A novel study on the degradation of styphnic acid from water by cold plasma technology

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Abstract— *Cold plasma technology exhibits many advantages in practical application. Due to these reasons the use of cold plasma technology for environmental treatment is receiving great attention. Here a novel study on the degradation of styphnic acid from water by cold plasma technology has been presented in detail, such as establishment of cold plasma reactor structure, determination of efficiency in degradation of styphnic acid by cold plasma radiation under different experimental conditions. The obtained results have shown that cold plasma might be used for degrade styphnic acid with high efficiency.*

Keywords— cold plasma, degradation, acid styphnic.

I. INTRODUCTION

Styphnic acid (TNR) or 2,4,6 trintro-1,3 benzenediol with formula$C_6H_3N_3O_8$ is used in manufacturing dyes, pigments, inks, medicines, explosives (led styphnate) [1]. Styphnic acid is one of aromatic nitro compounds, with synonyms: 2,4,6-trinitroresorcine, 2,4,6- trinitroresorcinol ranging from slight to strong oxidizing agents. It may explode in the presence of a base such as NaOH or KOH even in the presence of water or organic solvents. So that this compound is always kept away from heat, sparks and avoided from mechanical shock [2]. Styphnic acid can cause eye, skin and being harmful if inhaled, swallowed or absorbed through the skin. It is also toxic for blood, kidney and nervous system, causing cancer and aquatic life *[3]*. Like aromatic nitro compounds, the styphnic acid contaminated water may be treated by many methods such as physical, chemical [4].

In recent years, plasma plays an important role in variety of industrial applications. including material processing, environmental treatment and many more. There are increasing interests in the plasma discharges in liquids because of its potential applications for various fields like biological, environmental, and medical technologies. In this paper a novel study on the degradation of TNR from water using cold (non thermal) plasma technology was presented. The chief aim of study is to degrade TNR from plant wastewater resulting from the manufacture of lead styphnate to avoid explosive hazard. Plasma is an ionized gas that is the fourth state of matter after solid, liquid and gas. Plasma technology has been studied and applied for wastewater treatment in recent years, involving many advantages compared with chlorination, ozonation and UV. Principle of plasma is based on the formation of free radicals and strongly oxidative species under electric discharge with high voltage through a dielectric barrier in air at atmosphere pressure as following [5-8]:

- Reactions producing ozone

$$O_2 + h\nu \rightarrow O + O$$

$$O_2 + O \rightarrow O_3$$

- Reactions producing free species

$$O_3 + OH^- \rightarrow O_3^{\bullet -} + {}^{\bullet}OH$$

$$O_3^{\bullet -} \rightarrow O^{\bullet -} + O_2$$

$$O^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH + OH^-$$

The main oxidative species is hydroxyl free radical with the high reduction potential 2.80 V might degrade recalcitrant organic compounds like TNR from water as follows:

$$C_6H_3N_3O_8 \xrightarrow{oxidative species\,(^{\bullet}OH)} \text{Products}$$

II. EXPERIMENTAL PART

2.1 Chemicals:

Styphnic acid 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),
- DR/890 Colorimeter, HACH, for COD analysis.

The schematic structure of plasma reactor shown in the Fig 1.

