The Oxidation Reaction Of 2-Nitroaniline In The Presence Of Some Supported Catalysts And Hydrogen Peroxide

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ABSTRACT

Different supported catalysts were studied in the presence of hydrogen peroxide as a method for oxidation of 2-nitroaniline which is a hardly degradable aromatic derivative. Among some transition metal ions, supported catalysts of (Ferro chloride) immobilized in silica gel is selected for detailed study. The effect of pH, the initial concentration of hydrogen peroxide, the amount of catalyst and the influence of temperature were...
studied. Optimum conditions for the wet oxidation of this organic pollutant were investigated. Experimental kinetic study was carried out, using visible spectrometry techniques and Chemical Oxygen Demand (COD). It was found from the observed data that the oxidation rate is a first order kinetics with respect to pollutant/s concentration (COD), hydrogen peroxide concentration and the amount of catalyst used per treated water volume. The reaction rate was dependant on the immobilized transition metal, temperature and the pH of the reaction media.

**Keywords:** Advanced oxidation method (AOM) - hardly oxidized impurities- 2-nitroaniline - supported catalyst-Transition metals-silica gel- \( \text{H}_2\text{O}_2 \).

**INTRODUCTION:**

Efficiency of water treatment is strongly dependent upon the method, pollutant nature and intended use of the water. (Bergendahl, J, et. al, 2004). In this context water treatment at the same industrial location is recommended for elimination of aromatic or aromatic derivatives organic water pollutants. The treated water could be reused (recycled) in addition to the environmental aspects and/or municipal regulations.

Advanced oxidation method (AOM) was used for clean oxidation of the organic pollutants, where mostly \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) are the final products of this oxidation technique. The main oxidizer in AOM is the hydroxyl free radical \( (\text{OH}^-) \) with a relatively high oxidation potential. (Hoigné J. and H. Bader., 1976.) Hydroxyl free radical is preferable over other halogen oxidants because of their by-products (Eric D. H., et al, 2002). The hydrogen free radical can be produced by different methods from the hemolytic dissociation of \( \text{H}_2\text{O}_2 \) in the presence of a homogeneous catalyst like \( \text{Fe}^{2+} \), (Rush J.D. et, el, 1985) or heterogeneous catalyst like \( \text{TiO}_2 \) with ultraviolet radiation (254nm), (Cunningham, J. et, el.,1994). Other methods including the presence of \( \text{O}_3 \) together with \( \text{H}_2\text{O}_2 \) (Hood E. D., et. al., 2002) can be also used to eliminate hardly oxidized organic pollutant. (Ronald J., et. el, 1997).

Many studies were conducted concerning the elimination of water pollutants by AOM such as phenol derivatives (Masende, Z.P.G., et. al., 2002 ), (Zacharia P.G. 2004), (aromatic pesticides (Pignatello, J.J, 1991), (Sun, Y. et. al., 1991), fuel additives, dyes (Ajeta, E. M., et. el, 1988) and some other pharmaceutical drugs (Hoigné J. and Bader H., 1983), where good results have been achieved.
In water treatment processes we focus on the method which is a cheap, clean and high oxidation potential for non biodegradable organic pollutants. Supported catalysts with the advantage of reusability were involved in some studies (Gemeay A. H., et. al. 1990), (Monfared H H, et. al. 2004), Monfared H H, 2004). Silica, alumina and cation exchange resins were investigated; where Co²⁺, Cu⁺¹, and Ni²⁺ complexes were involved. In cases of using supported catalysts, the ease of catalyst separation after the process, beside the efficiency of such systems gave a successful model of organic pollutant mineralization.

In this present oxidative a transition metal ion supported in silica gel is investigated for the oxidative mineralization of 2-nitroaniline which is studied as an organic pollutant. The effect of the process parameters such as H₂O₂ initial concentration, the amount of catalyst, pH and temperature are studied to determine optimum conditions of the oxidation of the investigated organic pollutants.

**EXPERIMENTAL:**

**Materials.**

2-nitroaniline, tetraethoxysilane, ethanol and H₂O₂ 35% w/w were analytical grade from (Akross, Belgium). Sulfuric acid 98 % was analytical grade of (Merck-Germany). Potassium dichromate K₂Cr₂O₇, Fe(NO₃)₂, FeCl₂, CoCl₂, Co(NO₃)₂, Cu(NO₃)₂, Potassium hydrogen phthalate (KHP) and MnO₂ powder analytical grade were analytical grade products from (B.D.H - England) and were used without further purification. Na₂HPO₄ was analytical grade, purchased from (Akross -Belgium). Water used was distilled to the level of 60 mg/L (TDS).

