Kinetic Model for the Oxidative Degradation of Aqueous p-Nitrophenol by Fenton’s Reagent

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This work investigates the oxidative degradation of p-Nitrophenol (PNP) pollutant in aqueous solution using an environmentally friendly advanced chemical oxidation (Fenton’s) process. Degradation experiments of PNP present in aqueous solutions in the concentration range between 3.597 x 10^{-3} moles/L (500 ppm) and 7.188 x 10^{-3} moles/L (1000 ppm) were carried out in a batch reactor. This work describes a mechanistic study for the reaction kinetics between the PNP and hydroxyl (•OH) radical. A model of mechanistic study was planned for degradation of an aqueous PNP in Fenton’s process and that model was used for the calculation of rate constant of the reaction showing the influence of hydroxyl radicals on PNP degradation. Around 96.80 % of degradation was achieved after 60 min of reaction time [700 ppm of PNP concentration, 0.1006 moles/L H_2O_2, 1.798 x 10^{-3} moles/L of Fe^{2+} catalyst and pH 3]. Our main purpose was to determine the reaction rate constant between PNP and the hydroxyl radical. The reaction rate constant for the reaction of PNP removal with 'OH radicals is estimated as 2.76 x 10^{10} L/mole-s.

Keywords: Fenton’s Process, p-Nitrophenol, Environmental Remediation, Hydroxyl Radicals, Rate Constants

Introduction
Wastewater discharged from various industries contains significant amount of the phenolic compounds which have been paid much attention due to their high toxicity and persistence in the environment\(^1\). PNP is also very toxic, mutagenic and carcinogenic and regarded as a priority pollutant by USEPA (United States Environmental Protection Agency)\(^2,3\). Thus, it is needed to minimize the impact of PNP on the aquatic biota. Several advanced oxidation processes (AOPs) using 'OH radicals could be known for PNP removal such as ozonation\(^4\), Electro-Fenton process\(^5,6\), microwave assisted catalytic oxidation\(^7\), photochemical treatment\(^8\) and for other phenolic compounds also\(^9,11\). AOPs include the generation of the highly reactive and short-lived hydroxyl radical (HO') species for the removal of organic compounds\(^12\). This report shows the development of the kinetic model for the oxidative degradation of PNP using ferrous salt and strong oxidant hydrogen peroxide.

Materials and method

Materials
Analytical grade chemicals were used in experimental runs. The solutions were synthesized with distilled water. The chemicals used were p-Nitrophenol (purity > 99 %, Lobachemie), H_2SO_4 (Merck), H_2O_2 (30 % w/w) (Merck), NaOH (Merck) and iron (II) sulphate. Instruments and analytical procedures: The pH of synthetically prepared PNP solution was measured with a MRC UK make, model: PH200 pH-meter. Unknown concentration of aqueous PNP was obtained with the measurement of absorbance value at a maximum wavelength of 350 nm and % degradation for PNP was calculated\(^13\). The measurement of the absorbance was taken with Shimadzu 1800 UV-Vis spectrophotometer by quartz-cell having a path-length of 1 cm. The form of the equation obtained from the curve of calibration for PNP was found to Y_{PNP} = 0.0251X_{PNP}+0.036; R^2=0.9916; where, Y_{PNP} is the absorbance value at maximum wavelength of 350 nm and X_{PNP} is value of the concentration of aqueous PNP in ppm.

Method
All experiments were carried out in a 500 mL glass beaker (batch reactor). The aqueous solution for PNP of known concentration was prepared synthetically in a round bottom flask and then its pH was maintained using 1 molar solution of sulphuric acid and 1 M NaOH solutions as and when required to bring it to 3. A known amount of iron (II) sulphate was added into the solution. Later on, the required quantity of oxidant
hydrogen peroxide was poured in the solution to generate \( \cdot \)OH radical (a strong oxidizing agent). Continuous stirring at 600 rpm was maintained using a Teflon-coated magnetic stirring bar for uniform mixing and the initial time of reaction start up was noted down. Samples were withdrawn from the reactor at every 2.5 min of time interval for 10 min and 10 min of time interval for next 50 min. This procedure was performed for 60 min of reaction time and samples were taken out for each corresponding intervals.

