Degradation on 2,4,6-Trinitrophenol by cold plasma technology

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Abstract— *Cold plasma exhibits many advantages in environmental treatment without additive reagent required. The 2,4,6-Trinitrophenol (TNP) might be degraded with high efficiency using cold plasma. The main factors influencing the TNP degradation have been studied. The kinetics of the TNP process proposed fits to the pseudo- first order reaction. The overall reaction rate expression was established to be* $-r = 0.024C_{TNP}$ *at low TNP concentration*

Keywords— Cold plasma, 2,4,6-Trinitrophenol, degradation by plasma.

I. INTRODUCTION

Since the late of 20th century, plasma field as a new study filed has been interested in the great attention of many scientists in over the word [1]. The plasma chemistry is focused on studying about the energetic particles (electrons and ions) in plasma participated in chemical reactions. The plasma can be divided into two kinds such as thermal plasma and cold plasma depending on the electron temperature and ion temperature [1,2]. According this principle, thermal plasma has electron temperature equal to ion temperature, while for cold plasma, the electron temperature is higher than the ion temperature. The cold plasma produced in water solutions forms the basis of an innovative advanced oxidation technology of water treatment. So that recently cold plasma has been considered to be a useful method in environmental pollution treatment technology concluding solid, liquid and gas wastes [3,4]. Because, the degradation of these substances has been based on the strongly active species (free radicals) generated from cold plasma process. Cold plasma is produced by gas discharge or combined with air in atmosphere that results in highly oxidative species such as electrons, ions, radicals, excited atoms and molecules [5]. So that use of cold plasma technique is an environmentally friendly and cost – effective alternative due to without any additional chemical reagents used and therefore their disposal is not required. Cold plasma can be classified into many types in which dielectric barrier discharge (DBD) is one of these. In this paper cold plasma with DBP (shortly called cold plasma) used to degrade 2,4,6 –Trinitrophenol will be presented in detail.

2,4.6-Trinitro phenol TNP (picric acid) is an organic compound with the formula $(O_2N)_3C_6H_2OH$, mass molecule 229.10 $g \cdot mol^{-}$, pka = 0.38, which used in munitions explosives or in medicine and dyes [6]. 2,4.6-Trinitrophenol is toxic that causes headache, vertigo, nausea, vomiting, diarrhea, inflammation of kidney and acute hepatitis and red colored urine may be produced [7].

In this paper the 2,4,6-trinitrophenol in waste water treated by cold plasma (DBD) will be studied in detail including degradation efficiency and the experimental conditions under that provides the highest efficiency.

II. EXPERIMENTAL PART

2.1 Chemical

The experimental method was carried out based on the previous work published in previous paper. It includes the following items:

- 2,4,6-Trinitrophenol with analytical purity grade purchased from China.

Other chemicals such as methanol (Merck, Germany), and NaOH, H_2SO_4, H_2O_2 with analytical purity grade purchased from China too.

2.2 Apparatus

- HPLC Model HP 1100, using *diode-array detector*. (DAD), Agilent (USA),
- Spectrophotometer UV- Vis Agilent 8453 (USA),
- The schematic structure of plasma reactor shown in the Fig 1.

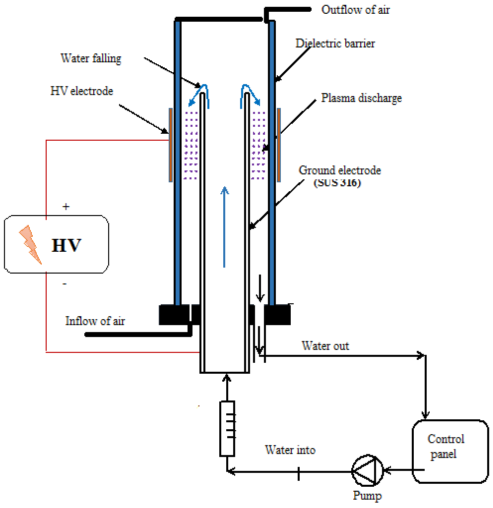

FIG.1. SCHEMATIC STRUCTURE OF PLASMA REACTOR

2.3 Experimental procedure

The experimental procedure is focused on studying the following items:

2.3.1 Formation of cold plasma

The appearance of cold plasma will carried out under conditions like electric current varying from 3.5 to 22 mA and electrode potential increasing from 7 to 21 kV (HV). Plasma intensity appeared is recognized by the naked eyes and through TNP degradation efficiency.

