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Degradation of 2,4-Dinitrophenol by Photo Fenton Process

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2,4-Dinitrophenol (2,4-DNP) is a priority pollutant that may enter environment from petrochemical, textile and dye stuff manufacturing. Due to ineffectiveness of biological processes in treatment of such a waste, advanced oxidation process (AOP) as a promising alternative has been introduced. Photo-Fenton process is an advanced oxidation process that we considered in this study. An 8.3 L cylindrical photo reactor equipped with 2 UV lamps, these two lamps with nominal power of 110 W emits radition at 254 nm. The photon flux of the reactor was 12 μ Einstein S^{-1}. The results show 100 % disappearance of the 2,4-DNP during 40 min reaction time was obtained when H_2O_2 concentration of 75 mg L^{-1} was used. The elimination of all 2,4-DNP was combined with 21 % TOC removal. Also raising the initial H_2O_2 concentration direct to more oxidation of the contained organic matter. 50 % of COD conversion was obtained when 75 mg L^{-1} H_2O_2 was used, while it reached to 61 % when H_2O_2 was increased to 100 mg L^{-1}. Increasing the initial Fe^{2+} from 45 to 75 mg L^{-1} direct to increase 2,4-DNP degradation from 54 up to 87 %. However, it was noticed that, the reaction reach a concentration at which catalytic reaction effect is weak and addition of the iron salt above this point (75 mg L^{-1}) did not improve the degradation, but rather perceptible decrease in the degradation rate occurred.

Key Words: Advanced oxidation, Degradation, 2,4-Dinitrophenol, Photo fenton.

INTRODUCTION

Nitrophenols (NP) are among the most widely used industrial organic compounds. They are frequently used as raw materials or intermediates in the manufacture of explosives, pharmaceuticals, pesticides, pigments, dyes, wood preservatives and rubber chemicals. These compounds pose significant health risks since they are carcinogenic. The US Environmental Protection Agnecy has listed 2-nitrophenol (2-NP), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (2,4-DNP) as priority pollutants and recommeneded restricting their concentrations in natural waters to < 10 ng/L [1].

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It may enter the environment from industrial discharges (nitrobenzene plant, textile and dye stuff manufacturing), spills or possibly as a breakdown product of certain pesticides containing 2,4-DNP moieties. 2,4-Dinitrophenol which exists as a yellowish crystalline solid, is soluble in water (5.6 g L^{-1} at 18 ºC) and is volatile with steam and it has strong acid properties, with pKa value of 4.03[2].

Due to its low molecular weight and toxic nature, the conventional chemical coagulation method and the biological treatment become ineffective. Hence, the advanced oxidation processes (AOPs), which generate strong oxidant of hydroxyl radicals (OH^-), appear to be a promising alternative for the removal of such a material.

Only a few studies using AOP for the destruction of 2,4-DNP have been published. Lipczynska-Kochany[3,4] indicated that photolysis in the presence of hydrogen peroxide and the Fenton reaction are effective in oxidixing aqueous 2,4-DNP. Stover *et al.*[5] studied the effect of ozone on the biodegradability of 2,4-DNP and found that ozone increases lightly the biodegradability of 2,4-DNP. Tanaka *et al.*[6] studied the photocatalytic degradation of 2,4-DNP in aqueous TiO_2 suspension and reported a significant decomposition of 2,4-DNP. There is not any report on 2,4-DNP degradation by photo Fenton.

The rate of degradation of organic pollutant with Fenton reagents can strongly accelerated by irradiation with UV-light. The combination of UV light with Fenton (photo-Fenton) is advantageous, not only it leads to ferrous catalyst recycling by reduction of Fe^{3+}. By this, the concentration of Fe^{2+} increases and therefore the reaction is accelerated[3].

The increased in efficiency of the photo-Fenton proces is attributed to the photo reductioin of ferric ion, the eficient use of light quanta and the photolysis of Fe^{3+} organic intermediate chelates.

