Catalytic degradation of 3,5-dimethylphenol with goethite and hydrogen peroxide


Abstract—Phenolic compounds are one class of organic contaminants with high toxicity. In the present work, we study the degradation of 3,5-dimethylphenol (3,5-DMP) in heterogeneous phase with Fe(III)(hydr)oxides (goethite). The transformation of 3,5-DMP in aqueous suspension has been investigated under monochromatic irradiation at 365 nm. The disappearance of 3,5-DMP was efficient upon irradiation of 3,5-DMP-goethite (10^4 mol/l, 1 g/l) suspension. The effects of pH, oxygen, initial concentration of DMP and goethite are demonstrated. The involvement of HO^\* radicals has been ruled out because of the non-influence of tertibutanol used as a scavenger. The 3,5-DMP-goethite-H_2O_2 (10^4 mol/l, 1 g/l, 10^2 g/l) system was performed in dark before studying the photochemical reaction. It was found that the photodegradation of 3,5-DMP was significantly accelerated in comparison with the 3,5-DMP-goethite system. The optimal levels of H_2O_2 required for the process are also examined.

Index Terms—3,5-dimethylphenol, H_2O_2, goethite, Photodegradation.

I. INTRODUCTION

Fe(III)(hydr)oxides are among the most chemically reactive components of suspended matter in aquatic systems. These species are among the components of matter suspended more chemically reactive in the atmosphere water [1]. Fe(III)(hydr) oxides absorb light up to 600 nm. Most of them have semiconductor properties and then can behave as photocatalysts even though a very efficient positive holes-electrons recombination tacken place [2].

Major iron oxides include goethite (α-FeOOH), hematite (α-Fe_2O_3), maghemite (γ-Fe_3O_4), lepidocrocite (γ-FeOOH) and magnetite (Fe_3O_4); they have been used as catalysts to degrade organic contaminants. Many early studies have been focused on the photoinduced reductive dissolution of Fe(hydr)oxides in natural water and atmospheric water droplets [3]-[8].

It is well known that the photodissolution of iron oxide is accelerated in the presence of organic compounds [1]. Mazellier et al showed that upon irradiation at 365 nm of goethite-phenol in aqueous suspension, the degradation of the phenolic pollutant is observed together with the formation of various photoproducts [9]. The photooxidation of environmental contaminants such as halogenated, EDTA and sulfur dioxide has been also reported in the presence of iron oxides by Faust et al [10]. Pelizzetti et al observed the transformation of atrazine photoinduced by Fe_2O_3 in acidic medium, but they did not give any mechanism for this reaction [11]. Recently, the use of goethite with hydrogen peroxide was found to effectively oxidize organic compounds due to the catalysis on goethite surface and ferrous ion generation [12]-[13]. Lin et al found that n-butyl chloride was oxidized by hydroxyl radicals generated from the interaction of hydrogen peroxide with goethite particles [14]. Lu also indicated that 2-chlorophenol can be decomposed with H_2O_2 catalyzed by goethite [12]. Ming-Jer Liou et al studied the catalytic degradation of nitro aromatic explosives (picric acid and ammonium picrate) with goethite and hydrogen peroxide process [15]. We et al reported that the combination of goethite and hydrogen peroxide provide rapid degradation of dimethyl sulfoxide (DMSO) in the neutral pH [16].

The study of the phototransformation of aromatic compounds in aqueous iron oxide-H_2O_2 system can provide valuable insights into the fate of this pollutants and the effect on characteristics of mineral particles in the environmental aquatic system. The primary objective of this study was to investigate DMP decomposition by goethite in the neutral pH. The effects of oxygen, pH, initial concentration of DMP and goethite are examined. In the second step, the photoreaction of DMP at goethite-water interface in the presence of H_2O_2 was considered and the concentration changes of organic compound and H_2O_2 were studied and compared.