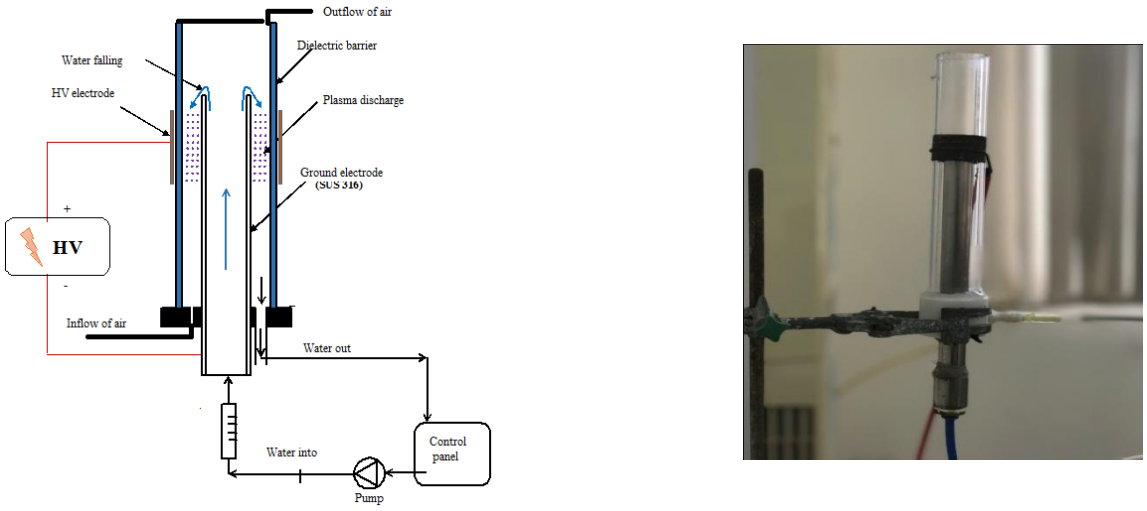


FIG.1. SCHEMATIC STRUCTURE OF PLASMA REACTOR

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 TNR degradation efficiency.

2.3.2 Degradation of TNR 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 TNR 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 TNR is carried out under the conditions such as: volume of sample is 500 mL containing a certain concentration of TNR, pH of samples from 3.2 to 11 at different electric power. After an interval of reaction time, a certain volume of sample is taken out to measuring the TNR concentration left, by HPLC method as suggested in [9].The removal of efficiency of styphnic acid 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 styphnic acid at the initial and t reaction time, mg/L.

The average rate of TNR degradation is also calculated by the expression:

$$r = \frac{(C_{t_1} - C_{t_2})}{\Delta t}$$

Here r denoted the average reaction rate (mg/l.min), Δt is the time interval from t_1 to t_2, min.

2.3.3 Study on increasing degradation efficiency

The experimental method was implemented like 2.3.2 but using H_2O_2 in addition

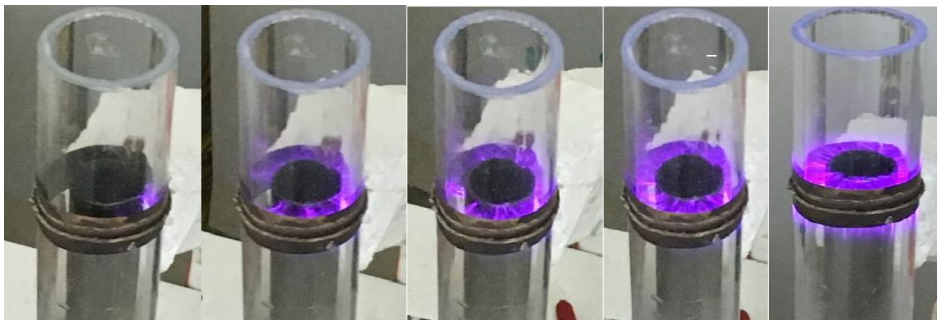
2.3.4 Study on other factors influencing degradation efficiency of TNR

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

III. RESULTS AND DISCUSSION

3.1 The appearance of plasma

The images of plasma discharges in reactor are presented in Fig.2



U= 7 kV I = 3.5 mA	U= 14kV I=5.5 mA	U=16kV I= 10 mA	U=19 kV I = 16 mA	U= 21kV I = 22 mA

FIG.2. THE APPEARANCE OF PLASMA IN VARYING CONDITIONS OF U AND I

Under condition such as U = 21kV, I =22 mA, intensity of plasma radiation is observed to be the highest.

3.2 The degradation of TNR in varying plasma discharge

The results of TNR degradation about efficiency and reaction rate, under the varying plasma discharge such as U and I were presented in Table 1 and in Fig.3.