Experimental runs were taken placed at a room temperature of 25°C. Unknown aqueous PNP concentration at various times of the reaction was measured by getting the absorbance at maximum wavelength of 350 nm. Experimental runs were conducted in two parts. In part one, total six number of experiments (E-01, E-02, E-03, E-04, E-05 and E-06) was carried out by taking the initial concentration ratio (R) value to 20. The initial concentrations of PNP and oxidant was varied for each run as R equals to the ratio of the initial concentration of oxidant hydrogen peroxide to PNP. Ferrous ion concentration (Fe\(^{2+}\)) was fixed to 1.798 x 10\(^{-3}\) mol/L throughout the experiments. Molar concentration of PNP was taken into account and their corresponding oxidant concentration was calculated from initial concentration ratio (R). Values of initial concentration of PNP were 7.188 x 10\(^{-3}\), 6.469 x 10\(^{-3}\), 5.750 x 10\(^{-3}\), 5.031 x 10\(^{-3}\), 4.313 x 10\(^{-3}\) and 3.594 x 10\(^{-3}\) (mol.L\(^{-1}\)) for experiments E-01 to E-06, respectively. The corresponding calculated values for oxidant concentration were 0.1437, 0.1293, 0.1150, 0.1006, 0.0862 and 0.0718 (mol.L\(^{-1}\)). Likewise, in second part, experimental runs (E-07, E-08, E-09, E-10, E-11 and E-12) were performed, but by taking the value of initial concentration ratio to 10. In this case, the values of initial PNP concentration were similar. But the calculated values of [H\(_2\)O\(_2\)]\(_0\) concentrations were varied as the value of R changed to different value. Those values are 0.0718, 0.0649, 0.0575, 0.0503, 0.0431 and 0.0359 (mol.L\(^{-1}\)) respectively. The slope value - (d[B]/dt)\(_0\) was obtained from the experimental results from the experimental runs (E-01 to E-12) with the discussed operating conditions previously. Those values are 57.58 x 10\(^{-6}\), 59.64 x 10\(^{-6}\), 57.22 x 10\(^{-6}\), 54.04 x 10\(^{-6}\), 49.88 x 10\(^{-6}\) and 38.44 x 10\(^{-6}\) (mol/Ls) for E-01 to E-06, respectively at a value of R 20. For next six runs (E-07 to E-12) at R equals to 10, the values of slope are 64.64 x 10\(^{-6}\), 58.87 x 10\(^{-6}\), 53.95 x 10\(^{-6}\), 50.29 x 10\(^{-6}\), 45.92 x 10\(^{-6}\) and 38.85 x 10\(^{-6}\) (mol/Ls), respectively.

**Results and Discussion**

This model of reaction kinetics was formulated using the process of oxidative degradation for PNP by ferrous salt and oxidant hydrogen peroxide and used to find out the rate constant of reaction showing attack of the \( \cdot \)OH radicals on PNP.