EXPERIMENTAL

Iron sulphate heptahydrate ($FeSO_4.7H_2O$) and hydrogen peroxide (30 %, v/v) were used as the reactant and sulphite solution as quenching agent. All chemical compounds were purchased from Merck and used without further purification.

All experiments ware carried out in an 8.3 L cylindrical photo reactor equipped with 2 UV lamps placed in its center. These two lamps with nominal power of 110 W emits radiation at 254 nm, also the photon flux of the reactor was 12 μ Einstein S^{-1}. The reactor was equipped with a recirculating pump that provides good mixing. All the reactions were performed at atmospheric pressure and room temperature.

Photodegradation procedure: All the experiments were carred out in batch mode. In each experiment a 2,4-DNP solution of 100 mg/L was prepared with millipore water in a mixing tank. The required concentrations of iron added. The photo-reactor was filled with the solution and it was stirred for 5 min. A 30 % aqueous hydrogen peroxide solution was injected into the reactor at different concentrations and the UV light was switched on at the same time. During the experiments, samples were withdrawn from the reactor at several time intervals, tested for H_2O_2 concentration and quenched with sodium hydrogen sulphite to avoid further reactions. The samples were stored for 2,4-DNP, TOC and COD analysis. All the experiment was done as standard methods for exmination of water and wastewater.

The 2,4-DNP concentration was measured by reverse phase high performance liquid chromatography HPLC analysis was performed with Knauer liquid chromatograph equipped with Knauer pumps (D-14163) and Knauer UV-vis detector (K-2500).

The reversed phase column used was a C_{18}(4 mm i.d. × 200 mm length, waters). The mobile phase was a mixture of water, methanol and acetic acid (65:33:2 %) isocratically delivered by a pump at a flow rate of 0.5 mL min^{-1}, the wavelength of the UV absorbance was set at 280 nm to assure reasonable measurement. The standard solution and the tested concentration measurements was repeated six times, obtained results were averaged and gave as a maximum 5 % standard deviation of the mean value.

RESULTS AND DISCUSSION

Effect of initial H_2O_2 concentrations: Photo-Fenton reactions at different molar concentration of H_2O_2 were carried out to find out the influence of hydrogen peroxide in 2,4-DNP degradation.

Fig. 1 presents the evolution of 2,4-DNP, COD and TOC removal as function of H_2O_2 initial concentration during photo-Fenton reaction according to the following conditions: 100 mg L^{-1} 2,4-DNP, fixed initial Fe^{2+} concentration 15 mg L^{-1}, 40 min irradiation time and different H_2O_2 concentration. It can be seen that, rising the initial H_2O_2 concentration direct to more oxidation of the contained organic matter. 50 % of COD conversion was obtained when 75 mg L^{-1} H_2O_2 was used, while it reached to 61 % when H_2O_2 was increased to 100 mg L^{-1}. This implies that the photo Fenton reaction could be used for total mineralization of organic compound to CO_2 and H_2O.

Elimination of all 2,4-DNP was also combined with 21 % TOC removal. Which indicates that small conversion of the contained organic material was mineralized to CO_2 and water.

H_2O_2 has an important role in $OH^{\wedge}$ production in photo-Fenton reaction, the degradation rate was found to be dependent on the initial H_2O_2 concentration, at free pH and small initial Fe^{2+} concentration 15 mg L^{-1}. It was also observed that H_2O_2 consumed rapidly over the reaction periods and this leads to significant degration of 2,4-DNP.

It was expected that increasing the concentration of H_2O_2 reduced the rate of degradation of 2,4-DNP, due to 'self-scavenging' effect of $OH^{\wedge}$ by H_2O_2 eqn. 4[7,8] and this may be used to get an optimum value for hydrogen peroxide needed for total degradation. Even though the hydroperoxy radical ($HO_2^{\bullet}$) formed in this process, its reactivity with organic compounds is low[9].

$$OH^{\wedge} + H_2O_2 \longrightarrow HO_2^{\wedge} + H_2O \tag{1}$$

However, in present experiments this effect has not been detected. Although all 2,4-DNP was disappeared from the reaction solution, increasing initial H_2O_2 guide to oxidize the formed intermediates.