2.3.2 Degradation of TNP from water in varying electric power

To increase the degradation of process, the plasma is in direct contact with the thin film of water falling via a grounded electrode. The TNP contaminated water sample is always circulated through reactor during the reaction proceeding, with the rate of 415 mL/minute and the air rate blowing with 3 liter/min. The degradation of TNP is carried out under the conditions such as: volume of sample is 500 mL containing a certain concentration of TNP, pH of samples from 3.2 to 11 at different electric powers. After an interval of reaction time, a certain volume of sample is taken out to measuring the TNP concentration left, by HPLC method as suggested in [9].The removal of efficiency of TNP is calculated using the expression:

$$H = \frac{(C_0 - C_t)}{C_0} \times 100, (\%)$$

Here H is removal efficiency of TNR. C_0 and C_t are concentrations of TNP at the initial and t reaction time in mg/L.

The average rate of TNP degradation (r) is also calculated by the expression:

$$-r = \frac{(C_{t2} - C_{t1})}{\Delta t}, mg/L.\min$$

Here r denoted the average reaction rate (mg/l.min), Δt is the time interval from t1 to t2, min.

2.3.3 Study on increasing degradation efficiency of TNP

The experimental method was implemented like 2.3.2 but adding H_2O_2

2.3.4 Study on other factors influencing degradation efficiency of TNP

- Influence of initial concentration of TNP, the experiments are carried out like in 2.3.2 but varying initial concentration of TNP.
- Influence of pH, the experiments was implemented like in 2.3.2, but the pH varying from 3.2 to 11.

III. RESULTS AND DISCUSSION

3.1 Influence of electric powers on TNP degradation

The results of TNP degradation efficiency and reaction rate, under the varying electric powers such as varying U and I were presented in Table 1 and in Fig.2**.** Under the conditions such as U =21 kV, I = 22 mA, the plasma discharge can reach the highest power. The results of influence of electric power are presented in Table 1 and Fig.2.

TABLE 1
INFLUENCE OF ELECTRIC POWERS ON TNP DEGRADATION

Reaction times, min	TNP/plasma								
	I=10mA, U=16kV			I=16mA, U=19kV			I=22mA, U=21kV		
	C_t, mg/L	H, %	r, mg/L.min	C_t, mg/L	H, %	r, mg/L.mim	C_t, mg/L	H, %	r, mg/L.min
0	135.30			135.30			135,30		
30	109.01	19.43	0.88	84.20	37.77	1.70	41.86	69.21	3.11
60	89.20	34.07	0.66	50.19	62.90	1.13	11.65	91.54	1.01
90	68.59	49.31	0.69	25.08	81.47	0.84	2.11	98.59	0.32
120	52.82	60.96	0.53	13.05	90.36	0.40	0.70	99.63	0.05