**Oxidative degradation of PNP by Fenton’s process**

Oxidative degradation of PNP using the ferric salt and hydrogen peroxide were conducted by varying oxidant concentrations and PNP. Ratio for both the concentration (R= [H\(_2\)O\(_2\)]\(_0\)/ [B]\(_0\)) was kept constant among values 10 and 20. Various operating conditions with [Fe\(^{2+}\)]\(_0\) 1.798 x 10\(^{-3}\) mol/L are discussed previously. There was an increment in the rate of the degradation -(d[B]/dt) when dose of [H\(_2\)O\(_2\)]\(_0\) was increased. Figure 1 indicates the changes of concentration of PNP Vs reaction time for experimental runs conducted to R value 20. There was a decrement for PNP concentration by effect of the generated hydroxyl radicals. Figure 1, Oxidation mechanism of PNP in Fenton’s process is a complex phenomenon. Whole set of reactions for its mechanism consists of the generation of the hydroxyl radicals i.e., OH\(^-\) from the reaction of hydrogen peroxide with ferrous salt (Fenton’s reagent) in acidic aqueous medium (pH~3) having rate constant \( k_1 \)\(^{14}\). The produced hydroxyl radicals further reacts with the PNP in order to oxidize it to simpler and harmless molecules of reaction rate constant \( k_2 \)\(^{15}\). Moreover, the scavenging effect of hydroxyl radicals was reported with the hydrogen peroxide and ferrous ions. The perhydroxyl radicals and water were produced with H\(_2\)O\(_2\) (rate constant \( k_3 \)). The scavenging action of OH\(^-\) radicals with ferrous ion gives rise to the generation...
of ferric ion and hydroxyl ions (rate constant \( k_3 \))\(^1\). There might be the two ways to specify the feasibility of ferric ion\(^1\). The reaction of ferric ion with hydrogen peroxide results in the generation of ferrous ions and hydrogen ions (H\(^+\)) (\( k_5 \))\(^1\). When ferric ions react with perhydroxyl radicals, there could be the generation of O\(_2\) along with ferrous ions and hydrogen ions (H\(^+\)) with rate constant \( k_6 \)\(^1\). The reactions with rate constant \( k_1 \) to \( k_4 \) indicate generation and the utilization of the hydroxyl radical (OH•) and thus, those reactions were used to determine the overall rate for the generation of hydroxyl radicals (Eq. No. 01):

\[
\frac{d[HO^*]}{dt} = k_1[H_2O_2][Fe^{2+}] - k_2[B][HO^*] - k_3[H_2O_2][HO^*] - k_4[Fe^{2+}][HO^*] \quad \text{(1)}
\]

When the reaction reaches to a state of chemical equilibrium (steady state condition for the hydroxyl radicals), the quantity \( \frac{d[HO^*]}{dt} \) equals to zero. Hence, the concentration of the hydroxyl radicals on simple rearrangement of above equation can be written in the form:

\[
[HO^*] = \frac{k_1[H_2O_2][Fe^{2+}]}{k_2[B]+k_3[H_2O_2]+k_4[Fe^{2+}]} \quad \text{(2)}
\]

Moreover, the rate equation for the degradation of PNP for its removal can be expressed in the form \( \frac{d[\text{PNP}]}{dt} = k_2[B][HO^*] \). Now, Value of [HO\(^*\)] radicals from Eq. No. 02 was substituted to this form. The further rearrangement of the obtained equation gives rise to the following equation in the form of \( Y = mX + C \):

\[
\frac{[\text{PNP}]_0[H_2O_2]_0}{[B]_0} = \frac{k_2+k_3R}{k_1k_2[Fe^{2+}]_0}[B]_0 + \frac{k_4}{k_1k_2} \quad \text{(3)}
\]