TABLE 1
INFLUENCE OF PLASMA DISCHARGE ON TNR DEGRADATION

Reaction time, min	TNR degradation								
	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.min	C_t, mg/L	H, %	r, mg/l.min
0	115.60			115.60			115.60		
30	94.75	18.04	0.70	75.28	34.88	1.34	15.25	86.80	3.34
60	79.21	31.48	0.52	45.13	60.96	1.01	1.34	98.84	0.46
90	66.97	42.07	0.41	20.26	82.47	0.83	0.77	99.33	0.02
120	54.48	52.87	0.42	7.72	93.32	0.42	0.00	100.00	0.03

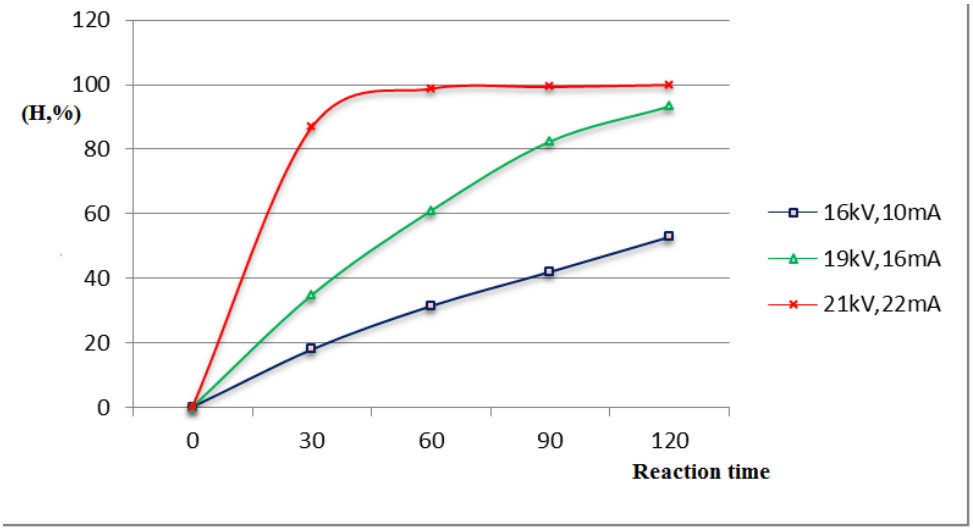


FIG.3. TNR DEGRADATION EFFICIENCIES VERSUS TIME

The obtained data have shown that the TNR degradation depends on the plasma discharge. Under the conditions such as U =21 kV, I = 22 mA, plasma discharge reaches the highest state.

3.3 Influence of pH on the TNR degradation

The results of influence of pH on the TNR degradation was presented in Table 2.

TABLE 2
INFLUENCE OF PH ON TNR DEGRADATION

Reaction time, min	TNR degradation								
	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	115,60			115.6			115.6		
30	75.28	34.88	1.34	77.08	33.32	1.28	74.36	35.67	1.37
60	45.13	60.96	1.01	46.62	59.67	1.02	43.59	62.29	1.03
90	20.26	82.47	0.83	20.14	82.58	0.88	16.87	85.41	0.89
120	7.72	93.32	0.42	7.07	93.88	0.44	2.2	98.10	0.49

The obtained experimental data has shown that at the pH =11, the TNR degradation efficiencies and reaction rate are higher at pH= 11.Due to that at this pH, the ozone resulting in plasma discharge is easily converted in hydroxyl radical. This radical is more reactive in alkaline medium the in acid or neutral one that has suggested in [10].

3.4 Influence of TNR initial concentration on degradation

The TNR degradation efficiency under cold plasma condition depends on the initial concentration of TNR, presented in Table 3 and in Fig.4.