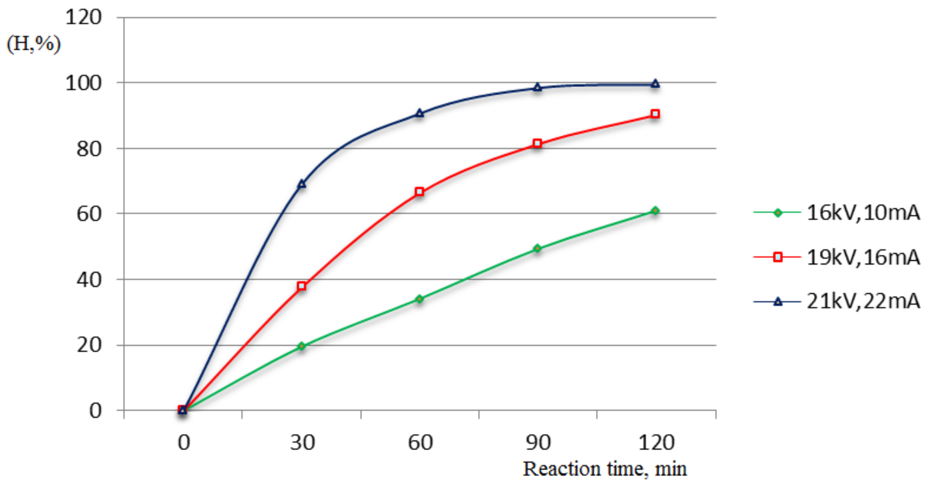

FIG.2. INFLUENCE OF ELECTRIC POWER ON TNP DEGRADATION

The obtained experimental data showed that the degradation efficiency and degradation rate for the same TNP concentration (135.30 mg/L) were enhanced with the increase of the used voltage. This is due to at higher voltage, electrons at the cathode surface are produce easily so that could increase the solution's electric field intensity and generate more oxidative, active particles such as O_3, $O^\bullet$,$^\bullet OH$, H_2O_2, so increasing degradation of TNP. This phenomena were explained in the work [8 -12].

3.2 Influence of the initial pH on the TNP degradation

As known, during discharge, plasma would be formed, producing oxidative particles including O_3, $O^\bullet$,$^\bullet OH$, H_2O_2at the gas - water interface in the reactor. These active particles must dissolve into water sample to initiate oxidation process to degrade TNP. The chemical activity of these particles in water sample depends on the pH-water. In water, the O_3- formation in plasma can react with H_2O molecules to form$^\bullet OH$, but O_3 would be decomposed at high pH and fairly stable at low pH [8]. The $^\bullet OH$-existence is higher in neutral or alkaline media than in an acidic one [13], so $^\bullet OH$ radical would be formed more at higher pH. Owing to these reason, the TNP degradation efficiency would higher in the weak or neutral reaction medium. The results of pH influencing the TNP degradation by cold plasma were presented in Table 2 and Fig.3.

TABLE 2
INFLUENCE OF pH ON TNP DEGRADATION

Reaction time, min	TNP/plasma								
	pH = 3.2			pH = 7.0			pH = 11.0		
	C_t, mg/L	H, %	r, mg/L.min	C_t, mg/L	H, %	r, mg/L.min	C_t, mg/l	H, %	r, mg/L.min
0	135.30			135.30			135.30		
30	84.10	37.84	1.71	86.20	38.29	1.64	90.66	32.99	1.49
60	50.19	62.90	1.13	50.00	63.05	1.21	54.74	59.54	1.20
90	25.08	81.47	0.84	26.00	82.78	0.80	30.35	77.57	0.81
120	13.05	90.36	0.40	11.30	91.65	0.49	16.10	88.10	0.48

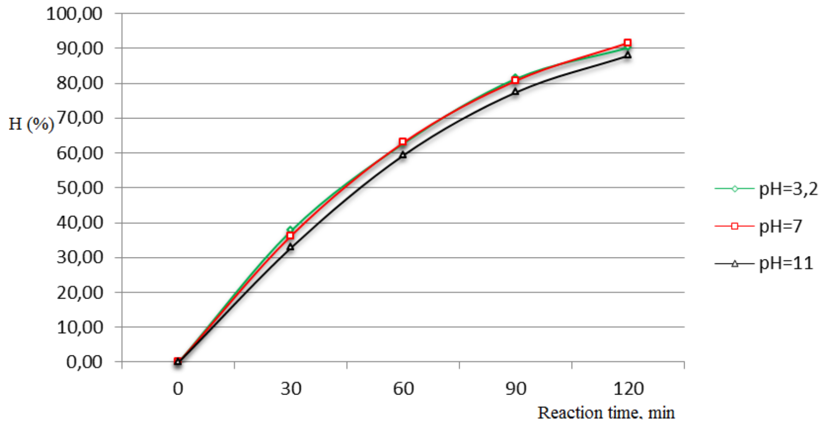

FIG. 3. INFLUENCE OF Ph ON TNP DEGRADATION

The experimental data showed that the TNP degradation efficiencies are higher in the pH range of 3.2 -7.0 than from 7 to 11. This is in accordance with the theory suggested above.