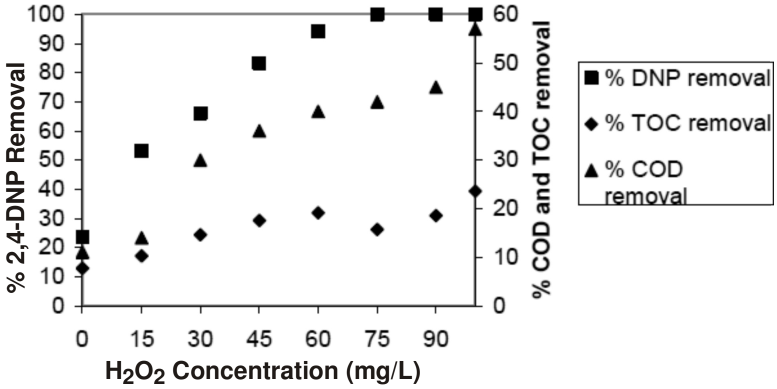

Fig. 1. 2,4-DNP, TOC and COD removal percentage as function of H_2O_2 in photo-Fenton process. $[Fe^{2+}]_i$ = 15 mg L^{-1} experimental time 40 min

The degradation rate of 2,4-DNP by photo-Fenton process was also studied based in first order kinetic model. The kinetic constant value and half-life time at different initial hydrogen peroxide concentrations are presented in Table-1.

TABLE-1
VALUES OF REACTION RATE CONSTANTS, HALF-LIFE TIME FOR 2,4-DNP DEGRADED BY PHOTO-FENTON AT DIFFERENT INITIAL H_2O_2 CONCENTRATIONS. $[Fe^{2+}]_i$ = 15 mg L^{-1} EXPERIMENTAL TIME 40 min AND FREE pH EVOLUTIONS

H_2O_2 (mg/L)	$t_{1/2}$ (min)	K_0
0	>40	0.0163
15	28	0.0266
60	8	0.1007
75	4.5	0.1062

Effect of initial iron ion concentration: Iron has important role in photo-Fenton reactions. Iron species in solution are considered to act as catalysts and have beneficial effect in forming oxidizing species in continuous cycle $Fe^{2+}/Fe^{3+}/Fe^{2+}$. So, it was decided to study the effect of iron in the degradation of 2,4-DNP to obtain the optimal Fe^{2+} amount.

Photo-Fenton reactions were carried out with various amounts of the iron salt and fixed H_2O_2 initial concentration.

Fig. 2 presents the evolution of 2,4-DNP, COD and TOC removal as function of iron initial concentration during photo-Fenton reaction according to the following conditions: 100 mg L^{-1}, 2,4-DNP, fixed initial H_2O_2 (15 mg L^{-1}), 40 min irradiation time and different iron initial concentrations.

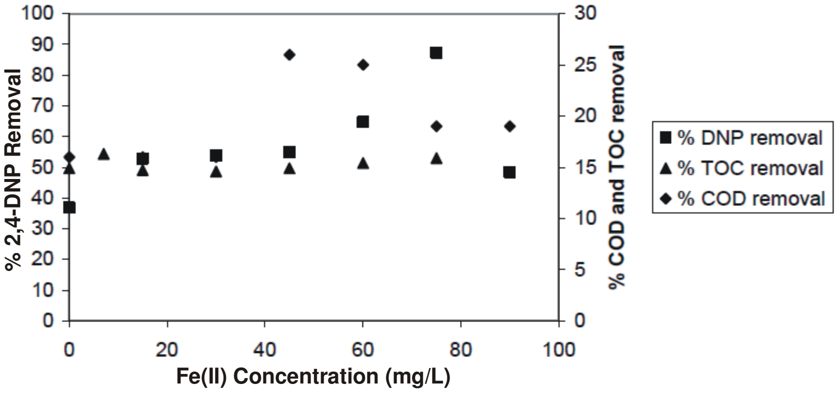

Fig. 2. 2,4-DNP, COD and TOC removal percentages as function of initial Fe^{2+}. $[H_2O_2]_i$ = 15 mg L^{-1} and reaction time 40 min and free pH evolution

