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Plasma Degradation of 1-Naphthylamine by Glow-discharge Electrolysis

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Abstract: A new method for degradation of 1-naphthylamine by glow discharge electrolysis is proposed. The degradation process was examined by using ultraviolet (UV) absorption spectrum and high performance liquid chromatography (HPLC). The chemical oxygen demand (COD) of sample was also measured. The results showed that 1-naphthylamine can be removed completely within 40 min in the absence of Fe^{2+} and within 2 min in the presence of Fe^{2+}. The optimum voltage used was at 600 V. The concentration of Fe^{2+} ion and the pH of solution exhibit an appreciable effect on the degradation rate. The COD of degradation sample was even higher than the original sample. This is because the benzene rings or naphthalene rings were destroyed and some organic acids were produced in this process.

Key words: Glow discharge electrolysis, 1-naphthylamine, degradation

INTRODUCTION

The permanent threat to natural environments, resulting from industrial activity and municipal infrastructures, focuses our continuing attention on the development of efficient technologies for the removal of anthropogenic pollutants from the environment. Among the various technologies, the advanced oxidation method is considered to be a potential way in several practical applications[1]. An economic analysis has been reported for the reagent on degradation of persistent organic pollutants in water for ground water remediation, where the addition of Fe^{2+} improves the efficiency by the elimination of the reducing species formed simultaneously with the OH• free radicals[2-5]. The use of the glow discharge electrolysis (GDE), chemical oxidation by hydroxyl radicals (•OH), is an area of active investigation. GDE may be efficient destroying 1-naphthylamine through hydroxyl radical processes. Hydroxyl radicals can be effectively generated by glow discharge electrolysis, which can remove organic amines and other organic compounds. It was considered to be an innovative technology to utilize in water treatment process[6,7].

1-naphthylamine is useful in growing food crops, which can make the seed germination and the control of weed[8]. It is also a dye intermediate, which is applied to yield direct dye, acidic dye and so on. Meanwhile, 1-naphthylamine is also an antioxidant in rubber and pesticide manufacture.

In this study, the effects of the initial concentration of Fe^{2+} and the effect of pH on the degradation of 1-naphthylamine (1-NA) were investigated, using HPLC and UV spectra to examine the degradation process. The chemical oxygen demand (COD) in the degradation process was also observed.

MATERIALS AND METHODS

The plasma degradation reactor was shown in Fig. 1, consist of an anode which was a platinum wire (0.5 mm in diameter) held in the brass support sealed into a glass tube. The cathode was a graphite plate (70 mm in diameter) suspended above the anode about 15 mm. The reaction cell was coated with an outer water jacket to keep the solution at a constant temperature. The electrolytic solution was prepared by dissolving reactants in a 250 mL of sodium sulfate (2 g L^{-1}). The supplied voltage used was 600 V and the range of electrolytic current was 120-150 mA. There was a magnetic stirring bar at the bottom of reactor to keep the solution mixed well. There was one door on the lid of the reactor used for taking samples during the experiments. The gas bubbles were produced in the glow discharge process. No gasses were introduced into the system in the present study.

The ultraviolet (UV) absorption spectra of reaction solutions were recorded by using a model UV-3400 Spectrometer (Hitachi, Japan) at intervals. In addition, a high performance liquid chromatography (HPLC) (ODS-18 reversed phase column; mobile phase: $H_2O/CH_3CN=50/50$) was used to analyze the degradation products. The chemical oxygen demand (COD) measurement was carried out using a COD analyzer. The pH of degradation solution was adjusted with NaOH or H_2SO_4 solution.