3.3 Influence of TNP initial concentration on degradation

Here there are three series of the initial TNP concentrations were selected for study their influence on the degradation reaction rate such as:

C_{TNP} = 91.02, mg/L, C_{TNP} =135.3, mg/L, C_{TNP} = 210.17, mg/L and

C_{TNP}= 50.46, mg/L C_{TNP}= 84.10, mg/L C_{TNP}= 149.67, mg/L

C_{TNP}= 25.26, mg/L C_{TNP}= 50.19, mg/L C_{TNP}= 105.00, mg/L

The TNP degradation rate was measured for 30 minute reaction listed in Table 3.

TABLE 3
INFLUENCE OF TNP-INITIAL CONCENTRATION ON DEGRADATION REACTION RATE

Series I	TNP concentration, mg/L	91.02	135.3	210.17
	Reaction rate, r mg/L/min	1.35	1.71	2.02
Series II	TNP concentration, mg/L	50.46	84.10	149.67
	Reaction rate, r mg/L/min	0.84	1.13	1.62
Series III	TNP concentration, mg/L	25.26	50.19	105.00
	Reaction rate, r mg/L/min	0.49	0.84	1.22

In the previous study [ ], the degradation rate expression of TNR by cold plasma fitted to the equation:

$$- r = \frac{k_1 C_{TNR}}{1 + k_2 C_{TNR}}$$

Using this expression, the rate expression corresponding the every series of the initial TNP concentration was calculated, resulted in as following:

For series I. $$-r = \frac{0.0247C_{TNP}}{1+0.0073C_{TNP}}$$

For series II $$-r = \frac{0.0231C_{TNP}}{1+0.0080C_{TNP}}$$

For series III. $$-r = \frac{0.0243C_{TNP}}{1+0.0098C_{TNP}}$$

The obtained rate expression showed that when C_{TNP} is small meaning the product of 0.0073, 0.0080 and 0.0089 with C_{TNP} very small the 1, the above rate expressions become:

For series I, $-r = 0.0247C_{TNP}$,

For series II, $-r = 0.0231C_{TNP}$

Fore series III,$-r = 0.0243C_{TNP}$

The overall rate expression could be resulted in:

This rate expression is fitted to the experimental data suggested in Table 3.

3.4 Increase of TNP degradation efficiency by plasma discharge combined with H_2O_2

The addition H_2O_2 into reactor with plasma might enhance TNP degradation, presented in Fig.4

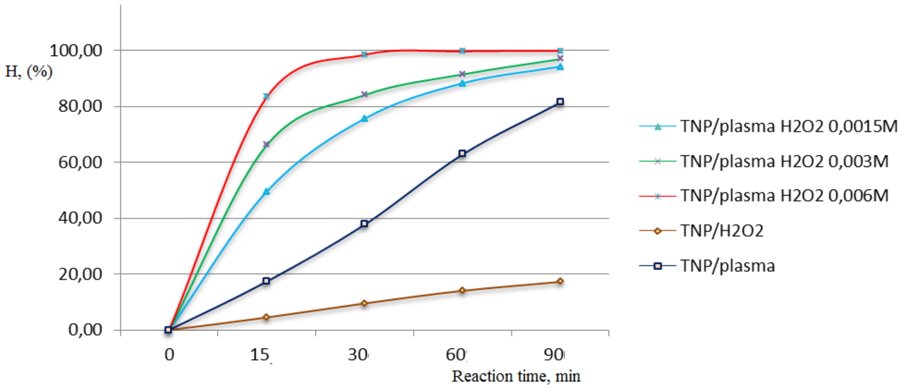

FIG. 4. INFLUENCE OF H_2O_2 ADDITION ON DEGRADATION EFFICIENCIES

The obtained experimental data have shown the presence of H_2O_2 increases the TNP degradation efficiency. The high efficiency might explain by the activation of H_2O_2 by plasma (UV) in plasma reactor to produce hydroxyl radical as following

