

Elimination of Organic Pollutants using Supported Catalysts with Hydrogen Peroxide

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Abstract

Picric acid (2, 4, 6, tri-nitro-phenol), which is a hardly-oxidized aromatic compound, was studied as a water pollutant. Different supported catalysts were tested in the presence of hydrogen peroxide as a method for elimination of the organic pollutant from waste water. Among some transition metal ions, Cobalt (II) nitrate immobilized in silica gel was selected for detailed study. The effect of pH, initial concentration of hydrogen peroxide, amount of catalyst, and temperature were studied to find the optimum conditions for the wet oxidation of this organic pollutant. Experimental kinetic study was conducted using visible spectrophotometric techniques and chemical oxygen demand (COD). Supported catalysts demonstrated experimentally some reusability. The present data show that the rate of oxidation is a first order with respect to pollutant concentration, hydrogen peroxide concentration and the amount of catalyst used. The dependence of the reaction rate on the nature of the immobilized transition metal, temperature, and pH of reaction media has also been discussed.

Keywords: Picric acid; Chemical oxygen Demand; Supported catalyst; Hydrogen peroxide; Advanced Oxidation Method.

Introduction

For hardly oxidized organic water pollutants, mostly from industrial sources, water treatment at the same industrial location is recommended. The treated water could be reused in addition to the environmental aspects and/or municipal regulations. Efficiency of water treatment is strongly dependent upon the method, pollutant nature, and intended use of the water.^[1]

Advanced oxidation method (AOM) means an environmentally-clean oxidation method for the organic pollutants in water. Mostly, CO₂ and H₂O are the products of the process. The main oxidizer in AOM is the hydroxide-free radical (OH[•]) with a relatively high oxidation potential.^[2] Hydroxyl free radical is preferable over other halogen oxidants because of their by-products.^[3] The OH free radical can be produced by different methods from the hemolytic dissociation of H₂O₂. In the presence of a catalyst like Fe²⁺,^[4] TiO₂ with ultraviolet radiation (254nm),^[5] or other methods including the presence of O₃ together with H₂O₂ and (H₂O₂ /UV/O₃ method) can be also used to eliminate organic pollutants.^[6]

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Many studies were conducted concerning the elimination of the hardly-oxidized water pollutants such as phenol derivatives, ^[7, 8] aromatic pesticides, ^[9, 10] fuel additives, dyes, ^[11] and some other pharmaceutical drugs. ^[12]

In this work, a transition metal salt supported in silica gel was investigated for producing hydroxyl free radicals from H₂O₂ in a practical rate, that is supposed to bypass the process of catalyst separation after water treatment whether homogeneous such as Fe²⁺ or very fine particles like TiO₂.^[4,5] The present method is supposed to save energy since no UV or ozone source is needed, also no high temperature is needed. Picric acid (2,4,6 tri-nitro-phenol) was taken as the model pollutant under investigation since it is one of the most oxidation persistent organic pollutants.^[13, 14]

An interpretation of the results is introduced, and the economical side is discussed.

Experimental

Different metal salts were tested concerning the resultant catalyst activity and reusability. Co (NO₃)₂ was selected among few tested salts. The effects of the reaction parameters such as H₂O₂ initial concentration, amount of catalyst, pH and temperature on the kinetics of oxidation of picric acid were investigated. Optimum conditions were followed.

Materials

Picric acid (2, 4, 6-trinitro phenol) was locally prepared by the nitration of phenol.^[15] Tetraethoxysilane, ethanol, and H₂O₂ (35% w/w) were obtained from Akross, Belgium. Sulfuric acid (96%) was purchased from Merck, Germany. The other materials used were also analytical grade products. Distilled water was used (TDS ≈ 60 mg/L).

Preparation of supported catalyst

Supported catalysts were prepared by mixing ethanol with tetraethoxysilane in the A of (3:1) ratio. A 0.60 M HCl aqueous solution was added drop by drop (using a burette) at 25°C, using magnetic stirrer. An aqueous solution of (0.10 M), NH₄OH was added in the same manner, and then the mixtures were stirred for further 30 minutes. The amount of 3.0 grams of the transition metal salt is added with continuous stirring until the mixtures start to solidify. The beakers of the products were covered by tinny porous aluminum foils and left for 48 hrs. Solid products were then crushed, further dried by heating at 100°C for another 24 hrs. The products were sieved in the range of 40-100 mesh. Portions of this range were taken only, and washed with distilled water repeatedly for 5-6 times and finally dried at 100°C for another 24 hrs.