II. EXPERIMENTAL

A. Chemicals

3,5-dimethylphenol (3,5-DMP) was a Reidel-de Haën product with a purity of 99.5%, ortho-phenantroline, sodium hydroxide, Hydrogen peroxide was a Labosi product with a purity of 30%, Tertibutanol was a Prolabo product with a purity of >99%, Acetonitril was analysis grade from Carlo Erba Reagenti, goethite (α-FeOOH) was synthesized according to the procedure described by Atkinson et al [17].
suspensions were prepared with ultra-pure water (Millipore simplicity-UV) and filtered through millipore filter 0.45 μm. The pH measurements were carried out with HANNA pH-meter to ± 0.1 pH unit. The pH of the solution was adjusted by adding NaOH (Prolabo, >97%) and HClO₄ (Merck, 60 %). The ionic strength was not controlled; the solutions were deoxygenated at room temperature by continuous nitrogen bubbling in the reactor.

B. Apparatus

The photoreactor was exposed to the radiation sources composed of low pressure mercury UV lamp type Philips HPW 125, (UV-A, λ_{max}=365 nm).

LC spectrophotometer Lambda–Max Model 481 was used to measure 3,5-DMP concentration with an accuracy of 3% (SD = 0.0030). HPLC experiments were carried out using a Waters chromatograph equipped with pump (Waters model 590). The chromatographic separation was performed with a C18 reverse phase column (5µm, 250 mm x 4.6 mm i.d.). The mobile phase was acetonitrile/water mixture (60/40, v/v) at a flow rate of 1 ml/min. the injection volume was 20 µL and the samples were monitored at 272 nm. The accuracy of HPLC is 2% (SD = 0.0028).

The crystal structure of the powdered goethite samples was verified by X-ray diffraction analysis with diffractometer (Siemens) and using Nicolet 5 SXC FT-IR spectrometer by dusting on the KBr.

C. Analysis

The presence of Fe(II) in the filtered aliquots was checked out by complexometry with ortho-phenantroline [18]. 3,5-DMP degradation was followed by HPLC.

III. RESULTS

A. Characterization of 3,5-DMP

The spectra depicted in Fig.1 of 3,5-DMP (10^{-4} mol/l) in aqueous solution represents a weak band at 272 nm which corresponds to transition of benzenic cycle n-π* and a shoulder around 218 nm. The molar absorption coefficient was evaluated to 1550 M^{-1}cm^{1}.

B. Thermal behavior of 3,5-DMP- goethite system in aqueous solution

A dark investigation of the system was performed before studying the photochemical behavior. Under our experimental conditions [3,5-DMP] = 10^{-4} mol/l, [goethite]=1g/l, the UV-Visible spectrum of mixture in aqueous solution as a function of time presents no appreciable variation Fig.2. The absence of any detectable adsorption is completely in agreement with the previous study of Patrick Mazellier [9].

C. Photochemical behavior of 3,5-DMP- goethite system

UV-Visible absorption spectra

When the mixture 3,5-DMP-goethite was irradiated at 365 nm, a decrease in absorbance was observed all along the spectrum (Fig.3). The peak at 272 nm diminished under UV irradiation illustrating the degradation of 3,5-DMP.
The concentration changes of 3,5-DMP were followed by HPLC (Fig.4). For our experimental conditions, data are in a good agreement with a pseudo-first-order reaction, as evidenced by plotting \( \ln \left( \frac{C_0}{C} \right) \) versus irradiation time (insert in Fig.4).

\[
C = C_0 \exp (-kt)
\]

\[
\ln \left( \frac{C_0}{C} \right) = kt
\]

Where, \( C \) is the concentration of 3,5-DMP at time \( t \) (min) and \( C_0 \) is the initial concentration of 3,5-DMP. The rate constant \( (k) \) was calculated to be \( 8.5 \times 10^{-5} \text{ min}^{-1} \). The correlation constant was calculated to be \( R^2=0.99 \).

**Influence of pH**

We varied the pH value of the suspensions below and above the zpc (Zero-point-charge) value of goethite (zpc = 8 [19]).

The solution containing a mixture of 3,5-DMP-goethite \((10^{-4} \text{ mol/l, } 1 \text{ g/l})\) was irradiated at 365 nm. The pH of which was equal to 3, 6.25, 9. It is important to note that in our conditions, no release of Fe(II) was observed in the solution. Additionally, the monitoring of the reaction by HPLC show a not significant pH effect on the disappearance of 3,5-DMP (Fig.5).