TABLE 3
INFLUENCE OF INITIAL CONCENTRATION ON TNR DEGRADATION

reaction time min	TNR degradation								
	C_{TNR} =61.72 mg/L			C_{TNR} =115.6 mg/L			C_{TNR} =175.03mg/L		
	C_{TNR} mg/L	H, %	r, mg/l.min	C_{TNR} mgL	H, %	r, mg/l.min	C_{TNR} mg/L	H, %	r, mg/l.min
0	61.72			115.60			175.03		
30	27.15	56.01	1.15	75.28	34.88	1.34	132.25	14.16	1.43
60	9.72	84.25	0.58	45.13	60.96	1.01	99.19	31.90	1.10
90	1.36	97.80	0.28	20.26	82.47	0.83	72.23	53.02	0.90
120	0.00	100.00	0.05	7.72	93.32	0.42	53.15	69.63	0.64

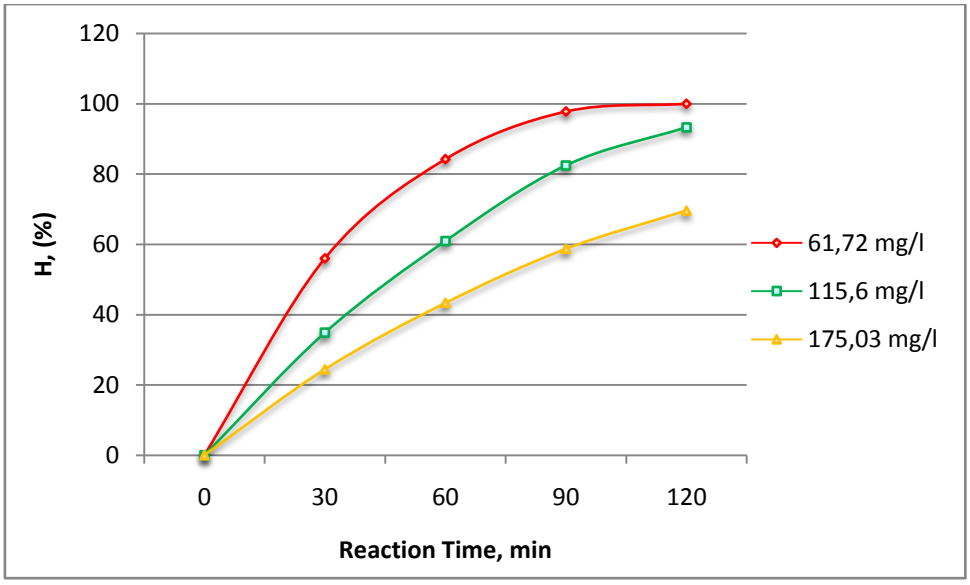


FIG. 4. TNR DEGRADATION EFFICIENCIES AT DIFFERENT CONCENTRATIONS

The obtained experimental data have shown that at the same plasma discharge and at the initial concentration of TNR of 61,72 mg/L, after 120 min, the TNR degradation efficiency reach 100 %, at the same time the TNR degradation efficiencies are 93.32 and 69.63 % for the TNR initial concentrations of 11.60 and 175.03 mg/L respectively. This is really true due to the plasma discharge limited.

3.5 Increase of TNR degradation efficiency by plasma discharge combined with H_2O_2.

The addition H_2O_2 into plasma reaction might enhance TNR degradation, presented in Fig. 5.

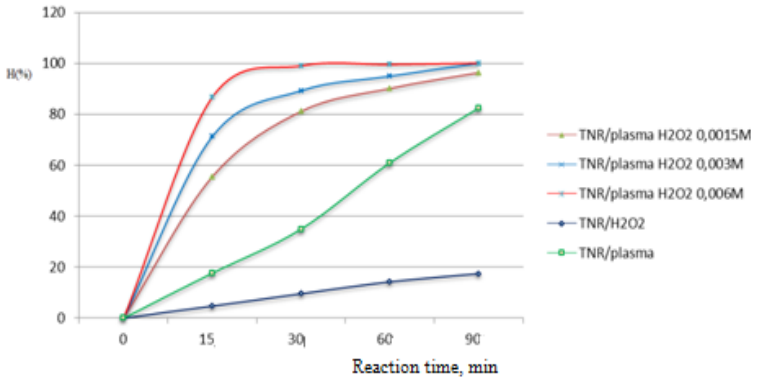


FIG. 5. TNR DEGRADATION EFFICIENCY BY PLASMA COMBINED WITH H_2O_2

The obtained experimental data have shown the presence of H_2O_2 increases the TNR 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 follows:

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

The increase of hydroxyl radical leads toincrease the TNR degradation efficiency.

3.6 Proposed TNR degradation rate expression by cold plasma

The degradation of TNR in water sample under the plasma discharge is due to the formation of oxidative species, mainly hydroxyl free radical ($OH^{\bullet}$). Under the same condition of plasma discharge, the total oxidative species are constant amount, the TNR degradation rate expression is normally is following:

$$r = - k[OH][TNR] = - k_{app}[TNR]$$

Here denoted $k[OH] = k_{app}$ = constant.

In this case the degradation rate of TNR should be proportional to TNR concentrations. The plot in Fig. 6 (a) has shown there is no proportional to TNR concentration. In the other hand there is a good proportional relationship between 1/rate and 1/TNR concentration Fig.6 (b).

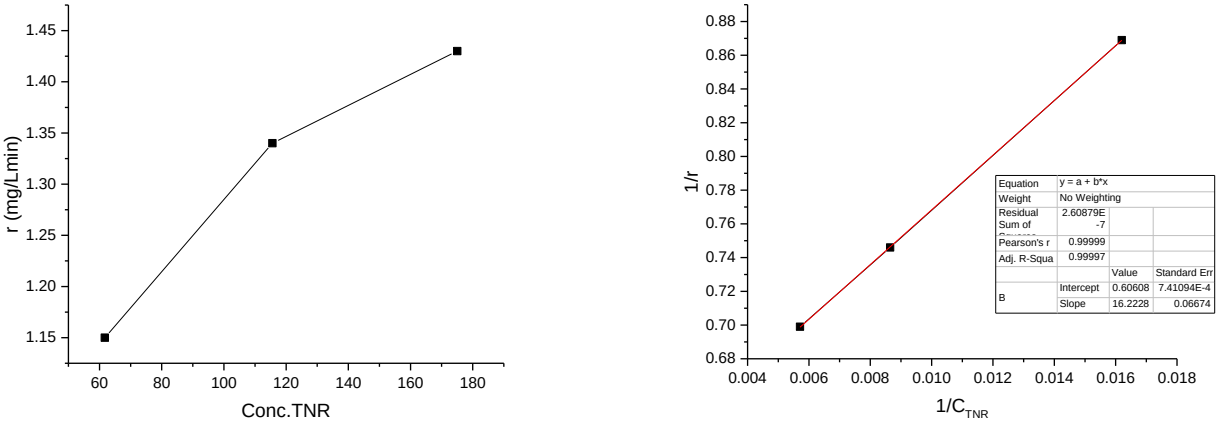


FIG. 6. THE PLOTS OF THE REACTION RATE AND TNR CONCENTRATION

But from data in the Table 3 the rate expression of TNR degradation fits to the formula as follows:

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

Here k_1 and k_2 are constants, [TNR] is TNT initial concentration. This proposed expression is in accordant with the work [11]. The $k_1$and k_2 will be determined in the further article.

IV. CONCLUSIONS

In this paper a novel study of cold plasma technology was presented. The use of cold plasma discharge for degradation of TNR from water was studied in detail. The main factors such as the reaction time, pH, TNR initial concentration, H_2O_2 and electric power influencing on the plasma resulting in and on TNR degradation efficiency were determined. By cold plasma, the TNR degradation efficiency might reach 100% for 120 min, when the initial TNR concentration is 61.72 mg/L.

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