The above equation (03) was used to solve the kinetic rate constant between PNP and oxidant species i.e., hydroxyl radicals (\( k_2 \)) and the rate constant \( k_1 \). It includes four rate constants (\( k_1, k_2, k_3 \) and \( k_4 \), respectively). The value of rate constant \( k_3 \) was found by Shen et al. (2017), being \( k_3 = 3.3 \times 10^7 \) L/mole-sec\(^2\) and value of \( k_4 \) was found by Fischbacher and Sonntag (2017) as \( 3.2 \times 10^8 \) L/mole-sec\(^2\). Say, \( Y = \frac{[\text{PNP}]_0[H_2O_2]_0}{[B]_0} \), \( X = [B]_0 \) and \( R = \frac{[H_2O_2]_0}{[B]_0} \) = ratio of the concentrations of oxidant and PNP at initial operating conditions. According to above equation (03), a plot of \( Y \) Vs \( X \) must give straight line for each series of experimental runs keeping same \( R \). In addition, \([Fe^{2+}]_0\) kept constant throughout experiments for degradation of the p-NP. The value of slope form plot can be written as: \( \text{slope} = \frac{k_2+k_3R}{k_1k_2[Fe^{2+}]_0} \). In this equation of slope, the values of the rate constant \( k_1 \) and \( k_2 \) is unknown. Thus, if slope can be calculated for the experiments performed with \( R \) equals to 20, one will have two simultaneous equations to solve. Figure 2 reports the plots for the calculation of rate constant \( k_2 \) in PNP degradation at \( R = 20 \) and 10 respectively (Figure 2 (a) for \( R \) value 20 and Figure 2 (b) for \( R \) value 10). Parameters needed for calculation of left hand side term of equation (03), including the value of \( \frac{(-d[B])}{dt}_0 \) are given in earlier discussion. Implementing the least square regression analysis, the slope was calculated to a value 2222.6 for \( R = 20 \) and to 1069.7 for \( R \) equals 10. The calculated values of \( Y \) are 16.5387, 14.0248, 13.0007, 10.7009, 9.50031 and 8.51303 for given values of \( X \) at a varying concentration of PNP from 500-1000 ppm at \( R \) value to 20. Now from the equation (03), we have, \( \frac{k_2+k_3R}{k_1k_2[Fe^{2+}]_0} = \frac{k_2+3.3 \times 10^7+20}{k_1k_2(1.798 \times 10^{-5})} = 2226.2 \) and \( \frac{k_4}{k_1k_2} = \frac{3.2 \times 10^8}{k_1k_2} = 0.0454 \). The value obtained for \( k_2 \) was found to be \( 2.76 \times 10^{10} \) L/mol-s and for \( k_1 \) was \( 0.2553 \) L/mol-s. This value of rate constant for reaction showing attack of •OH radicals on PNP is usually found in the range of \( 10^8-10^{10} \) L/mol-s 22, 23. Attempts were also taken to find out the rate constant \( k_2 \) keeping all other experimental conditions as same and for a value of \( R \) to 10. The calculated values of \( Y \) are 7.984, 7.131, 6.128, 5.032, 4.5 and 4.4 for given values of \( X \) at a varying concentration of PNP from 500-1000 ppm. A similar calculation as above is required to calculate the value of \( k_2 \) and \( k_1 \), Fig. 2 — Calculation of rate constant \( k_2 \) in oxidative degradation of PNP in Fenton’s process for the initial concentration ratio (R) equals to (a) 20 (b) 10
respectively at R value to 10. Figure 2 The hydroxyl reaction rate constant ($k_2$) was found to be $5.74 \times 10^9$ L/mol-s which is well in range and $k_1$ is $0.5801$ L/mol-s. Figure 3 shows the patterns obtained for reaction profiles at different initial concentrations of PNP from 500-1000 ppm and the % degradation of PNP with respect to time by Fenton’s reagent. It was observed that the % degradation of PNP was 93.71% at 500 ppm concentration of PNP and 94.34% at 700 ppm concentration for 60 min of reaction time. There was no significant change for the % degradation of PNP up to 700 ppm concentration. But, beyond 700 ppm, there was a decrease in the value of % degradation of PNP. It was 90.93% for 800 ppm, 86.64% for 900 ppm and 82.34% for 1000 ppm concentration of PNP.

Conclusions

Fenton’s process can be applied effectively for the oxidative degradation of the phenolic derivatives found in an industrial wastewater. Fe$^{2+}$ plays a crucial role is regenerated throughout the experiments. As an outcome, oxidant hydrogen peroxide is the limiting reactant in the Fenton process. Even though the chemistry of the Fenton’s process consists of a slightly complicated mechanism, an attempt has been made to study the mechanistic model of the reaction kinetics for the degradation of aqueous phenolic compound PNP. The main purpose of this model is to determine the rate constant between PNP and $^{1}$OH radicals. The value obtained for $k_2$ (kinetic reaction rate constant between hydroxyl radicals and PNP) is $2.76 \times 10^{10}$ L/mol-s.

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References