**Fe(II) formation**

Fe(II) produced by charge separation in the photoredox reaction was followed by complexometry. The result shows that the level could not be detected under our conditions. This result confirms the no dissolution of goethite in our experimental conditions.

**Influence of goethite concentration**

The effect of different concentration of goethite on the degradation rates of 3,5-DMP was also examined. The experiments were carried out varying the goethite amount from 0.5 to 2 g/l. The efficiency of 3,5-DMP photodegradation was found to increase with goethite concentration. The fastest degradation occurred when 1.5 g/l goethite was used.

An additional excess in goethite concentration slow down the reaction rate (Fig.6).
The increase in the photodegradation due to the increase in the total surface area available for photocatalytic reaction as the concentration of goethite increased. However, when goethite was overdosed, the intensity of incident UV light was attenuated because of the decreased light penetration and increased light scattering, which embeded. In all cases the initial rate of 3,5-DMP loss was calculated (Table I).

Influence of 3,5-DMP concentration

The disappearance of 3,5-DMP upon irradiation at 365nm was studied as function of the initial concentration of the substrate. Fig.7 represents the kinetics of 3,5-DMP disappearance mixture at different initial 3,5-DMP concentrations. The result obtained shows that the disappearance of 3,5-DMP is faster for the lowest concentration of substrate.

Influence of oxygen

In order to give implication of the oxygen role in mechanistic degradation of pollutant, the 3,5-DMP-goethite system was irradiated at 365 nm in deoxygenated and aerated solutions. The corresponding kinetics of 3,5-DMP disappearance represented in Fig.8, illustrate that the oxygen seems to be necessary for 3,5-DMP degradation.

Irradiation in the presence of tertiobutanol

Tertiobutanol 1%(v/v) used as a hydroxyl radicals scavenger, was added to some 3,5-DMP-goethite suspensions in order to give evidence for the formation of HO\(^{•}\) radicals. The results clearly showed that the degradation of 3,5-DMP was not affected by the presence of alcohol. Based on this
result we confirm that HO* radicals are not involved in the process of 3,5-DMP degradation (Fig.9).

![Graph](image)

Fig. 9. 3,5-DMP degradation upon irradiation of 3,5-DMP-goethite (10^-4 mol/l-1g/l) at 365 nm: (a) In the presence 1% of tertiobutanol, (b) In the absence of tertiobutanol.

**Mechanism**

The products of 3,5-DMP transformation are the same as those observed by Mazellier et al. The dissolution of Fe(hydr)oxide is not detected so the process leading to degradation of 3,5-DMP take place on the goethite surface. It has been proved that under irradiation, the electronic surface properties of goethite may be modified and photoadsorption of 3,5-DMP can occur.

A proposed mechanism of DMP degradation which is given in scheme 1 was already discussed by Mazellier et al is similar in our case.

![Scheme](image)

Scheme. 1. Pathway of 3,5-DMP degradation at the surface of goethite.

**D. Phototransformation of 3,5-DMP -goethite-H_2O_2 system**

- **Thermal behavior**

The experiments were carried out to study the effect of H_2O_2 on efficiency of DMP degradation. We preliminary studied the stability of the goethite at neutral pH after addition of H_2O_2.

The dark investigation of the 3,5-DMP-goethite-H_2O_2(10^-4 mol/l, 1 g/l, 5x10^-3 mol/l) and 3,5-DMP-H_2O_2 (10^-4 mol/l, 5x10^-3 mol/l) systems were performed at room temperature in order to evaluate the contribution of direct oxidation of 3,5-DMP by H_2O_2. In absence of goethite, low oxidation of 3,5-DMP is observed; the rate of disappearance of 3,5-DMP reached 4/2 after 25 hours of reaction. Other than, the addition of goethite accelerates the rate of reaction as is illustrate in Fig. 10. This phenomenon is explain by the production of hydroxyl radicals by Fenton reaction which will occur in the system goethite-H_2O_2 as reactions (1)-(2).

\[
\alpha\text{-FeOOH} + 2\text{H}^+ + \frac{1}{2}\text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{H}_2\text{O} \quad (1)
\]

