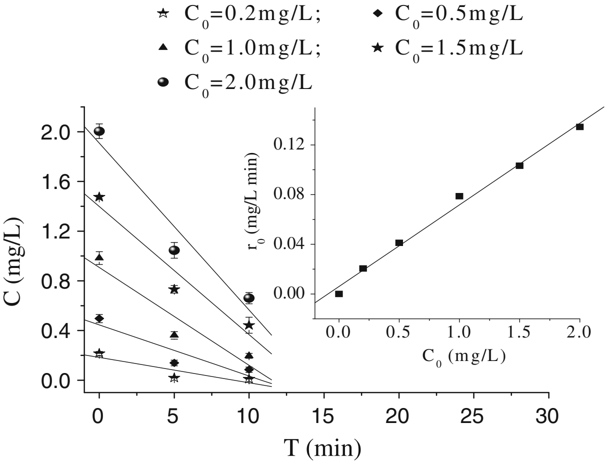


Fig. 5 Influence of the initial concentration on the degradation of APAP in aqueous solutions containing KSF (KSF 0.2 g/L, H_2O_2 0.5 mM, pH 4.0). Initial APAP concentrations (C_0) are specified in the figure. *Inset*: linear fit to the curve of initial rate r_0 as a function of initial APAP concentration C_0

shown in the inset of Fig. 5, the dependence of r_0 versus initial APAP concentration C_0 is linear. Therefore, the apparent degradation kinetics of APAP in solution is described by the pseudo first-order equation as below:

$$r = -\frac{dC}{dt} = kC$$

As a result, the reaction order versus APAP is one. The reaction rate constant k calculated from the straight line in the inset of Fig. 5 is (0.07 ± 0.01) min^{-1} at the typical reaction conditions (KSF 0.2 g/L, H_2O_2 0.5 mM, pH 4.0).

Sequential degradation experiments

Sequential degradation experiments with a fixed reaction time of 30 min were performed to test the stability and recycle of the catalyst. As shown in Fig. 6, in the primary stage, 94% of 0.5 mg/L APAP in the 500 mL reaction solution was decomposed after 30 min of reaction, while in the following recycle process, the degradation efficiency of APAP decreased to 44% (third run) and 37% (fourth run). And in the fourth run, the reaction time was prolonged to almost 3 h; the degradation efficiency was increased to 94% which was the same as that in the first run. This trend indicates that although KSF will gradually lose its catalytic power toward the degradation of APAP in the sequential load of APAP, higher degradation efficiency could also be achieved by prolonging the reaction time. Nevertheless, further work on the stability of KSF is needed for real application in the future.

Possible mechanisms of the degradation of APAP

The reaction mechanism of APAP degradation in the Fenton system seems to be rather complicated. Here we discuss the primary processes and the content of primary reaction products qualitatively.

The initial stage of oxidation is reaction 3 between APAP and $^{\bullet}$OH radical produced in the Fenton system (reaction 1) leading to the formation of dihydroxycyclohexadienyl radicals (further—radicals of an A-type). Reaction 3 shows an example of this reaction for the case of the formation of an ortho-A radical. A-radicals are the primary intermediates of the reaction between APAP and $^{\bullet}$OH radical [30]. A-radicals could dehydrate (reaction 4) to the *N*-acetyl-4-aminophenoxyl radical (RO$^{\bullet}$, Scheme 1) [30, 31]. This reaction is base and acid catalyzed [30]. Another possibility is the disproportionation reaction between the A-radicals (reaction 5) leading to the formation of dihydroxy products. This reaction seems to be sufficient in neutral solutions.