**Instruments.**

1. CECEIL/CE 1020 Spectrophotometer (CECEIL instrument, Cambridge – has been used for spectroscopic measurements.

2. A Hanna pH meter was used to adjust the pH of different solutions.

3. Thermo-stated water bath was used for fixing temperatures (±0.5°C) in the range of (10-50°C).
Methodology:

Supported catalyst was prepared by mixing ethanol with tetraethoxysilane in the proper molar ratio (3:1), a 6.0 M HCl aqueous solution is added drop by drop while stirring at room temperature (25°C), another aqueous solution of (1.0 M NH₄OH) is added in the same manner. 3.0 grams of the transition metal anhydride salt is added with continuous stirring until the mixture start to solidify, solid products were crushed, dried by heating at 100°C for 24 hrs. The products were sieved in the range of 40-100 mesh, the partition of this range powders were washed with distilled water and finally dried at 100°C for another 24 hrs.

Kinetic investigation was performed such that: In each experimental run, reaction vessels were prepared with the appropriate volume of the reaction solution, Dark glass reaction vessels were let opened to atmospheric air. Absorbance readings were taken at different intervals of the reaction time. Samples were read spectro-photometrically with 0.05 mg/L detection limit at 415 nm $\lambda_{\text{max}}$ which was determined experimentally. The isolation method (pseudo-first order method) was applied in all kinetic experiments, always $[\text{H}_2\text{O}_2]_0$ was relatively high with respect to the initial concentration of 2-trinitroaniline, the (observed rate constant) $k$ was the slope of the obtained straight line after plotting $(\ln C_0/ C)$ against time.

Standard COD solutions were prepared from the stock potassium hydrogen phthalate (KHP) solution from 50 to 900 (mg/ L). A calibration plot between COD (mg/L) and absorbance was obtained. Samples for chemical oxygen demand determination (COD) were taken at different time intervals, dealt with MnO₂ to decompose any remaining H₂O₂ present in order to prevent the interference of H₂O₂ with COD measurements, (Talinli-I; Anderson-GK, 1992). Filtration was performed to separate the MnO₂ catalyst. Standard method of WHO with detection limit of (50 mg/L) has been conducted for the determination of COD. (Walling, C.,1975). COD values were plotted against time.

Different reaction parameters such as (the amount of solid catalyst, initial concentrations of H₂O₂, temperature change and reaction pH) were investigated and the resultant rate constants were plotted against readings (or values) of each parameter to clarify the relation graphically.

H₂O₂ concentration through the reaction was followed by titration against KMnO₄ in acidic media and then plotted against time. The significance of that is to clarify if there is a side decomposition reaction of
the present H₂O₂ to produce H₂O and O₂ or not which clarifies if there is a 
hydrogen peroxide waste or not.

Alfa naphthol ethanolic solution was used to detect the absence of 
free Fe²⁺, Fe³⁺ ions in the reaction solution. KSCN solution was used also 
for the same propos.

Sodium hydrogen phosphate (Na₃HPO₄) 0.07M, Sodium dihydrogen 
phosphate, 0.01M  H₂SO₄ and 0.01M NaOH have been used to adjust the 
pH at the value between (3 and 11) for the reaction media.

RESULTS

The oxidation of 2-nitro aniline was studied in the presence of some 
supported transition metal salts and H₂O₂. The obtained results (Table 1) 
indicate that the oxidation reaction has different rates according to the 
transition metal salt used. The catalyst including FeCl₃ was selected for 
further detailed study due to its reactivity.

Table 1: Reusability and reactivity of supported catalysts in the 
oxidation of 2-nitro aniline as a water pollutant. [H₂O₂]₀ = 4000 mg/L, T= 
(30±0.5)°C, pH ~ 7.0, 0.5 g/L solid catalyst, no stirring.

<table>
<thead>
<tr>
<th>Metal salt</th>
<th>CoCl₂</th>
<th>Co(NO₃)₂</th>
<th>Cu(NO₃)₂</th>
<th>CoCO₃</th>
<th>FeCl₃</th>
<th>Free</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₁/₂, 1st reuse, hr.</td>
<td>105</td>
<td>68.0</td>
<td>55.0</td>
<td>117</td>
<td>05.4</td>
<td>659.0</td>
</tr>
<tr>
<td>T₁/₂, 2nd reuse, hr.</td>
<td>197</td>
<td>231</td>
<td>60.0</td>
<td>458</td>
<td>06.4</td>
<td>721.0</td>
</tr>
<tr>
<td>T₁/₂, 3rd reuse, hr.</td>
<td>576</td>
<td>766</td>
<td>173</td>
<td>631</td>
<td>31.1</td>
<td>778.0</td>
</tr>
</tbody>
</table>

The role of each H₂O₂, 2-nitroaniline and COD through the course of 
the oxidation was studied (Fig 1). Decay curve of H₂O₂ shows that there was 
no clear decomposition of H₂O₂ to produce H₂O and O₂ whereas 2-
nitroaniline and COD were clearly observed. The results shown in figure1 
demonstrate also the situation of 2-nitro aniline derivatives (partial 
oxidation intermediates).