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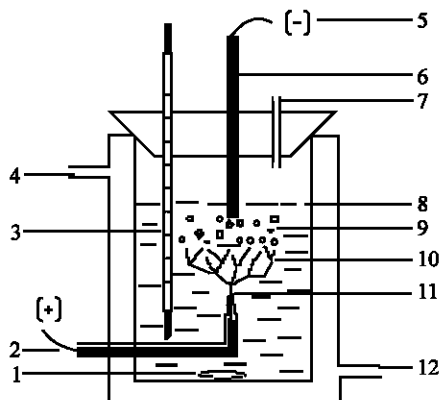
Fig. 1: Experimental setup of the glow discharge process.
1: stirring bar, 2: anode, 3: thermometer, 4: cooling
water outlet, 5: cathode, 6: graphite, 7: gas outlet,
8: solution level, 9: gas bubbles, 10: glow
discharge area, 11: platinum wire, 12: cooling
water inlet

RESULTS AND DISCUSSION

Typical current-voltage relationship: Figure 2 shows the
typical current-voltage characteristics in the degradation
process, which can be divided into several sections.
There is a linear section below 200 V (A→B), called the
conventional electrolysis proceeded with small gases
leaving the wire anode. When the voltage was raised up
to 200 V (B), the small flashes of light could be seen
around the anode. Between 200 V and 380 V (B→C), the
readings of both current and voltage fluctuated widely
and the flashes of light was vanished. From 380 to 520 V
(C→D), the current become stabilized and a smooth pale
sheath of vapor appeared. Over the voltage of 520 V
(D→E), the continuous reddish glow was brought into
view. The intensity of light emission increased with
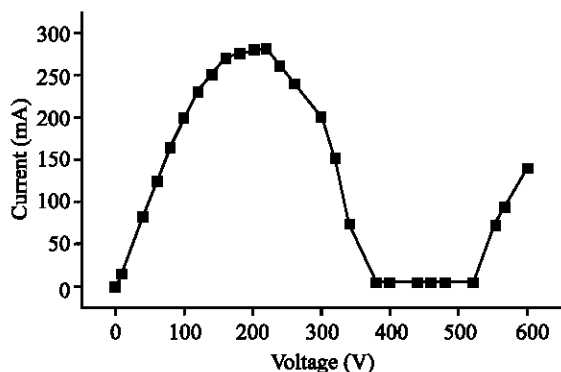increasing voltage, while the current was substantially

Fig. 2: The current-voltage characteristics in the
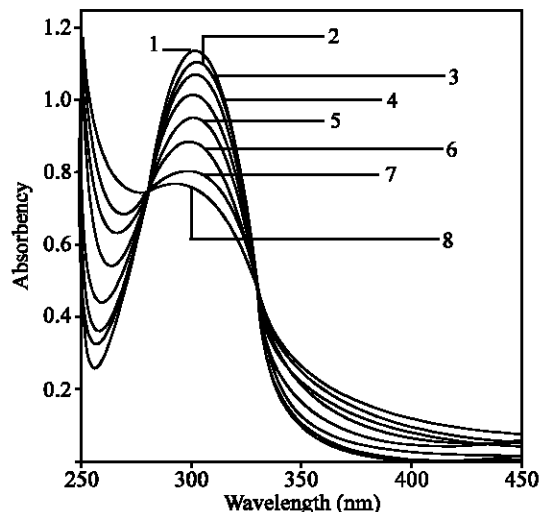degradation process

Fig. 3: UV spectra of the 1-naphthylamine at different
time in GDE. 1: untreated 1-naphthylamine
solution, 2: 30 sec, 3: 1 min, 4: 2 min, 5: 4
min, 6: 6 min, 7: 8 min, 8: 10 min

unchanged up to 300 mA. While if the voltage was too
high, it would consume energy and destroy the anode.
Hence, in this experiment, the degradation voltage was
kept at 600 V.

UV absorption spectra of 1-naphthylamine: Figure 3
shows the UV absorption spectra of 1-naphthylamine, the
medium was sodium sulfate solution and the initial
concentration of 1-naphthylamine was 30 mg L^{-1}. The UV
spectrum of sample shows a strong absorption near
300 nm before the reaction, which was reduced
gradually after 30 sec and reduced further 10 min later.
That is, the 1-naphthylamine was removed gradually in
this process. As illustrated in Fig. 3, the increase of
absorption near 254 nm may be due to accumulation of
glow discharge products, such as H_2O_2, O_3, etc.[9], or the
intermediates of the 1-naphthylamine decompositions.