$$H_2O_2 + h\nu \rightarrow HO^{\bullet} + {}^{\bullet}OH$$

The increase of hydroxyl radical leads to increase the TNP degradation efficiency. This was suggested in previous work.

3.5 Proposed kinetic TNP degradation by cold plasma

As suggested above the TNP degradation rate by constant plasma obeyed the equation:

$$-r = \frac{k_1C_{TNP}}{1+k_2C_{TNP}}$$

At the low TNP concentration (when $1 >> k_2C_{TNP}$) , the reaction rate becomes

$$- r = k_1C_{TNP} = 0.024C_{TNP}$$

It means the reaction follows a pseudo-first order kinetic. The experiment was carried out with the TNP concentration of 91.02 mg/L to degrade by constant condition of plasma for the different times listed in Table 4 as follows:

TABLE 4
THE CHANGE OF TNP CONCENTRATION FOR THE TIME

Reaction time, min	0	30	60	90
TNP conc. mg/L	91.02	50.46	25.26	10.71

Using these data, the integral expression corresponding the pseudo-first order reaction was determined:

$$\ln(C/C_0) = - 0.0244t$$

and its plot was presented in Fig.5.

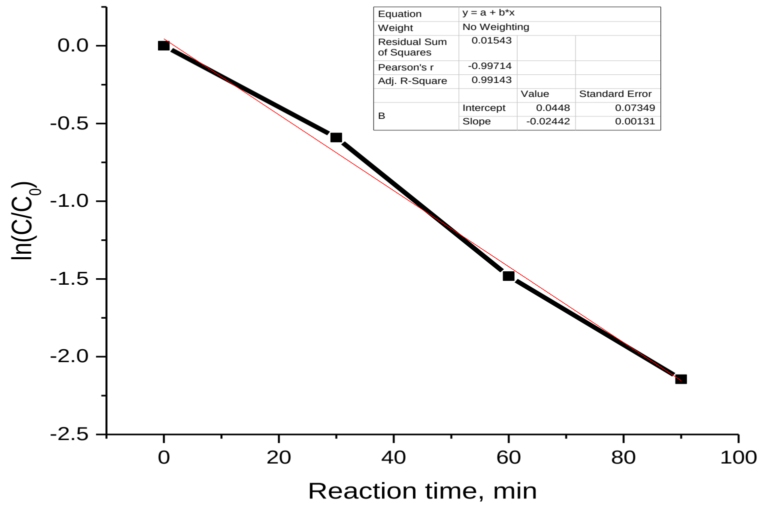

FIG.5. THE PLOT OF $\ln(C/C_0)$ VS. TIME

The obtained reaction rate constant is similar with the author [14].

IV. CONCLUSION

Cold plasma technology has been applied in environmental treatment with the many advantages. The main principle of cold plasma technology is based on the oxidative particles including free radical $^{\bullet}OH$ and active ions or molecules generating in situ under the high electric voltage to degrade pollutants from wastewater. The cold plasma has been used to degrade TNP in water samples resulting in high efficiency. The influence of main factors such as pH, reaction time, additive H_2O_2, TNP concentration was studied. The cold plasma used to degrade TNP yielded high efficiency at the range of pH 3.2-11 and its efficiency enhancing with additive H_2O_2. The kinetics of the TNP degradation under cold plasma has been suggested, following the pseudo - first order reaction at the low TNP concentration.

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