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Original Research

Degradation of 2,4,6-Trinitroresorcinol in Aqueous Solution by Cold Plasma Technology

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Abstract

The degradation of 2,4,6-Trinitroresorcinol (TNR) in aqueous solution by dielectric barrier discharge system was investigated and the effect of some factors that might affect the degradation process was also further examined. The results showed that TNR could be effectively removed from aqueous solution by cold plasma. Under the experimental conditions, the TNR removal efficiency was proportional to the input electric power and the circulating flow rate, but inversely proportional to the initial pH, initial concentration and electrode distance. Initial pH significantly influenced on the TNR removal efficiency. Accordingly, in acidic medium, the TNR removal efficiency was higher than that in neutral and alkaline medium and is highest at pH = 3.2. The presence of some oxidizing agents in the solution such as H_2O_2, $Na_2S_2O_8$, O_2 greatly increased the TNR removal efficiency under the effect of cold plasma. The TNR removal efficiency increased gradually by the range of plasma/H_2O_2 > plasma/O_2 > plasma/$Na_2S_2O_8$ > plasma. The TNR degradation process in the presence and absence of the oxidizing agents all abided by the regulation of first order reaction kinetics.

Keywords: 2,4,6-Trinitroresorcinol, cold plasma, dielectric barrier discharge, kinetics

Introduction

2,4,6-Trinitroresorcinol (TNR) or styphnic acid with formula $C_6H_3N_3O_8$ is a nitrophenol compound that is widely used in the explosives industry. Wastewater containing nitrophenols has the characteristics of high chroma, high toxicity, and low biodegradability. Under natural conditions, it is difficult for nitrophenols to be removed because of their high stability and solubility, leading to a long-term retention and an accumulation in the environment, causing serious pollution to the environment and hazard to humans [1]. Like nitrophenol compounds, the TNR contaminated water could be treated by many methods such as adsorption, advanced oxidation processes (AOPs), chemical reduction or bioremediation. However, there was some issues about economics, equipment, or efficiency when applying these methods [2].

Nowadays, cold plasma technology such as dielectric barrier discharge (DBD) is promising in environmental pollution control. This is a new and advanced technology due to its many advantages compared to other traditional technologies, by forming a plasma that produces ultraviolet (UV), ozone (O_3), H_2O_2 and hydroxyl free radicals (•OH) in situ through electrical discharge at the surface of the electrode exposed to liquid or air [3-6] . Therefore, it can degrade the organic pollutants into CO_2, H_2O, and small-molecule

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carboxylic acid by the active particles produced during the discharge process [7]. The mechanism of the active species formation is described as follows [8, 9]:
(i) The process of ozone formation under the action of electric sparks:

$$O_2 + h\nu \rightarrow O + O \quad (1)$$

$$O + O_2 \rightarrow O_3 \quad (2)$$

(ii) The process of free hydroxyl formation when ozone is dissolved in water:

$$O_3 + OH^- \rightarrow O_3^{\bullet -} + {}^\bullet OH \quad (3)$$

$$O_3^{\bullet -} \rightarrow O^{\cdot -} + O_2 \quad (4)$$

$$O^{\bullet -} + H_2O \rightarrow {}^\bullet OH + OH^- \quad (5)$$

(iii) The process of free hydroxyl formation when energy electrons collide with water vapor molecules:

$$e^- + H_2O \rightarrow {}^\bullet OH + {}^\bullet H + e^- \quad (6)$$

(iv) The process of forming free hydroxyl when atomic oxides react with water vapor molecules:

$$O + H_2O \rightarrow {}^\bullet OH + {}^\bullet OH \quad (7)$$

The impact of the high energy electrons of plasma and ozone chemistry on water molecules will result in more ${}^\bullet OH$, $H^\bullet$ and H_2O_2 [3-5, 10].

$${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2 \quad (8)$$

$${}^\bullet OH + O_3 \rightarrow {}^\bullet HO_2 + O_2 \quad (9)$$

$${}^\bullet H + O_3 \rightarrow {}^\bullet OH + O_2 \quad (10)$$

$${}^\bullet HO_2 + O_3 \rightarrow {}^\bullet OH + 2O_2 \quad (11)$$

$${}^\bullet HO_2 + {}^\bullet H \rightarrow H_2O_2 \quad (12)$$

Thus, cold plasma produces ozone, H_2O_2, UV light and radicals ${}^\bullet OH$, ${}^\bullet H$, ${}^\bullet O$, especially free radicals ${}^\bullet OH$ - a very strong oxidizing agent (oxidation potential of ${}^\bullet OH$ is 2.8 eV [11], which is much higher than that of other oxidizing agents), which are capable of decomposing most organic compounds. In addition, the combination of these agents also results in AOPs, which are capable of handling a wide variety of recalcitrant organic compounds presented in wastewater.

The degradation of TNR in aqueous solution by cold plasma technology has not yet been studied. This is the reason why this study was conducted to investigate the possibility of TNR degradation from aqueous solution by cold plasma. Furthermore, the degradation processes of TNR in the presence of O_2, H_2O_2 and $Na_2S_2O_8$ were also examined.

Materials and Methods

Materials

Analytical purity grade of solvents, chemicals and 2,4,6-Trinitroresorcinol were obtained from Merck, U.S.A and used without further purification. All the solutions were prepared prior to carrying out experiments and kept at room temperature.

Experimental Setup

The schematic diagram of dielectric barrier discharge (DBD) system is shown in Fig. 1. It consists of a homemade high voltage power supply and a coaxial cylindrical reactor. The outer quartz glass tube has inner and outer diameters of 28 and 34 mm, respectively. The inner tube is a stainless steel (SUS 316) ground electrode with a diameter of 21 mm. The two coaxial tubes were fixed on a Teflon insulated base. The plastic base was drilled for removing water from the plasma reactor. The outer electrode is made of copper foil glued to the outside of the quartz tube with a length of 20 mm. The TNR solution was circulated by a diaphragm pump with a flow rate of 450 mL/min and was made to flow as a film on the outer surface of the inner tube. The voltage of insulating glass tubes was always high to obtain electrical sparks, which spread around the pipe evenly without pipe breakdown. A high voltage source (from 10 to 19 kV) was connected the electrodes. DBD-cold plasma was obtained between a water layer and the inner surface of tube, because of sparks discharged in air between the outer surface of water layer and inside quartz tube. An air blower (Quairium SB-348A, China) was employed to supply air (3 L/min) inside and outside the quartz tube of plasma chambers for enhancing ozone generation and ozone dissolution in water. For every experiment, 500 mL solutions were added into the reactor.

Sample Preparation

TNR solution at initial concentration of 150 mg/L and a volume of 500 mL was used to test the effect of input power, circulating flow, initial pH value, electrode distance and oxidizing agents on the degradation by cold plasma. The input power of 250 W and circulating flow of 450 mL/min was employed to investigate the effect of initial pH value, electrode distance and oxidizing agents on the degradation by cold plasma.

Analytical Methods

TNR concentration was measured via a high performance liquid chromatography (Agilent, USA, 1100 Series) with a Hypersil C18 (200 × 4 mm) column as stationary phase. The mobile phase consisted of 65% acetonitrile and 35% water, the flow rate was

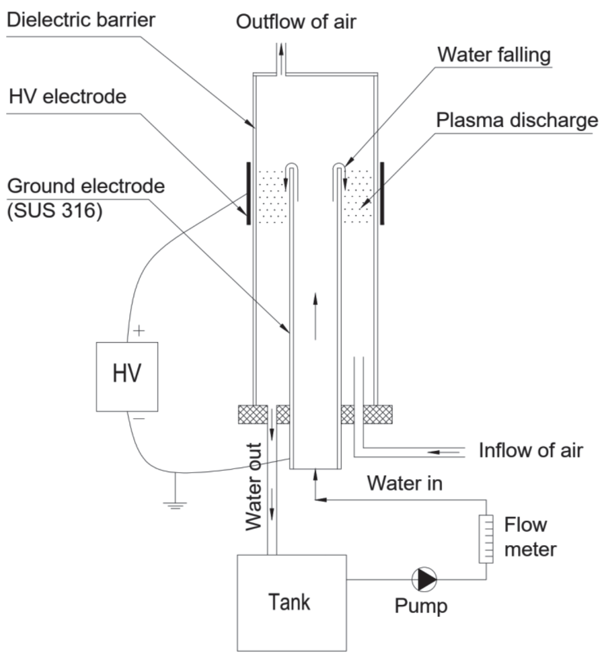

Fig. 1. Schematics of batch reactor configuration for plasma treatment.

0.35 mL/min, and the injection volume was 5 µL. The column temperature was kept at 25ºC and a UV detector was set at 420 nm. The solution pH value were measured using a pH meter (Oaklon, USA).

The degradation efficiently for each sample was calculated from the following Eq:

$$\eta = \left(\frac{(C_0 - C_t)}{C_0}\right) \times 100\% \qquad (13)$$

...where η was TNR degradation efficiency (%); C_t was TNR residual concentration at a given time *t* (mg/L); C_0 was TNR initial concentration (mg/L).

Results and Discussion

Effect of the Input Power on Degradation of TNR

Fig. 2 showed the degradation efficiency of TNR with different input powers using cold plasma. It was indicated that TNR could be effectively removed from aqueous solution by cold plasma and increasing input power favored the degradation process. With initial TNR concentrations of 135 mg/L, the discharge time of 120 min, 52.8%, 90.3% and 100% of TNR was removed when the input powers were 130, 250 and 370 W, respectively. However, regarding the strength of quartz tube, at the input power of 370 W, there is an appeared phenomenon of puncture of quartz tube by electric sparks. Therefore, the input power of 250 W was chosen for the next experiments.

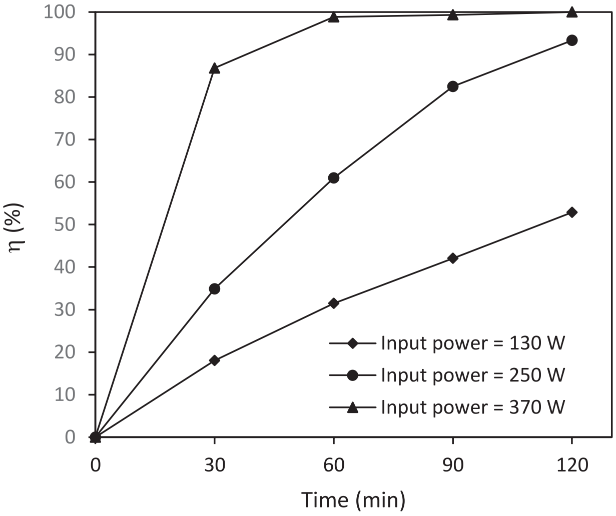

Fig. 2. Degradation efficiency of TNR with different input powers.

Effect of the Initial Concentrations on Degradation of TNR

The results in Fig. 3 show that, when the initial TNR concentration increases, the discharge time also increases. With the initial TNR concentration of 61.7 mg/L, after 120 minutes of discharge, the removal efficiency of TNR reached 100%. Meanwhile, with the initial concentration of 115.6 mg/L and 175 mg/L, the removal efficiency of TNR after 120 minutes was only 93.32% and 69.63%, respectively. In addition, an increase in the initial TNR concentration also enhanced the degradation rate due to the increased contact between the pollutant molecule and the oxidizing agents formed from the cold plasma.

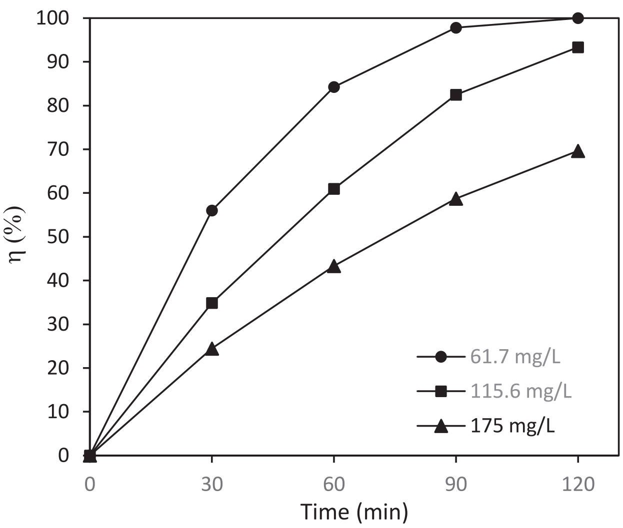

Fig. 3. Effect of the initial TNR concentrations on TNR degradation.

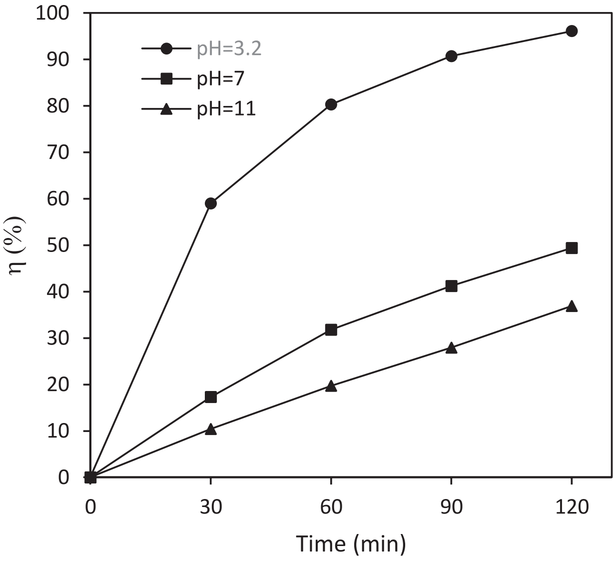

Fig. 4. Effect of the initial pH on TNR degradation.

Effect of the Initial pH on Degradation of TNR

The process of discharging electric sparks in the air not only forms oxidizing agents such as ozone, H_2O_2, UV light ... and •OH radicals, but also produces nitrogen compounds such as nitrates (NO_3^-), nitrites (NO_2^-) that make reduce the pH of the solution during discharge [3, 4, 6, 9, 10, 12, 13]. Therefore, in order to study the effect of initial pH on the removal efficiency of TNR, Borat buffer solution was used. The initial pH values of the TNR solution were selected as 3.2, 7.0 and 11.

The results in Fig. 4 show that TNR degradation efficiency in acidic medium is much higher than that in neutral and alkaline medium. This can be explained by the fact that an acidic medium is more conducive to the formation of O_3 and •OH than an alkaline medium due to the oxidation potential of oxidizing agents such as O_3, H_2O_2 and radical •OH in an acid medium lower in alkaline medium [5, 14]. Moreover, in acidic medium, H_2O_2 compounds can be decomposed into two •OH radicals by cold plasma (Eq. 14). In addition, in alkaline medium, there is an increase in reaction between H_2O_2 with OH radicals (Eq. 15) [15-18].

$$H_2O_2 + h\nu \rightarrow {}^{\bullet}OH + {}^{\bullet}OH \quad (14)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (15)$$

In addition, Grabowski (2006) [7] reported that the amount of O_3 generated in the plasma region is the highest at low pH (pH = 3.27). This is also one of the reasons why the TNR degradation efficiency in acidic medium is higher than that of neutral and alkaline medium.

Effect of Circulating Flow on Degradation of TNR

Research on the effect of the solution circulation on the TNR removal performance was performed in three circulation modes: 176, 450 and 833 mL/min. In which, the circulating flow of 176 mL/min is the smallest one that meets the amount of water creating a thin film of water evenly around the stainless steel tube electrode (Fig. 1). The results of the decomposition efficiency of TNR are presented in Fig. 5.

The results in Fig. 5 show that the higher the circulating flow, the greater the TNR removal efficiency. The result can be explained by the fact that when the circulating pump flow is large, the high level of fluid disturbance leads to uniform distribution of contaminants in the system, improving treatment efficiency. Moreover, when the circulating flow increases, combined with increasing the contact surface between the liquid and gas phases, the phase contact surface is always refreshed, leading to the mass transfer rate of oxidizing particles such as O_3, H_2O_2, •OH is enhanced, therefore the organic compounds treatment efficiency is improved [7].

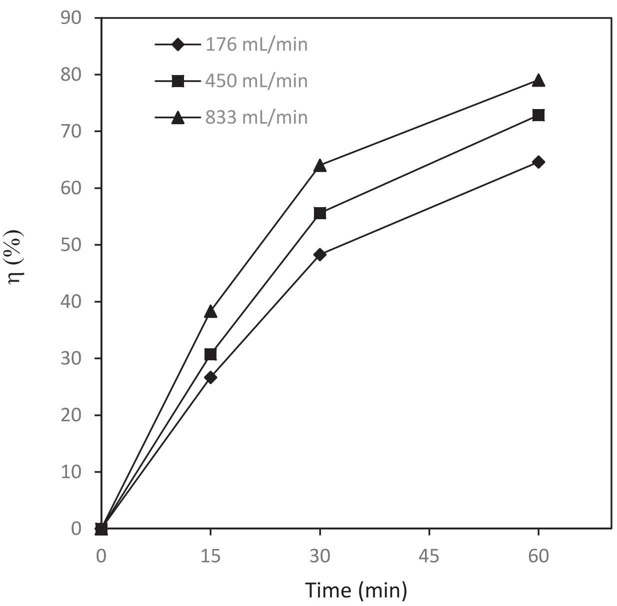

Fig. 5. Effect of circulating flow.

Effect of Electrode Distance on Degradation of TNR

The electrode distance has a great effect on the discharge to form cold plasma. Under the same conditions, when the distance between the two electrodes decreases, the potential (U) of plasma is reduced, which means reducing the power of the generator, saving electrical energy. The studies of H. Krause et al. [19] and Y. Zhang et al. [20] both stated that the voltage decreases when narrowing the gap between the two electrodes. However, a too narrow

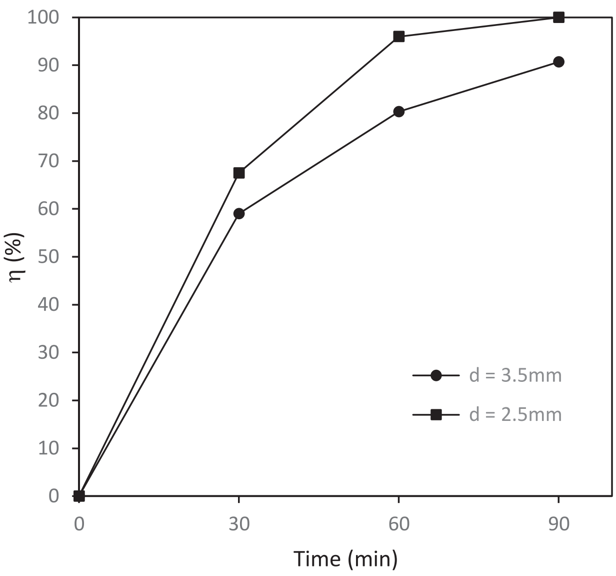

Fig. 6. Effect of electrode distance.

gap will reduce the plasma volume, which in turn can impair the ability to degrade organic compounds.

In this study, the stainless steel central electrode tube with an outer diameter of 21 mm was replaced with a 23 mm diameter tube to reduce the electrode distance from 3.5 mm to 2.5 mm.

The results in Fig. 6 show that when the electrode distance decreases from 3.5 mm to 2.5 mm (1.4 times reduction), the voltage between the two poles decreases from 19 kV to 16.5 kV (input power decreases from 250 W to 215 W) and the plasma volume (figure wall between 2 electrodes) decreased 1.35 times. However, the TNR removal efficiency enhanced quite significantly. Specifically, with electrode distance d = 2.5 mm, the TNR removal efficiency reaches 96% after 60 minutes of discharge. Meanwhile, with electrode distance d = 3.5 mm, TNR removal efficiency is only 80.3 in the first 60 minutes of discharge. The reason may be that increasing the inner electrode diameter from 21 mm to 23 mm will also increase the contact surface area between the liquid and plasma by approximately 1.2 times, thereby increasing the transfer efficiency of oxidizing agents such as O_3, H_2O_2, •OH… from the gas to the liquid phase, leading to enhanced TNR removal efficiency.

This result shows that reducing the electrode distance (1.4 times) not only reduces the input power (1.16 times reduction) but also improves the TNR removal efficiency (the TNR removal efficiency increases 1.1 times).

Effect of Some Oxidizing agents on Degradation of TNR

The purpose of this study is to evaluate the ability to activate some oxidants in the cold plasma reaction system to improve the removal rate of TNR. The factors selected to study include:

(i) H_2O_2: Adding H_2O_2 (with molar ratio TNR/H_2O_2 = 10) to the plasma reaction system to increase the original concentration •OH in the solution based on the reaction:

$$H_2O_2 + 2O_3 \rightarrow 2{}^\bullet OH + 3O_2 \quad (16)$$

$$H_2O_2 + h\nu \rightarrow 2{}^\bullet OH \quad (17)$$

$$H_2O_2 + O_3 + H_2O + h\nu \rightarrow 4{}^\bullet OH + O_2 \quad (18)$$

(ii) $Na_2S_2O_8$: Adding $Na_2S_2O_8$ (with molar ratio TNR/$Na_2S_2O_8$ = 10) to the plamsa reaction system to activate persulfate ions to create $SO_4^{-\bullet}$ radicals. $SO_4^{-\bullet}$ radical has very strong oxidizing properties with reduction potential E_0 = 2.6 V [6]. Non-selective reactivity of $SO_4^{-\bullet}$ radical with organic compounds similar to •OH radical (E_0 = 2.8 V) [11, 21]. The general reaction that activates persulfate to form sulfate $SO_4^{-\bullet}$ free radicals can be described as follows:

$$S_2O_8^{2-} \xrightarrow{activating\ agent} 2SO_4^{-\bullet} \quad (19)$$

Activating agents here can be temperature, UV light, transition metal, microwave, magnetite, etc.

(iii) O_2: The pure oxygen gas is introduced into the cold plasma reaction system at a flow rate of 3 L/min (redundancy) to enhance the ozone generation (O_3) according to the reactions (1) and (2).

The results in Fig. 7 show that all 3 chemicals added to the plasma reaction system have the ability to improve the TNR removal efficiency of the cold plasma. In particular, H_2O_2 gives the highest removal efficiency, many times higher than that of other reaction systems. Specifically, within the first 15 minutes of treatment, the TNR removal efficiency of the plasma/H_2O_2 system has reached 90%. It is higher 1.7 times of the plasma/O_2

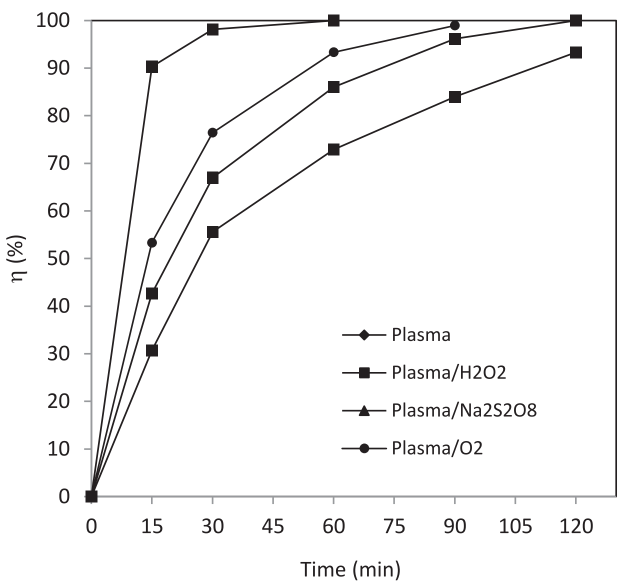

Fig. 7. Effect of some oxidizing agents on TNR degradation.

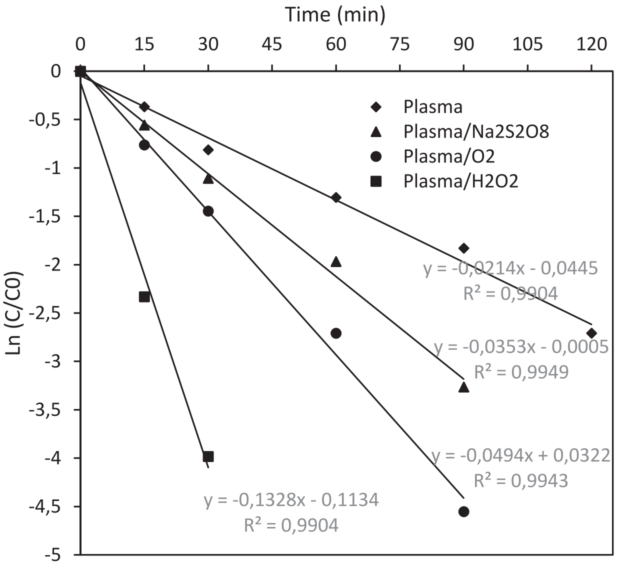

Fig. 8. Reaction kinetics for the degradation of TNR.

system, 2.1 times the plasma/$Na_2S_2O_8$ system and 2.9 times of the plasma/air system. And in just 60 minutes, the entire amount of TNR in the solution was removed. Meanwhile, for plasma/O_2 and plasma/$Na_2S_2O_8$, it takes 90 to 120 minutes to remove all pollutants. The reason may be that the addition of H_2O_2 will create more reactions based on advanced oxidation AOPs such as UV/H_2O_2; UV/H_2O_2/O_3; H_2O_2/O_3 compared with the addition of $Na_2S_2O_8$ and O_2. In addition, unlike the plasma/O_2 reaction system, which is a heterogeneous (gas/liquid) reaction, the reaction efficiency depends much on the mass transition of O_3 from the gas phase to the liquid phase, the reaction of the plasma/H_2O_2 system is a homogeneous reaction (liquid/liquid), it is capable of creating more direct oxidizing agents of pollutants.

As the degradation curves in Fig. 7 appeared to be exponential, an attempt was made to apply the data to the integral rate equation for the pseudo-first-order reaction Eq. (19).

$$ln\left(\frac{C}{C_0}\right) = -kt \qquad (20)$$

...where k denoted the rate constant (min^{-1}). Calculation results are shown in Fig. 8 below.

Fig. 8 shows that the linear correlation coefficient (R^2) of the degradation rate constant was quite high. It was 0.9904, 0.9949, 0.9943 and 0.9904 for for plasma, plasma/$Na_2S_2O_8$, plasma/O_2 and plasma/H_2O_2 systems, respectively. This means that the degradation process abided by the regulation of first order reaction kinetics.

Conclusions

A DBD plasma reactor was used for the degradation of TNR in aqueous solution. The results show that TNR could be effectively removed from aqueous solution by cold plasma. Under the experimental conditions, the TNR removal efficiency was proportional to the input electric power and the circulating flow rate, but inversely proportional to the initial pH, initial concentration and electrode distance. When the input power was 370W, the TNR removal efficiency was the highest, however due to the strength factor of quartz tube, the input power of 250W was chosen. Initial pH significantly influenced on the TNR removal efficiency. Accordingly, in acidic medium, the TNR removal efficiency was higher than that in neutral and alkaline medium and is highest at pH = 3.2. The presence of some oxidizing agents in the solution such as H_2O_2, $Na_2S_2O_8$, O_2 greatly increased the TNR removal efficiency under the effect of cold plasma. The TNR removal efficiency increased gradually by the range of plasma/H_2O_2>plasma/O_2>plasma/$Na_2S_2O_8$> plasma. The TNR degradation process in the presence and absence of the oxidizing agents all abided by the regulation of first order reaction kinetics.

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Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this article.

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