HPLC of the 1-naphthylamine: In order to study the
degradation process further, a HPLC was used to
analyze intermediates. Before degradation, the profile of
1-naphthylamine solution was shown in Fig. 4, only
one strong peak at 6.082 min was observed. After
15 min, many stronger peaks appear (Fig. 5), that is,
the 1-naphthylamine was oxidized into some of
intermediates in the glow discharge electrolysis
(GDE). At that time, the concentration removed of
1-naphthylamine was about 50%. If a solution of 2.0×10^{-3}
mol L^{-1} Fe^{2+} ion was added into the above solution, the
total of 1-naphthylamine was almost disappeared and the
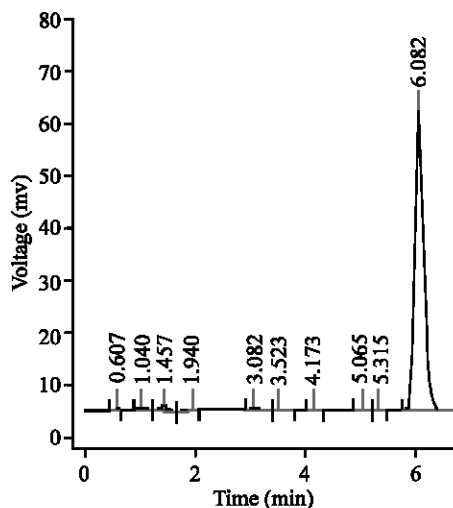corresponding intermediates were decreased rapidly

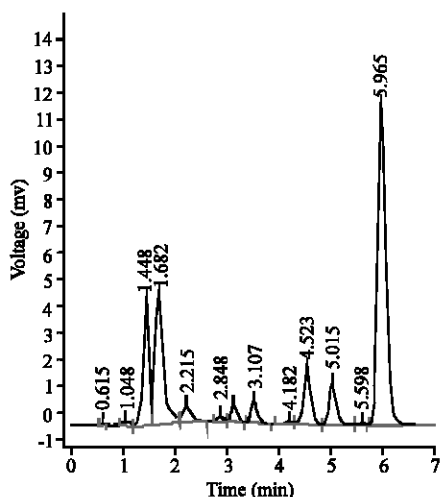Fig. 4: The high performance liquid chromatography of untreated 1-Naphthylamine (initial concentration = 30 mg L^{-1}) solution

Fig. 5: The high performance liquid chromatography of 1-Naphthylamine solution in 15 min (initial concentration = 30 mg L^{-1})

Table 1: pH and degradation rate of 1-naphthylamine under the degradation process

Condition	Time (min)	pH	Degradation rate (%)
	0	6.23	—
(a)	2	6.07	6.5
(a)	6	5.96	18.4
(a)	10	5.78	31.8
(a)	20	5.27	59.5
(a)	30	4.76	70.3
(a)	40	4.73	98.6
(b)	1	5.13	90.8
(b)	2	5.06	99.6

Note: (a) glow discharge in the absence of Fe^{2+} ion;
(b) glow discharge in the presence of Fe^{2+} ion (2.0×10^{-3} mol L^{-1})
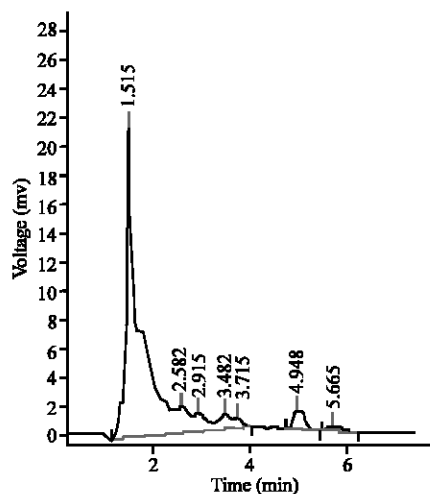
Fig. 6: The high performance liquid chromatography of 1-Naphthylamine solution with 2.0×10 mol L^{-1} Fe^{2+} in 2 minutes (initial concentration = 30 mg L^{-1})