Kinetics

The reaction solutions were prepared using water, picric acid and H₂O₂ standard solutions; the supported catalyst is finally added to start the reaction immediately, all quantities were chosen according to the desired run. Samples were taken at different time intervals. The decrease in the absorbance of picric acid as a function of time at 355 nm

and 25 ± 0.5 °C using CECEIL 1020 UV/ VIS spectrophotometer was recorded. 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 picric acid initial concentration, the observed rate constant k was obtained from the slope of the plotting of $(\ln C_0/C)$ Vs time. The same procedure was employed to study the effect of initial concentration of H_2O_2 , amount of supported catalyst, temperature, and pH.

Standard (Chemical Oxygen Demand) 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. COD value was plotted against time. Samples for COD were taken at different time intervals, treated with MnO_2 to decompose any remaining H_2O_2 present in order to prevent the interference of H_2O_2 with COD.^[16] MnO_2 catalyst was separated by filtration. Standard method of the world health organization (WHO) has been conducted for the determination of COD.^[17] The method depends on the complete oxidation of any organic content using K_2CrO_7 in concentrated sulfuric acid media at 150 °C temperature in closed Pyrex tubes for 150 minutes, then reading the Cr^{3+} ions spectrophotometrically at 600 nm. Phosphate buffer with HCl and NaOH were used to control the pH value which was adjusted using a Hanna pH meter.

Results

The influence of each kinetic parameter was investigated. The results summarized in (table 1) show that the oxidation reaction had different rates according to the transition metal salt used depending on $t_{1/2}$ values, among the other tested salts the best supported catalyst was $Co(NO_3)_2$ due to reactivity and reusability. The catalyst including $Co(NO_3)_2$ was selected for this detailed study. The reason of the observed, non-perfect reusability is thought to be the partial poisoning of the catalyst system or/and the partial leaching of the transition metal ions into the bulk (escaping from the surface of the catalyst).

Table 1. Reusability (1st, 2nd, 3rd and 4th reuse) of the supported catalysts Vs half lives in hours of degradative oxidation of picric acid in water. 100.0 mg/L picric acid, (25 ± 0.5) °C. $[H_2O_2]_0 = 5000$ mg/L, pH ~ 7.0, 0.500 g/L solid catalyst, no stirring).

Metal salt	$CoCl_2$	$Co(NO_3)_2$	$Cu(NO_3)_2$	$CoCO_3$	$FeCl_2$	Free
$T_{1/2}$, 1 st reuse, hr.	12.90	05.80	10.13	11.24	59.01	114.0
$T_{1/2}$, 2 nd reuse, hr.	14.82	12.80	06.80	12.50	61.00	139.0
$T_{1/2}$, 3 rd reuse, hr.	11.90	12.05	08.71	20.90	48.00	182.0
$T_{1/2}$, 4 th reuse, hr.	13.63	13.53	11.49	28.25	65.80	198.0

Decreases in the concentrations of H_2O_2 , picric acid, and COD were clearly observed. The results shown in (figure 1) also demonstrate the situation of the partial oxidation products of the picric acid. From the slight decay curve of H_2O_2 it may be

observed that mostly H_2O_2 decomposes into OH free radicals and it has no clear side decomposition to produce H_2O and O_2 . Concentration of partial oxidation products, which may be called derivatives of picric acid, was obtained by subtracting the picric acid concentrations at different time intervals in mg/l from the total COD in mg/l (which is assumed to represent the total concentration of picric acid and its derivatives). (figure 1) shows that new intermediate compounds start to form at the beginning of the reaction, the concentration of these compounds increased gradually by time, arriving to a maximum, and starts to decrease as a result of further oxidation. It is thought that detailed identification of the possible derivatives is not necessary since these derivatives are also degradable intermediates.