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^* + \text{OH} \quad (2)
\]

![Graph](image)

Fig. 10. 3,5-DMP degradation in different mixture

a) 3,5-DMP-goethite (10^-4 mol/l, 1g/l)

b) 3,5-DMP-H_2O_2 (10^-4 mol/l, 5x10^-3 mol/l)

c) 3,5-DMP-goethite-H_2O_2 (10^-4 mol/l, 1g/l, 5x10^-3 mol/l)

Moreover, as illustrated in Table II the Rate of elimination of 3,5-DMP at different times in different systems showed that 3,5-DMP is weakly degraded in the 3,5-DMP-goethite-H_2O_2 system in dark at room temperature.

<table>
<thead>
<tr>
<th>TABLE II</th>
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<tr>
<td>RATE OF 3,5-DMP ELIMINATION AT DIFFERENT TIMES IN DIFFERENT SYSTEMS</td>
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<tr>
<td>Systems</td>
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<tr>
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</tr>
<tr>
<td>3,5-DMP- goethite</td>
</tr>
<tr>
<td>3,5-DMP-H_2O_2</td>
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<tr>
<td>3,5-DMP-goethite-H_2O_2</td>
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</table>
The results obtained in the different systems studied show that:

- The presence of hydrogen peroxide improves slightly the rate of the degradation.
- The degradation of pollutant in the absence of light is low even for long time.

**Photochemical behavior**

**UV-Visible absorption spectra**

During irradiation at 365 nm, the temporal evolution of the UV-Visible spectra changes taking place in the studied system 3,5-DMP- goethite- H$_2$O$_2$ (10$^{-4}$ mol/l, 1 g/l, 5x10$^{-3}$ mol/l) is displayed in Fig.11. The diminution of the absorbance at 215 nm and the formation of two isosbestic points illustrate that a transformation occurred between different constituents.

![Graph 1](image1)

**Fig. 11.** Spectrum evolution of mixture 3,5-DMP- goethite- H$_2$O$_2$ (10$^{-4}$ mol/l, 1 g/l, 5x10$^{-3}$ mol/l) upon irradiation at 365 nm.

The concentration of 3,5-DMP was also measured by HPLC in the goethite-H$_2$O$_2$-UV system, upon irradiation at 365 nm (Fig.12).

The rate of disappearance of DMP in the absence of hydrogen peroxide is 2% after first hour of irradiation; however the addition of hydrogen peroxide increases the rate up to 21% during the same time. The rate constants (k) are: k = 8, 50x10$^{-5}$ min$^{-1}$ and k = 4,13x10$^{-3}$ min$^{-1}$ respectively proving of this fact.

![Graph 2](image2)

**Fig. 12.** 3,5-DMP degradation upon irradiation of 3,5-DMP-goethite (10$^{-4}$ mol/l, 1g/l) at 365 nm : a) In the absence of H$_2$O$_2$, b) In the presence of [H$_2$O$_2$] = 5x10$^{-3}$ mol/l.

The successful degradation of 3,5-DMP shows that the photodegradation process occurs via the photoexcitation of complex goethite-H$_2$O$_2$ may produce HO$^\cdot$ radicals. He et al proposed the mechanism of photodegradation of various aromatic compounds in goethite-H$_2$O$_2$ system at neutral pHs as reactions (3)–(6) [21].

\[
\begin{align*}
\equiv\text{Fe}^{\text{III}}\text{OH} + \text{H}_2\text{O}_2 & \rightarrow \equiv\text{Fe}^{\text{III}}\text{OOH} + \text{H}_2\text{O} & (3) \\
\equiv\text{Fe}^{\text{III}}\text{OOH} + \text{hv} & \rightarrow \equiv\text{Fe}^{\text{IV}}\text{=O} + \text{HO}^\cdot & (4) \\
\equiv\text{Fe}^{\text{IV}}\text{=O} + \text{H}_2\text{O} & \rightarrow \equiv\text{Fe}^{\text{III}}\text{OH} + \text{HO}^\cdot & (5) \\
\text{Organic compound} + \text{HO}^\cdot & \rightarrow \text{degradation products} & (6)
\end{align*}
\]

The photo-decomposition of 3,5-DMP is more quick in aqueous goethite-H$_2$O$_2$, due to the efficient production of HO$^\cdot$ by photolysis of the surface complex.