within 2 min, too (Fig. 6). These results suggested that the 1-naphthylamine could be degraded in a glow discharge electrolysis reactor and that the degradation was strongly dependent upon the presence of iron salt. It was indicated that the increased removal of 1-naphthylamine in the presence of Fe^{2+} ion was due to the well-known Fenton's reaction[10].

It also can be seen from the Table 1, which given the changes in degradation rate of 1-naphthylamine solution with treatment time for the conditions (a)-(b). This study have compared the rate of degradation of 1-naphthylamine between (a) glow discharge in the absence of Fe^{2+} ion and (b) glow discharge in the presence of Fe^{2+} ion.

Table 1 shows the comparison between the degradation in the absence and the presence of Fe^{2+}. If there is no Fe^{2+} ion, the completed degradation would last 40 min; in contrast to the reaction, in the presence of Fe^{2+} ion, it need only 2 min. The experimental data indicate that the Fe^{2+} ion can increase remarkably the reaction rate.

The experiments were also performed to determine the effect of Fe^{2+} concentration on the 1-naphthylamine degradation rates. The experimental data in Fig. 7 show the effects of iron concentration on the removal of 1-naphthylamine from a solution with an initial concentration of 1.0×10^{-4} mol L^{-1}, parts of 1-naphthylamine degradation occurs. However, as the iron concentration is increased up to 1.0×10^{-3} mol L^{-1}, the rate of 1-naphthylamine degradation increases dramatically and it even faster when the iron concentration was 2.0×10^{-3} mol L^{-1}. We can see that although Fe^{2+} concentration is increased to 1.0×10^{-2} mol L^{-1}, the rate of 1-naphthylamine degradation increased no longer. Thus, the decrease of the degradation in this case was caused by the over
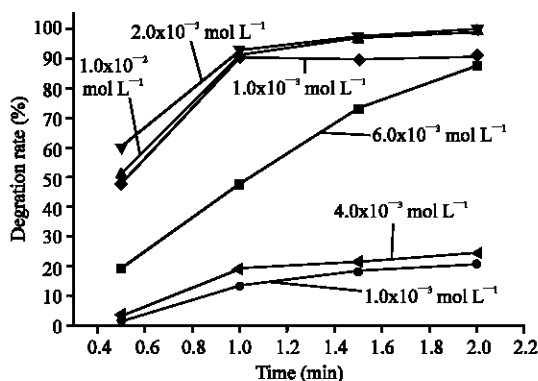
Fig. 7: Experimental results showing the effect of iron concentration on 1-NA degradation (initial 1-NA concentration =30 mg L^{-1})

oxidation of 1-naphthylamine. So, an optimal value of ferrous ion concentration applied for the degradation in this experiment is 2.0×10^{-3} mol L^{-1}.
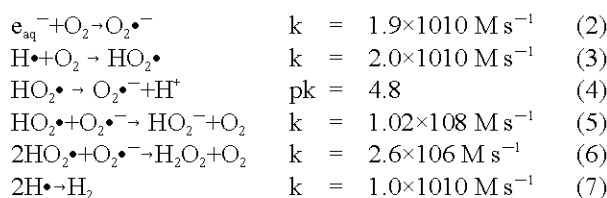
The reasons for the phenomena were presumed as follows:

There are three main reactive species in degradation, e.g., hydrogen atoms (H•), solvated electrons (e_{-aq}) and hydroxyl radicals (•OH), as well as reactive species such as H_2O_2, H_3O^+ and H_2 (Eq (1))[11].

$$H_2O_2 \to e_{aq}^- (2.6) + \bullet H (0.6) + \bullet OH (2.7)$$
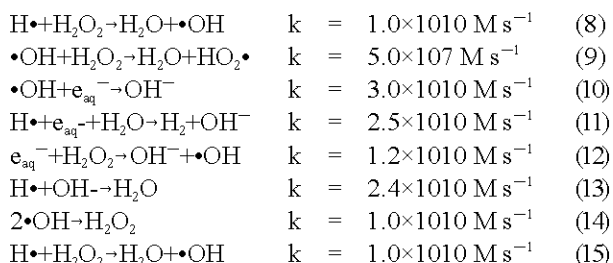$$+ H_2 (0.45) + H_2O_2 (0.7) + H_3O + (2.7) \qquad (1)$$
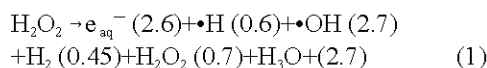
The distribution of these chemical species has been studied extensively[12-14] and the values in parentheses in Eq (1) are referred to as free energy G values. By definition G is the number of reactive species, excited states or other products formed or destroyed in a system absorbing 100 eV of energy.

The removal and ultimate destruction of organic chemicals in aqueous solution occurs primarily as a result of the reaction of three transient reactive species, H•, e_{aq}^- and •OH. However, in the presence of air, the H• and e_{aq}^- are scavenged by oxygen, forming $HO_2\bullet$ and O_2^- (Eqs (2)-(5)) at the lower doses[15].

$e_{aq}^- + O_2 \to O_2\bullet^-$	k	=	1.9×1010 M s^{-1}	(2)
$H\bullet + O_2 \to HO_2\bullet$	k	=	2.0×1010 M s^{-1}	(3)
$HO_2\bullet \to O_2\bullet^- + H^+$	pk	=	4.8	(4)
$HO_2\bullet + O_2\bullet^- \to HO_2^- + O_2$	k	=	1.02×108 M s^{-1}	(5)
$2HO_2\bullet + O_2\bullet^- \to H_2O_2 + O_2$	k	=	2.6×106 M s^{-1}	(6)
$2H\bullet \to H_2$	k	=	1.0×1010 M s^{-1}	(7)

Generally, $O_2\bullet^-$, •OH and H_2O_2 have a very high activity and the concentration •OH is higher than $HO_2\bullet$ and $O_2^-\bullet$, they are generally thought to contribute

minimally to the degradation of compounds (Eqs.(8)-(15))[16].

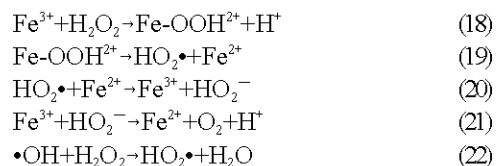|				
$H\bullet + H_2O_2 \to H_2O + \bullet OH$	k	=	1.0×1010 M s^{-1}	(8)
$\bullet OH + H_2O_2 \to H_2O + HO_2\bullet$	k	=	5.0×107 M s^{-1}	(9)
$\bullet OH + e_{aq}^- \to OH^-$	k	=	3.0×1010 M s^{-1}	(10)
$H\bullet + e_{aq}^- + H_2O \to H_2 + OH^-$	k	=	2.5×1010 M s^{-1}	(11)
$e_{aq}^- + H_2O_2 \to OH^- + \bullet OH$	k	=	1.2×1010 M s^{-1}	(12)
$H\bullet + OH \to H_2O$	k	=	2.4×1010 M s^{-1}	(13)
$2\bullet OH \to H_2O_2$	k	=	1.0×1010 M s^{-1}	(14)
$H\bullet + H_2O_2 \to H_2O + \bullet OH$	k	=	1.0×1010 M s^{-1}	(15)

In the presence of Fe^{2+} ion, the chemical mechanisms propose hydroxyl radicals as the oxidant species, which are generated in the following chemical equation[17]:

$$Fe^{2+} + H_2O_2 \to Fe^{3+} + OH^- + \bullet OH \qquad (16)$$
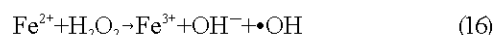
Hydroxyl radicals may be scavenged by reaction with another Fe^{2+} ion:

$$\bullet OH + Fe^{2+} \to Fe^{3+} + OH^- \qquad (17)$$

Fe^{3+} can catalytically decompose H_2O_2 following a radical mechanism that involves hydroxyl and radicals, including (16) and (17):

$Fe^{3+} + H_2O_2 \to Fe\text{-}OOH^{2+} + H^+$	(18)
$Fe\text{-}OOH^{2+} \to HO_2\bullet + Fe^{2+}$	(19)
$HO_2\bullet + Fe^{2+} \to Fe^{3+} + HO_2^-$	(20)
$Fe^{3+} + HO_2^- \to Fe^{2+} + O_2 + H^+$	(21)
$\bullet OH + H_2O_2 \to HO_2\bullet + H_2O$	(22)

Effect of the pH of solution: From the above equations, it was noted that H^+ ion was produced as a by-produced. The pH of degradation solution was measured and the results have been summarized in the Table 1. The results show that the pH of the solution decreased with increasing degradation in general. But we also want to know the effect of pH of the initial solution on the degradation rate. We change the pH from 3.5 to 7.5 in the same initial concentration and the same degradation time (15 min). The experimental data show that when the pH is about 5, the degradation rate of 1-naphthylamine is the largest (Fig. 8). The degradation rate was remain 72% at the pH 6~8. So the pH of untreated solution has also appreciable effect on the degradation of 1-naphthylamine.

COD measurements: The chemical oxygen demand (COD) of sample solution was determined during the degradation process of 1-naphthylamine, whose
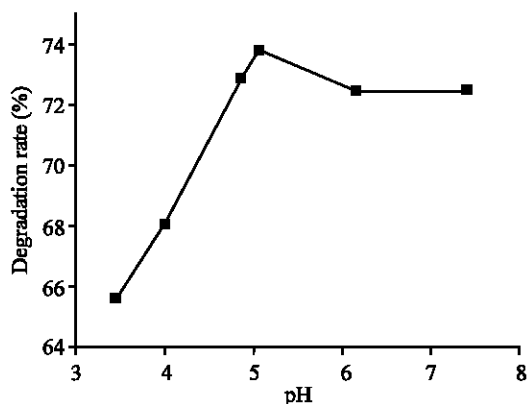
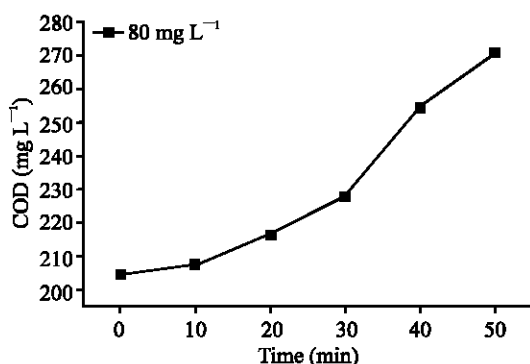Fig. 8: A plot of degradation rate vs. pH of the degradation solution

Fig. 9: The relationship between the COD of 1-naphthylamine and the degradation time

concentration was $80 \, mg \, L^{-1}$. The results are shown in the Fig. 9. The COD are rising with the lasting of degradation; this is due to a lot of action particles attacking the 1-naphthylamine from all parts in this process and gradually producing many small molecules of organic acid after opening the rings.

It can be concluded that 1-naphthylamine can exhaustively degraded by GDE in this set-up. Increasing the applied voltage is favorable for the removal of 1-naphthylamine. The degradation may be carried out with different way in the presence and absence of Fe^{2+}. In the presence of Fe^{2+} ion, the hydroxyl radicals may be as the oxidant species. The pH of untreated solution has also appreciable effect on the degradation. The COD were rising with the degradation time lasted. There is a need for further developments in the area of water treatment by GDE.

ACKNOWLEDGMENTS

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