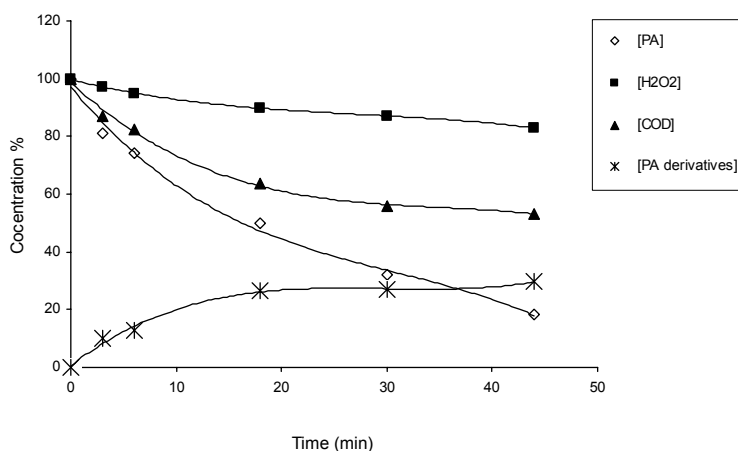


Figure 1. The rule of H_2O_2 , COD, picric acid and picric acid derivatives in the oxidation reaction. $[\text{H}_2\text{O}_2]_0 = 5000$ ppm, $[\text{Picric Acid}]_0 = 500$ mg/L, $T = (25 \pm 0.5)$ °C, $\text{pH} = 7.0$, 0.5 g /L solid catalyst, no stirring.

Effect of the initial concentration of H_2O_2 on the rate constant k was studied under the same other conditions. (Figure 2) shows that the observed reaction constant is increasing by increasing H_2O_2 concentration up to some level, and a plateau started to form at 500 mg/l.

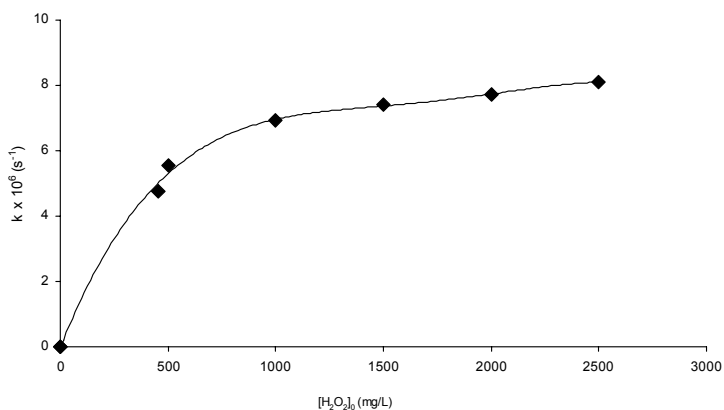


Figure 2. Effect of the initial concentration of H_2O_2 on the reaction kinetics, (0.5 g Catalyst, $T = 25^\circ\text{C}$, reaction bulk volume = 500 ml, $[\text{picric acid}]_0 = 100$ mg/L)

The effect of the amount of catalyst on the observed rate constant k was studied, from the results in (figure 3), it can be observed that the reaction rate increased with increasing the amount of catalyst up to 1 g /l then a plateau is obtained. From this plot, it is clear that the rate is a first order at low amounts of catalyst and is a zero order at relatively high amounts under the same reaction conditions.

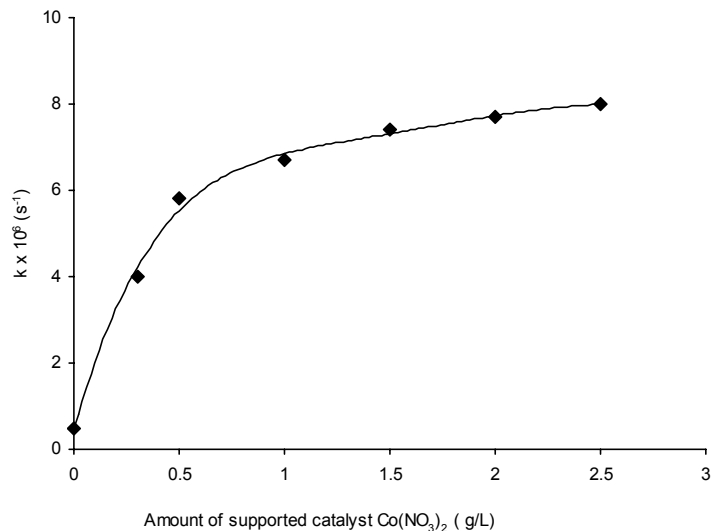


Figure 3. Effect of the amount of catalyst on the oxidation rate constant, $T=25^\circ\text{C}$, $[\text{H}_2\text{O}_2]_0=2000$ mg/L, $[\text{picric acid}]_0=100$ mg/L .

The influence of temperature on the oxidation reaction was studied in the range of $(10-45^\circ\text{C})$. This range is expected to cover the temperature variation of polluted water through different processes. It is clear in (figure 4) that a direct relationship was obtained between $\ln k$ and $1/T$, where a straight-line was obtained; meaning that the reaction has Arrhenius type behavior.

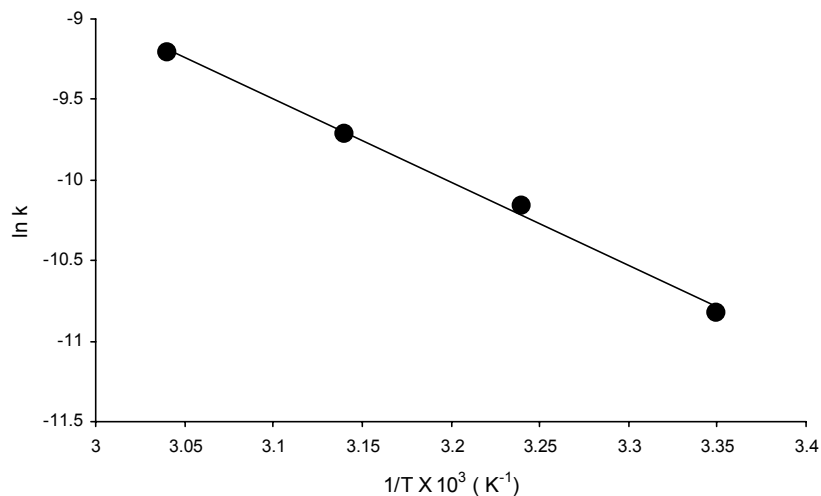


Figure 4. Plot of $\ln k$ vs. $1/T$ for the catalytic oxidation of picric acid in the presence of H_2O_2 , 1.5g Catalyst , $[\text{H}_2\text{O}_2]=2000$ mg/L , sample volume=500ml

The effect of pH on the oxidation of picric acid was examined. The reaction at three different values of pH 5.0, 7.0 and 9.0, in addition to a non buffered system was studied under the same reaction conditions (*1.5g Catalyst, $[H_2O_2] = 2000 \text{ mgL}^{-1}$, reaction volume=500mL, $T=25.0^\circ\text{C}$, no stirring*). The obtained rate constants were respectively 4.9, 4.6, 4.4 and $9.8 \times 10^{-5} \text{ s}^{-1}$. The rate constant values show that the oxidation is clearly inhibited by buffering.

Discussion

From the demonstrated results, it can be arrived that the advanced oxidation method, including supported catalyst, is an efficient method for the elimination of hardly oxidized aromatic compounds such as picric acid. The catalyst was efficient in the second, third, and fourth reuse with some percent decay in this efficiency due to poisoning.

The partial oxidation products started to appear at the beginning of the oxidation process, reaching steady concentration, and expected to show decreasing concentration values with time due to consequent oxidative degradation. The persistent color decay of picric acid followed by COD decay due to oxidation is the evidence of this method efficiency.

According to the above results, $\text{Co}(\text{NO}_3)_2$ supported catalyst was preferable among the other studied transition metal salts for its relative higher reactivity and reusability. Compared with aqueous $\text{Co}(\text{NO}_3)_2$, which was not reactive at all when tested in this research, different bonding were formed by the immobilization of Co^{2+} ion in silica that seems to serve the reaction by causing the dissociation of H_2O_2 into HO free radical. The basic aqueous systems had higher rates of oxidation than acidic systems that could be due to the role of OH^- in reaction step. The reaction is slower generally in buffered systems; it is thought that the presence of H_2PO_4^- , HPO_4^{2-} or PO_4^{3-} inhibited the oxidation process on the bases of scavenger influence of PO_4^{3-} , HPO_4^{2-} and H_2PO_4^- for OH free radicals.

The present water treatment method is expected to be a cheaper method than other advanced oxidation methods including U.V. radiation, ozone or each in addition to H_2O_2 , since no electric power is needed to produce UV radiation or ozone.^[18] This present method -where no electric energy is needed- is expected also to be cheaper than methods which entail very high temperatures.^[19]

The current method is clean since no further separation of homogeneous catalyst is needed. No free metal ions were found when tested by 2-nitronaphthol.^[20,21] The supported catalyst can be involved in a continuous type system (reactor) for industrial waste water treatment for a long time since the catalyst is reusable. The optimum conditions for a real reactor can be designed on the bases of this study results such as H_2O_2 concentration which should be equivalent to the COD of the pollutant/s, the amount of catalyst should be in the first order period with respect to

the flow rate of the treated water. Temperature is an activation parameter so the higher the temperature the more efficient is the system and so on.

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