The degradation rate of 2,4-DNP by photo-Fenton process was also studied based in first order kinetic model. The kinetoc constant value of half-life time at different initial iron concentrations are presented in Table-2.

TABLE-2
VALUES OF REACTION RATE CONSTANTS OF THE DEGRADATION OF 2,4-DNP AT DIFFERENT INITIAL Fe^{2+} CONCENTRATIONS. 2,4-DNP INITIAL CONDITON: $[H_2O_2]$ = 15, 40 MIN REACTION TIME AND FREE pH EVOLUTION

Fe (mg/L)	K_0
0	0.0117
15	0.0194
45	0.0198
75	0.0500
90	0.0167

Unlike the H_2O_2, it can be seen that at higher amount of iron no significant increase in the degradation rate. Kinetic constant values and half-life time are presented in Table-2. The results suggest that the maximum degradation of 2,4-DNP can be obtained at Fe^{2+} initial concentration around 75 mg L^{-1}. Moreover a slight decrease in the reaction constants when initial iron concentration augmented to 90 mg L^{-1}, as result of iron scavenging effect.

The degradation rate distinctly increased with increasing amounts of iron salt. However, it was noticed that the reaction reach a concentration at which catalytic reaction effect is weak and addition of the iron salt above 75 mg L^{-1} did not improved the degradation, but rather perceptible decrease in the degradation rate occured.

This may be explained due to the fact that during several elementary steps of reaction mechanism, iron can consume radicals with potentially negative effect in the reaction rate. Ghaly *et al.*[10] studied the degradation of *p*-chlorophenols by photo-Fenton reaction and they reported that higher addition of iron salt resulted in brown turbidity that slowed down the absorption of UV light required for photolysis and cause the recombination of hydroxyl radicals. In this case Fe^{2+} act as scavenger for $OH^{\hat{}}$ radicals. On the other hand, the use of large quantities of iron in solution has negative effect from the applied point of view, since it implies the need of an additional treatment step for Fe^{2+} removal. So, it is desirable that the ratio of H_2O_2 to Fe^{2+} should be as small as possible and both radicals recombination and sludge production from iron complex can be evaded. Under the studied conditions, increasing the initial Fe^{2+} from 45 to 75 mg L^{-1} direct to increase 2,4-DNP degradation from 54 up to 87 %.

Effect of initial pH: The effect of initial pH at photo-Fenton process is presented in Fig. 3. Maximum degradation was obtained at acidic pH (pH = 3.0), then the degradation decrease for pH above 4.5 because at higher pH value iron ions may precipitate as hydroxide and that reduced the transmission of the radiation.

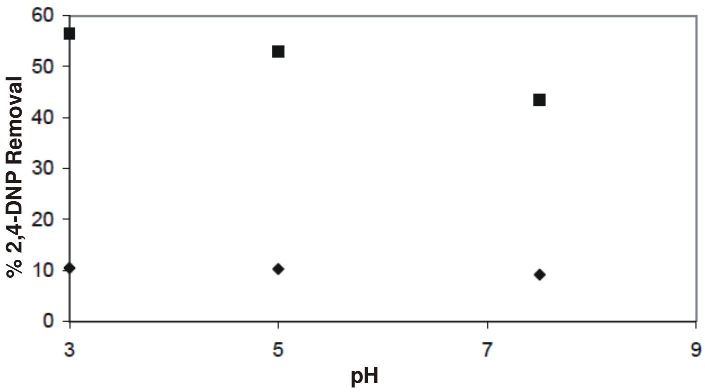

Fig. 3. Evolution of 2,4-DNP degradation as function of pH, $[H_2O_2]$ = 15 mg L^{-1}, $[Fe^{2+}]_i$ = 15 mg L^{-1} and reaction time 40 min