The total concentration of partial oxidation products was obtained by 
subtracting the 2-nitro aniline % concentrations at different time intervals 
from the % COD (which is assumed to represent the total % of 2-nitro 
aniline and its products).
The Oxidation Reaction Of...

Figure 1: shows also that new compounds are formed by the beginning of the reaction. The total concentration of these compounds increases by time passes through a maximum and then starts to decrease as a result of further oxidation.

Effect of the initial concentration of H$_2$O$_2$ on the observed rate constant $k$ was studied under fixed conditions of temperature, pH, amount of solid supported catalyst and initial 2-nitroaniline concentration, by applying pseudo first order condition i.e high excess of H$_2$O$_2$ concentration (fig 2). The oxidation reaction rate was increasing directly by increasing [H$_2$O$_2$]$_0$. The straight line relation was observed between hydrogen peroxide concentration and $k_{obs}$. The reaction is a first order reaction with respect to [H$_2$O$_2$] up to some concentration.
Effect of the amount of catalyst on the observed rate constant $k$ was studied (fig 3). The reaction rate was increasing directly by increasing the amount of catalyst. The relation is a first order in the beginning of the studied range.

The dependent of the oxidation reaction on the temperature was studied in the range of (30-60°C). An inverse relationship was obtained between “ln $k$” and “1/T” where a straight-line plot has been obtained. This means that the reaction shows Arrhenius type behavior.

The oxidation of 2-nitroaniline was studied in buffer solution of different pH values. The obtained results are cited in Table 2.

**Table 2: Influence of pH on the oxidation reaction rate, (0.500g Catalyst, $[H_2O_2]=4000$ mgL$^{-1}$, reaction volume=250ml, T=30.0°C, no stirring)**

<table>
<thead>
<tr>
<th>pH</th>
<th>No buffer</th>
<th>pH 3.0</th>
<th>pH 5.0</th>
<th>pH 7.0</th>
<th>pH 9.0</th>
<th>pH 11.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k \times 10^7$, s$^{-1}$</td>
<td>378</td>
<td>7.8</td>
<td>13.1</td>
<td>30.6</td>
<td>39.9</td>
<td>39.0</td>
</tr>
</tbody>
</table>
The oxidation rate increases by the increasing of pH value which indicated that there is some accelerating rule of OH⁻ in the reaction mechanism.

**DISCUSSION**

The foregoing results show that the optimum conditions of oxidation process of 2-nitroaniline according to reactivity and reusability were obtained in the presence of FeCl₃, at the highest temperature, at higher initial concentrations of H₂O₂ and at increasing amounts of solid catalyst used. The un-buffered aqueous systems have higher rates of oxidation than buffered systems. It can be interpreted that H₂PO₄⁻¹, HPO₄²⁻ and PO₄³⁻ may act as free radical scavengers in some step in the reaction mechanism. Basic buffered systems had less inhibitional influences than acidic ones. The last result may be referred to some promotional effect of OH free radical in the oxidation reaction.

Partial oxidation intermediates start to appear at the beginning of the oxidation process, reach maximum and then show decreasing concentration values with time due to further oxidation or mineralization.

The decreasing of the oxidation products concentration means that the method is efficient for the derivatives.

A suggested mechanism, similar to Fenton’s mechanism which is shown bellow, may include the rule of OH free radical. In literature Fenton’s reaction mechanism was clearly discussed (Hoigné J. and Bader H., 1976, Hoigné J. and Bader H., 1983 Walling, C., 1975 and Walling, C., 1982).

**Suggested Oxidation Mechanism of 2-Nitroaniline**

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

2) \( \begin{array}{c}
\text{NH}_2 \\
\text{NO}_2 \\
\end{array} \rightarrow OH^- \rightarrow \begin{array}{c}
\text{NH}_2 \\
\text{NO}_2 \\
\end{array} + H_2O \)

3) \( \begin{array}{c}
\text{NH}_2 \\
\text{NO}_2 \\
\end{array} \rightarrow OH/\dot{OH} \rightarrow \begin{array}{c}
\text{COOH} \\
\text{COOH} \\
\end{array} + NO_3^- \)

4) \( \begin{array}{c}
\text{COOH} \\
\text{COOH} \\
\end{array} \rightarrow OH^- \rightarrow CO_2^- + H_2O \)

5) \( \begin{array}{c}
\text{CO}_2^- \\
\text{Fe}^{3+} \\
\end{array} \rightarrow \text{CO}_2 + \text{Fe}^{2+} \)
The present water treatment method is expected to be a cheaper method than other advanced oxidation methods including U.V. radiation or ozone or each in addition to H$_2$O$_2$. (Greenberg, A. E., 1992).

The method was also found environmentally clean since no further separation of homogeneous catalyst is needed. Solid particles of the catalyst are easily separated.

References: