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

Dr. Hartany khaled *
Dr. El-sousy Khaled *
Dr. El-Ailah Hesham *
Dr. Rabah ahmed *

الملخص

في هذه الدراسة تم تفحص فاعلية بعضاً من العوامل الحفازة المدعمة في وجود فوق أكسيد الهيدروجين كطريقة لأكسدة 2-نيتروأنيلين كأحد الملوثات المستعصية على الأكسدة البيولوجية.

من بين عدة أملاح لعناصر انتقالية تم اختيار كلوريد الحديدوز المدعم في جل السيليكا للدراسة التفصيلية، وبهذا الصدد تم إجراء دراسة حركية التفاعل والعوامل المرتبطة بذلك، منها دراسة تأثير كل من الأس الهيدروجيني و التركيز الابتدائي لفوق أكسيد الهيدروجين وكمية العامل الحفاز ودرجة الحرارة. وركزت الدراسة على محاولة الوصول إلى الظروف المثلى للتفاعل. بناء على النتائج العملية، وجد أن التفاعل من الدرجة الأولى بالنسبة لكل من تركيز المادة الملوثة وتركيز فوق أكسيد الهيدروجين وكذلك كمية العامل الحفاظ. و تأثرت حركية التفاعل بطبيعة العنصر النتقالي داخل العامل الحفاز وبالنسبة لتأثير درجة الحرارة فلقد وجد التفاعل من نوع أرهينيوس وكان التأثير ايجابياً برفع الأس الهيدروجيني. وإجمالا وجدت هذه الطريقة ناجعة وفعالة وكذلك اقتصادية في تنقية المياه الصناعية من الملوثات العضوية المستعصية.

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

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*Department of Chemistry, Al-Aqsa University, Gaza, Palestine.
E-mail: khasousy@yahoo.com.

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-H_2O_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 CO_2 and H_2O are the final products of this oxidation technique. The main oxidizer in AOM is the hydroxyl free radical **(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 ***(Œric D. H., et el, 2002).*** The hydrogen free radical can be produced by different methods from the hemolytic dissociation of H_2O_2 in the presence of a homogeneous catalyst like Fe^{2+}, (Rush ***J.D. et, el, 1985)*** or heterogeneous catalyst like TiO_2 with ultraviolet radiation (254nm), ***(Cunningham, J. et, el.,1994).*** Other methods including the presence of O_3 together with H_2O_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 (Aieta, 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, el. 1990), (Monfared H H, et. el. 2004), Monfared H H, 2004). Silica, alumina and cation exchange resins were investigated; where Co^{2+}, Cu^{+1}, and Ni^{2+} 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 H_2O_2 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 H_2O_2 35% w/w were analytical grade from (Akross, Belgium). Sulfuric acid 98 % was analytical grade of (Merck-Germany). Potassium dichromate $K_2Cr_2O_7$, $Fe(NO_3)_2$, $FeCl_2$, $CoCl_2$, $Co(NO_3)_2$, $Cu(NO_3)_2$, Potassium hydrogen phthalate (KHP) and MnO_2 powder analytical grade were analytical grade products from (B.D.H - England) and were used without further purification. Na_2HPO_4 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 ($\pm 0.5^0C$) in the range of ($10-50^0C$).

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 (25^0C), another aqueous solution of (1.0 M NH_4OH) 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 100^0C 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 100^0C 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 λ_{max} which was determined experimentally. The isolation method (pseudo-first order method) was applied in all kinetic experiments, always $[H_2O_2]_0$ 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 MnO_2 to decompose any remaining H_2O_2 present in order to prevent the interference of H_2O_2 with COD measurements. ***(Talinli-I; Anderson-GK, 1992).*** Filtration was performed to separate the MnO_2 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 H_2O_2, 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.

H_2O_2 concentration through the reaction was followed by titration against $KMnO_4$ 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 H_2O_2 to produce H_2O and O_2 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 Fe^{2+}, Fe^{3+} ions in the reaction solution. KSCN solution was used also for the same propos.

Sodium hydrogen phosphate (Na_2HPO_4) 0.07M, Sodium dihydrogen phosphate, 0.01M H_2SO_4 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 H_2O_2. The obtained results (Table 1) indicate that the oxidation reaction has different rates according to the transition metal salt used. The catalyst including $FeCl_3$ was selected for further detailed study due to its reactivity.

Table1: Reusability and reactivity of supported catalysts in the oxidation of 2-nitro aniline as a water pollutant. $[H_2O_2]_o$ = 4000 mg/L, T= (30±0.5) ^{0}C, pH ~ 7.0, 0.5 g /L solid catalyst, no stirring.

Metal salt	**$CoCl_2$**	**$Co(NO_3)_2$**	**$Cu(NO_3)$**	**$CoCO_3$**	**$FeCl_3$**	**Free**
$T_{1/2,}$ 1^{st} reuse, hr.	105	68.0	55.0	117	05.4	659.0
$T_{1/2,}$ 2^{nd} reuse,hr.	197	231	60.0	458	06.4	721.0
$T_{1/2,}$ 3^{rd} reuse,hr.	576	766	173	631	31.1	778.0

The role of each H_2O_2, 2-nitroaniline and COD through the course of the oxidation was studied (Fig 1). Decay curve of H_2O_2 shows that there was no clear decomposition of H_2O_2 to produce H_2O and O_2 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).

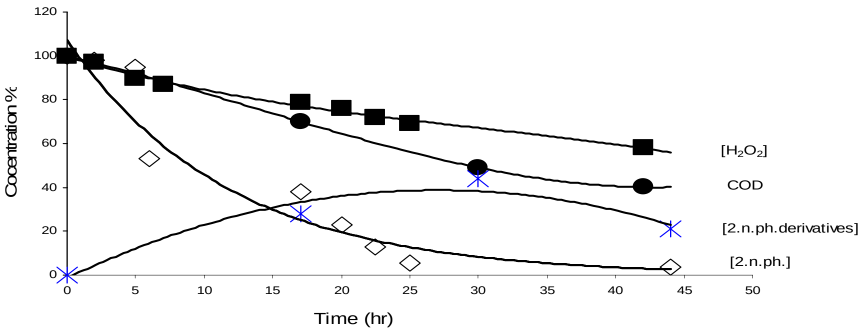


Fig. 1. The rule of H_2O_2, COD, picric acid and2-nitro phen derivatives in the oxidation reaction. [H_2O_2]o = 4000 mg/L, [2-nitro pheno]$_0$=600mg/L, T= (30±0.5)^{0}C, pH = 7.0, 0.50 g /L solid catalyst, no stirring.

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.

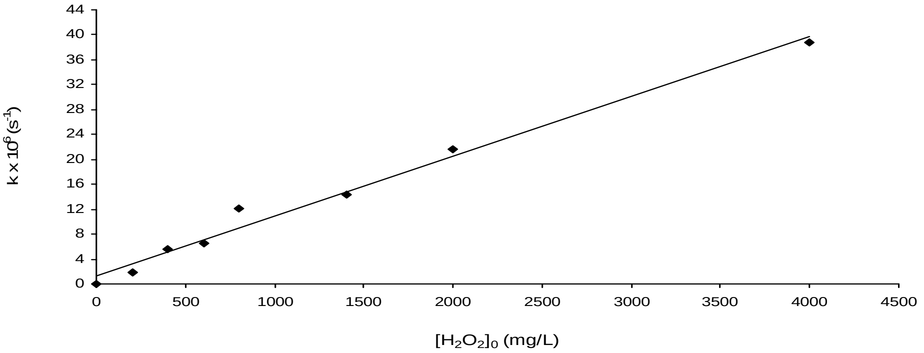


Fig. 2. Effecct of the initial concentration of H_2O_2 on the reaction kinetics, (0.5g Catalyst, T=30^{0}C, reaction bulk volume=250 ml , [2-ntro phenol]$_0$ = 80mg/L).

Effect of the initial concentration of H_2O_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_2O_2 concentration (fig 2). The oxidation reaction rate was increasing directly by increasing [H_2O_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_2O_2] up to some concentration.

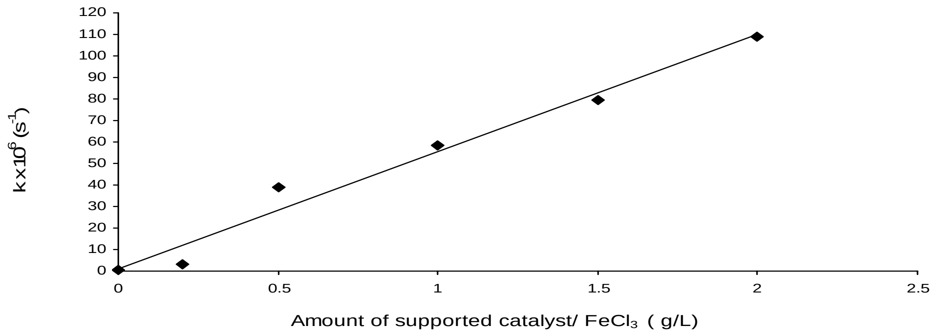


Fig. 3. Effect of the amount of catalyst on the oxidation rate constant, T=30^{0}C, $[H_2O_2]0$=4000 mg/L, [2-nitro phenol]$_0$= 80 mg/L.