pH value affects the oxidation of organic substances both directly and indirectly. During the photo-Fenton process the dominated reactions are Fenton, photolysis of hydrogen peroxide and photo-reducation of ferric ion, (eqn. 2 to 4), respectively[11].

$$H_2O_2 + Fe^{2+} \longrightarrow OH^{\hat{}} + Fe^{3+} + OH^- \quad (2)$$

$$H_2O_2 + UV \longrightarrow 2OH^{\hat{}} \quad (3)$$

$$Fe^{3+} + UV + H_2O \longrightarrow OH^{\hat{}} + Fe^{2+} + H^+ \quad (4)$$

As indicated in eqn. 2 the amount of $OH^{\hat{}}$ formed through Fenton process is affected by solution pH. The $OH^{\hat{}}$ can be efficiently formed under acidic conditions. On the contrary, H_2O_2/UV process is independent of pH conditions, according to eqn. 3.

It has been reported that photo-Fenton process can effectively remove toxic and refractory organics such as landfill leachate[12] nitrogen containing organics[13], colour in dye manufacturing wastewater[14] at pH 3, 3.5 and 5. In other words, the photo-Fenton process can remove pollutant under acidic and neutral conditions.

During photo-Fenton reaction there were pH drop from any initial pH to 2.8. The overall pH drop is corresponds to an increase in the $[H^+]$ concentration in solution[15] by a factor of almost 7. This suggests that at this pH value 2.8, eqn. 5 is controlling during the degradation process and not the $OH^{\hat{}}$ radical generation.

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^{\hat{}} + H^+ \qquad (5)$$

However, Fenton reaction leading the pH of the system in the opposite direction

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\hat{}} + OH^- \qquad (6)$$

It is known that superoxide radical $HO_2^{\hat{}}$ has a considerably lower one-electron standard potential $HO_2^{\hat{}}/O_2^-$ $E^o = 0.75$ V compared to the $OH^{\hat{}}$ radical with $(OH^{\hat{}}/OH^-)$ $E^o = 1.90$ V. This may give an explanation of the photo-Fenton rate slowing down as the reaction proceeds.

Effect of initial 2,4-DNP concentration: The change of initial 2,4-DNP concentrations was also studied. Fixed concentrations of hydrogen peroxide and iron(II) was chosen to study the degradation rate and all experiments were held at room temperature and free pH evolution. Experimental results are stipulated in Fig. 4.

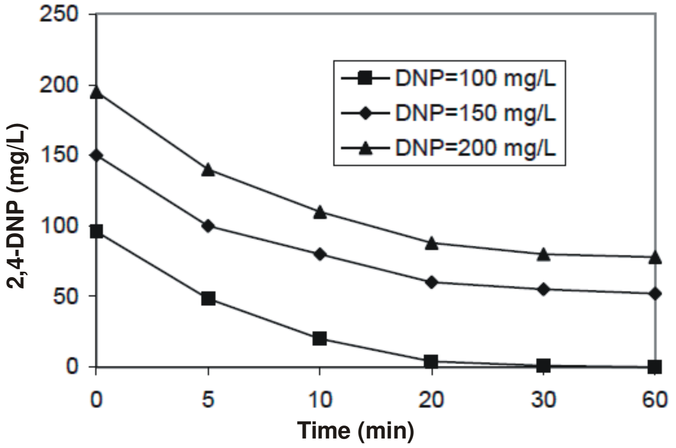

Fig. 4. 2,4-DNP evolution as function of time for different initial concentrations, initial condition; are $[H_2O_2]_i = 75$ mg L^{-1}, $[Fe^{2+}]_i = 15$ mg L^{-1} and free pH evolution

From Fig. 4 it can be noticed that, 2,4-DNP degradation concentration follow zero order kinetic, average zero order kinetic constant of 0.0045 mol min^{-1} was obtained.