**Effect of pH**

The pH value of solution is significant factor acting in the course of reaction. The system has been investigated in this study from 3 to 9 pH value. The results illustrate that 3,5-DMP degradation seems to be the most efficient at acidic medium (pH=3) (Fig.14).
This phenomenon is probably related to the PZC. Indeed, since the point of zero charge (PZC) of goethite is about 8.0 [19], a lower pH value (<8) causes changes on the surface to be positively charged, this favors adsorption of the pollutant [22]. Moreover, it will be noticed that the photo-Fenton is more efficient in acidic media. This is in agreement with Ju et al which reported that the rate degradation of Mordant Yellow (MY10) was more rapid in acidic media (pH = 5), in which [MY10] = 0.1 mM and [goethite] = 0.5 g/l and [H₂O₂] = 1 mM [22].

**Effect of H₂O₂ concentration**

The effect of H₂O₂ concentration on photodegradation of 3,5-DMP in the 3,5-DMP-goethite-H₂O₂ system is presented in Fig.15.

The reaction rate of 3,5-DMP degradation accelerated by increasing the concentration of hydrogen peroxide. Thus, more hydroxyl radicals were produced when the concentration of H₂O₂ was increased from 10⁻³ to 10⁻² mol/l.

Nevertheless, further increase in the H₂O₂ concentration from 10⁻² to 5x10⁻² mol/l would result in the decrease of degradation of 3,5-DMP. This fact is due to the scavenging effect of hydroxyl radicals by hydrogen peroxide existing at high concentration. The, hydroperoxy radicals are predominantly produced in this case [23]. Moreover, these hydroperoxy radicals are much less reactive and do not contribute to oxidation of DMSO [16].

\[
\text{HO}^* + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^* + \text{H}_2\text{O} \quad k_{\text{H}_2\text{O}_2} = 4.5 \text{ M}^{-1}\text{s}^{-1} \quad (7)
\]

\[
2\text{HO}_2^* \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (8)
\]

Wu et al also found that the degradation of DMSO was significantly improved by increasing the concentration of H₂O₂ to 2.9 x10⁻¹ mol/l [16].

**Contribution of HO^* in photochemical process**

The mixture 3,5-DMP-goethite-H₂O₂ (10⁻⁴ mol/l - 1g/l - 5x10⁻³ mol/l) was irradiated at 365 nm in the presence of 1 % of tertbiobutanol used as a scavenger of HO^* radicals. An important effect of tertbiobutanol on the course of reaction is noticed (Fig.13). This result implies the involvement of HO^* radicals in the process of 3,5-DMP degradation.

**IV. CONCLUSION**

From the results, the following conclusion can be drawn:

The study of mixture 3,5-DMP-goethite in aqueous solution, was thermally stable (in the dark at room temperature) when the solution ages; there was neither DMP degradation nor reductive dissolution of goethite.

The photodegradation of 3,5-DMP at 365nm induced by goethite in the aqueous suspension was highlighted.
The photodegradation of 3,5-DMP in aqueous solution by using goethite has been studied in the pH range from 3.0 to 9.0 and there was no significant effect on the disappearance of 3,5-DMP.

The optimum dosage of goethite at the experimental condition was 1.5 g/l, it was found that adding more goethite inhibited the degradation of 3,5-DMP.

The non-intervention of HO• radicals has been proved and the formation of Fe(II) could not be detected in 3,5-DMP-goethite-UV system.

The degradation of 3,5-DMP was accelerated by adding H₂O₂ in 3,5-DMP-goethite suspension.

The optimal condition for DMP photodegradation has been substantially determined by adding 10⁻² g/l of hydrogen peroxide. The photodegradation of 3,5-DMP by this system involves the attack by HO• radicals.

Although H₂O₂ is essential to generate HO•, very high levels of H₂O₂ could reduce degradation of DMP because of scavenging effect.

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