The characteristic feature of phenoxyl radicals (RO$^{\bullet}$), regardless of their nature and generation mode, is their combination reaction yielding dimeric products (dihydroxybiphenyls—reaction 6) or disproportionation [32, 33]. In our case, the

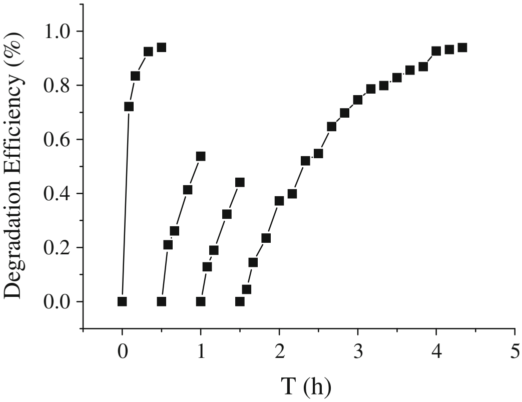
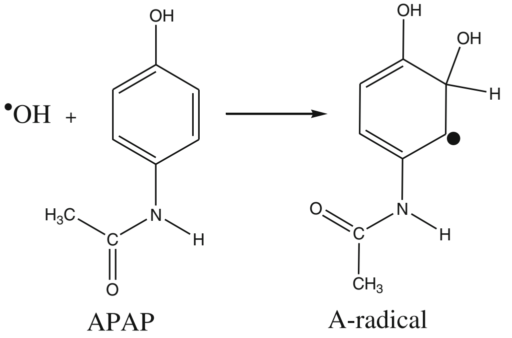


Fig. 6 Time profile of APAP degradation efficiency during the sequential degradation of APAP (APAP 0.5 mg/L, KSF 0.2 g/L, H_2O_2 0.5 mM, pH 4.0)

products of disproportionation are *N*-acetyl-*p*-benzoquinoneimine (NAPQI) and the parent compound (reaction 7). Formation of NAPQI is followed by its hydrolysis (reaction 8) yielding *p*-benzoquinone. It was shown [31] that in the absence of oxygen, isomeric dihydroxybiphenyls produced via the dimerization of $RO^\bullet$ (reaction 6) are the main reaction products.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \tag{2}$$



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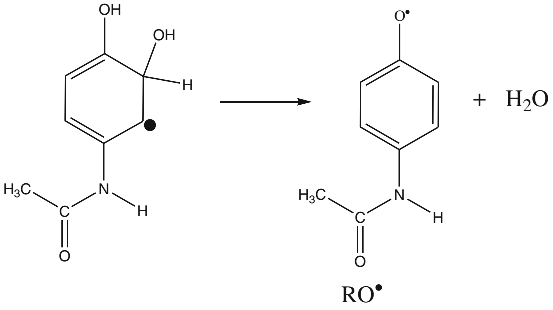

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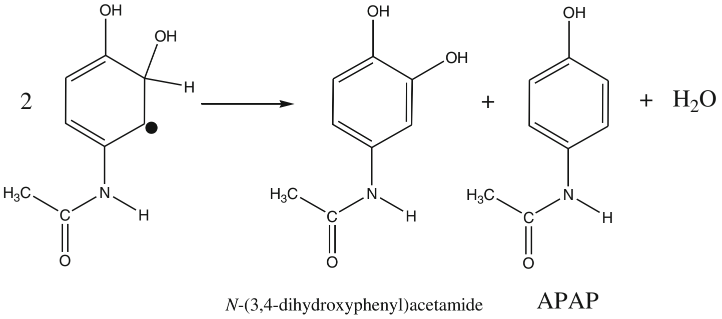

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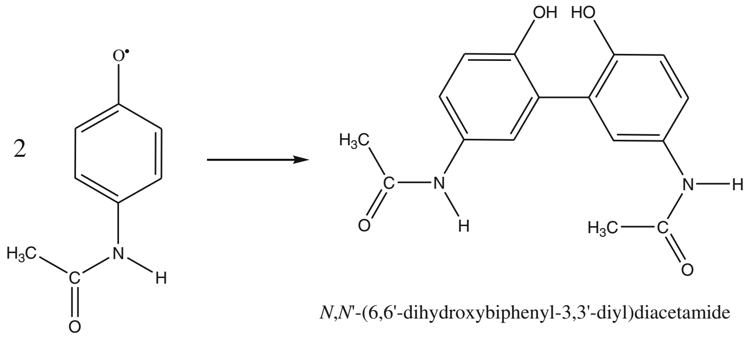