Although it was started with the same reactant concentrations (75 mg L^{-1} H_2O_2 and 15 mg L^{-1} Fe^{2+}), it was noticed that the rate of degradation is related to initial contaminant concentration. 100 % of 2,4-DNP was removed when 75 mg L^{-1} initial H_2O_2 concentrations was used, while it is only 60 % for 200 mg L^{-1} H_2O_2. It is interesting to note that, for all 2,4-DNP initial concentrations, TOC % is in the same order of magnitude (Fig. 5).

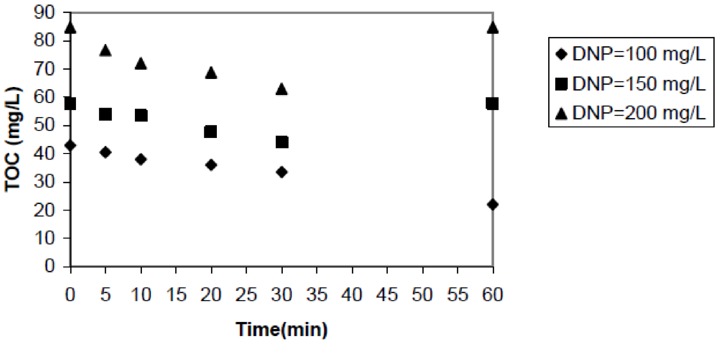

Fig. 5. Evolution of TOC *vs.* reaction time for different 2,4-DNP initial concentrations, initial condition; $[H_2O_2]_i$ = 75 mg L^{-1}, $[Fe^{2+}]_i$ = 15 mg L^{-1} and free pH evolution

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REFERENCES

1. S. Zonglian, G. Mengchun, J. Chunji, C. Youyuan and Y. Jianwei, *Process Biochem.*, **40**, 3017 (2005).
2. A. Goi and M. Trapido, *Proc. Estonian Acad Sci. Chem.*, **50,** 5 (2001).
3. E. Lipczynska-Kochany, *Chemosphere*, **22**, 529 (1991).
4. E. Lipczynska-Kochany, *Chemosphere*, **24**, 1369 (1992).
5. E.L. Stover, L.W. Wang and D.R. Medeley, *Ozone Sci. Eng*., **4**, 177 (1982).
6. K. Tanaka, W. Luesaiwong and T. Hisanaga, *J. Mol. Catal. A*., **122**, 67 (1997).
7. M.I. Stefan, A.R. Hoy and J.R. Bolton, *Environ. Sci. Technol*., **30**, 2382 (1996).
8. S.F. Kang. C.H. Liao and H.P. Hung, *J. Hazard. Mater. B*, **65**, 317 (1999).
9. F. Herrera, C. Pulgarin, V. Nadtochenko and J. Kiwi, *Appl. Catal. B: Environ.*, **17**, 141 (1998).
10. M.Y. Ghaly, G. Hartel, R. Mayer and R. Haseneder, *Wat. Manage*., **21**, 41 (2001).
11. B.C. Faust and J. Hoigne, *Atoms Environ*., **22**, 79 (1990).
12. S.M. Kim, S. Geissen and A. Vogelpohl, *Wat. Sci. Technol*., **35**, 239 (1999).
13. P. Maletzky and R. Bauer, *Chemosphere*, **24**, 1369 (1998).
14. J.W. Kang, H.M. Hung, A. Lin and M.R. Hoffmann, *Environ. Sci. Technol*., **33**, 3199 (1999).
15. M.P. Ormad and J.L. Ovelleiro and J. Kiwi, *Appl. Catal. B: Environ.*, **32**, 157 (2001).

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