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^{0}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.

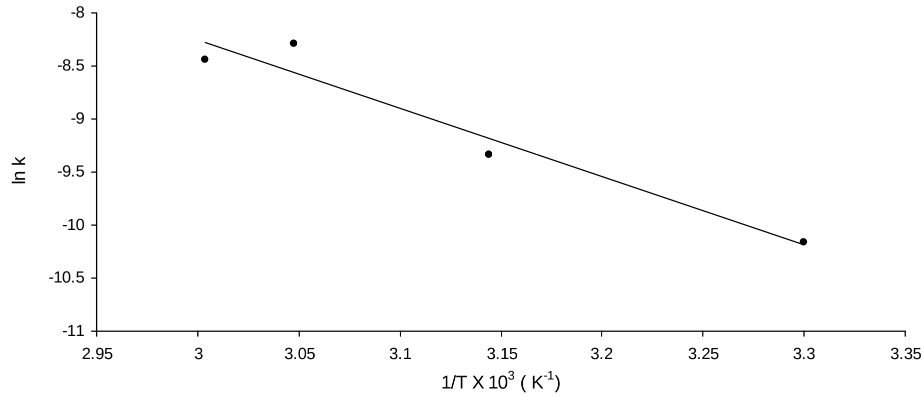


Fig. 4. Plot of lnk vs. 1 / T for the catalytic oxidation of 4-nitro phenol in the presence of H_2O_2, 0.500g Catalyst , $[H_2O_2]$=4000 mg/L , sample volume=250ml.

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, $[H_2O_2]_0$ = 4000 mgL^{-1}, reaction volume=250ml, T=30.0^{0}C, no stirring)

pH	No buffer	pH 3.0	pH 5.0	pH 7.0	pH 9.0	pH 11.0
k x10^7, s^{-1}	378	7.8	13.1	30.6	39.9	39.0

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

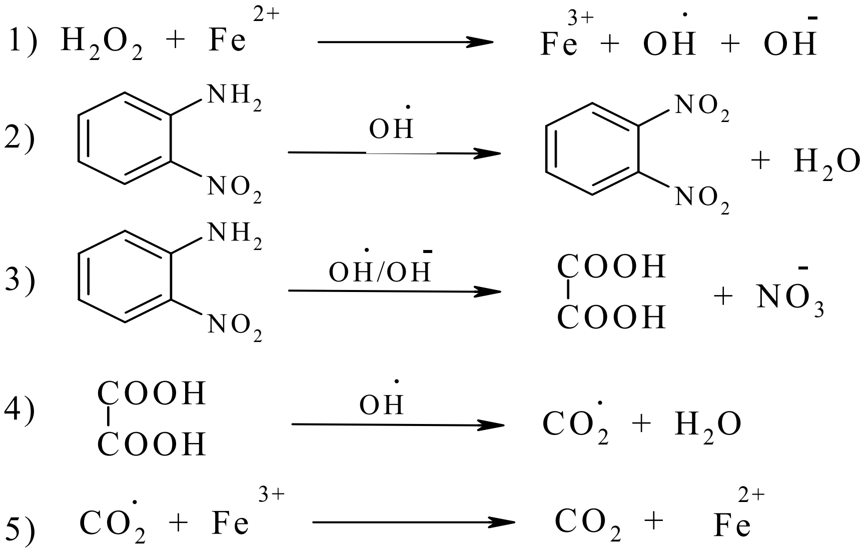
The foregoing results show that the optimum conditions of oxidation process of 2-nitroanline according to reactivity and reusability were obtained in the presence of $FeCl_3$, at the highest temperature, at higher initial concentrations of H_2O_2 and at increasing amounts of solid catalyst used. The un-buffered aqueous systems have higher rates of oxidation than buffered systems. It can be interpreted that $H_2PO_4^{1-}$, HPO_4^{2-} and PO_4^{3-} 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 starts 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



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_2O_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.

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