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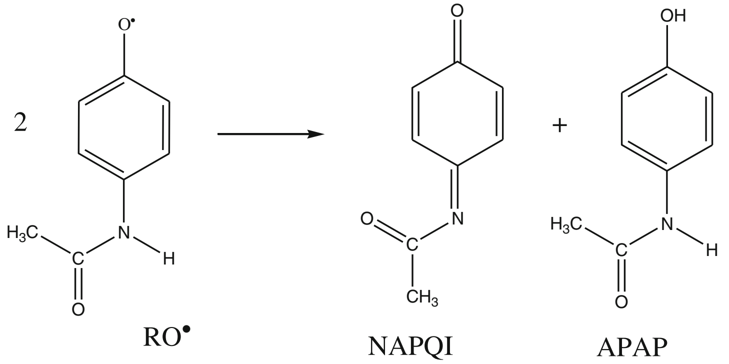

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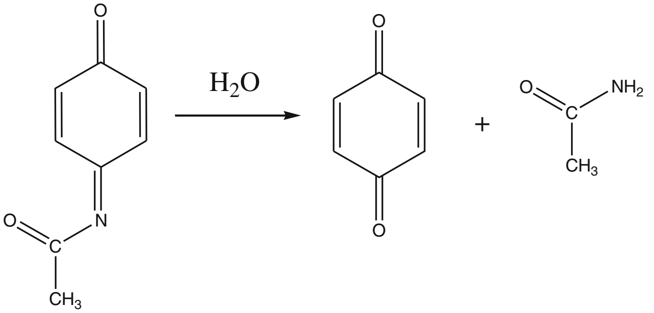

(8)

When APAP is degraded by the Fenton reagent, the reactions between a phenoxyl radical and a superoxide radical anion formed in the Fenton system (reaction 9) could be sufficient. This reaction is typical of all the phenoxyl radicals [34]. These processes lead to either electron transfer, reducing the $RO^{\bullet}$ radical to the anion RO^{-} (reaction 7) or the addition of the superoxide radical to give the corresponding peroxide anion (reaction 11) [35, 36].

$$HO_2^{\bullet} + OH^{-} \leftrightarrow O_2^{\bullet-} + H_2O \qquad (9)$$

$$RO^{\bullet} + O_2^{\bullet -} \rightarrow RO^{-} + O_2 \tag{10}$$

$$RO^{\bullet} + O_2^{\bullet -} \rightarrow ROO_2^{-} \tag{11}$$

In the case of APAP, reaction 11 leading to the formation of the peroxide anion ROO_2^{-} was shown to be favored [31].

Therefore, the degradation of APAP in the Fenton system leads to the formation of ROO_2^{-} anion, dihydroxybiphenyls and dihydroxyphenylacetamides as the main stable primary products. Minor products are NAPQI and *p*-benzoquinone. Among these compounds, NAPQI can bind to proteins, exerting a toxic effect [37]. The content of primary products is pH dependent. Primary products are, of course, the subjects of further oxidation.

Conclusions

APAP in aqueous solutions can be oxidized effectively in the presence of montmorillonite KSF and H_2O_2. KSF provides iron which reacts with H_2O_2 to produce $^{\bullet}OH$ radical through Fenton reaction mechanism. The optimal concentration of KSF and H_2O_2 was 0.2 g/L and 0.5 mM, respectively, for 0.5 mg/L APAP at pH 4.0. The degradation rate of APAP catalyzed by KSF was strongly pH-dependent and acidic pH facilitates the degradation. The degradation kinetics of APAP followed the pseudo first-order law. Thus, the present study proved the feasibility of using KSF as a new catalyst for the degradation of APAP in heterogeneous Fenton system.

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