

# Application of electrochemical plasma on iron electrodes for treating 2,4-Dichlorophenoxyacetic acid (2,4-D) and 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) in water environment

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## Research Article

**Keywords:** electrochemical plasma, cold plasma, high-voltage DC, iron electrode, treatment 2,4-D pollution, treatment 2,4,5-T pollution

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33 quantitatively by a calibration curve from GC-MS 6890-5975 Agilent system or high  
34 performance liquid chromatograph HPLC 1100 Agilent system. The treatment process  
35 can be controlled to achieve optimum performance by technological factors such as input  
36 voltage, distance between anode and cathode electrodes, initial concentration of 2,4-D and  
37 2,4,5-T as well as flowing air through solution. The analysis results showed that the  
38 degradation efficiency of 2,4-D and 2,4,5-T reached at 99.98%; 99.83%, respectively.

39 **Keywords:** electrochemical plasma; cold plasma; high-voltage DC; iron electrode;  
40 treatment 2,4-D pollution; treatment 2,4,5-T pollution.

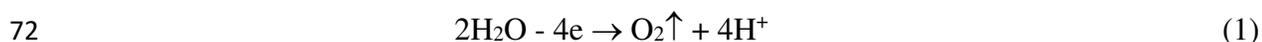
## 41 **1. Introduction**

42 Plasma is the fourth state of matter, plasma is classified based on temperature and is  
43 divided into high thermal plasma and cold plasma. Thermal plasma occurs at high  
44 temperatures ranges from  $10^6$ ÷ $10^8$  K. Thermal plasma is the fusion reaction, solar wind,  
45 stars. Cold plasma occurs in low temperature ranges from  $300$ ÷ $2\times 10^4$  K (Bogaerts et al.  
46 2001; Vijay et al. 2014). It usually is the process of electric discharge at high voltage from  
47  $0$ ÷ $40$  kV and can be generated by many different techniques such as AC voltage, DC  
48 voltage, pulse voltage (Reddy et al. 2012; Locke et al. 2006). The cold plasma can be  
49 classified into various categories such as electric discharge in air, electric discharge in  
50 solution, electric discharge in low pressure or electric discharge in high pressure. It also  
51 depends on the characteristics of the dielectric layer. On the other hand, under various  
52 electric discharge conditions will lead to the generation of  $\text{OH}\cdot$ ,  $\text{O}\cdot$ ,  $\text{H}\cdot$  free radicals as  
53 well as  $\text{O}$ ,  $\text{H}$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$  active species were different (Sengupta et al. 1994; Sengupta et al.  
54 1998; Burlicaa et al. 2004; Kogelschatz et al. 2002; Joshi et al. 1995; Nishioka et al. 2009;  
55 Ruma et al. 2018; Barni et al. 2019). These are agents that has high redox properties  
56 (Kanazawa et al. 2012). For these reasons, cold plasma has many practical applications,  
57 such as it is used in the medical to treat cancer or use in the surface treatment or the using  
58 for material manufacture industry and food preservation technique. Especially, it is used  
59 commonly in environmental treatment such as waste water treatment, exhaust gas  
60 treatment, drinking water treatment (Li et al. 2013; Stara et al. 2009; Dojcinovic et al. 2009;  
61 Jiang et al. 2014; Sayed at al. 2015); EL-Tayeb et al. 2016; Tanino et al. 2020). One of the  
62 way is used to treat pollutant compounds is method using high voltage DC, combined with

63 iron electrode. The process of electric discharge direct in solution create free radicals and  
 64 other active pecies such as OH•, H<sub>2</sub>O<sub>2</sub> (Lukes et al. 2012; Tachibana et al. 2011). In  
 65 addition, the corrosion process on iron anode electrode also produces Fe<sup>2+</sup> ions, which  
 66 play as Fenton agents role and making increase the degradable efficiency of pollutant  
 67 organic substances (Dors et al. 2007; Trung et al. 2010; Abdelmaleka et al. 2008; Hao et al.  
 68 2007; Grymonpre et al. 2004).

69 The free radicals and other active species can be formed according to the mechanisms  
 70 following:

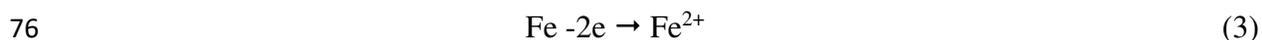
71 The electrolysis reaction releases oxygen gases on the anode electrode:



73 The electrolysis reaction releases hydrogen gases on the cathode electrode:



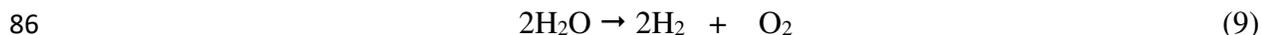
75 The electrolysis reaction dissolve iron anode electrode:



77 The mechanisms generate the free radicals and the active species ( Anpilov et al. 2001;  
 78 Itikawa et al. 2005; Porter et al. 2009):



83  
 84 Plasma decomposes water by the reaction mechanism follow ( Kirkpatrick et al. 2005):



87 The Fenton reaction produces OH• free radicals according to the reaction (Chen et al.  
 88 1997):



## 90 **2. Experimental procedures**

### 91 **2.1. Materials**

92 The power source is used in the study is the high voltage DC, the voltage is regulated  
93 stepless from 0 to 20 kV, power capacity from 0 to 30 kVA, the electrode material uses  
94 in the reaction is made of Fe, the electrode diameter  $\varnothing = 3$  mm, the electrode length  $l = 250$   
95 mm, the iron electrode is molded by surrounding epoxy layer, the iron electrode area that  
96 contact with water is 7.068 square millimeter. The reaction vessel is made of heat resistant  
97 glass and it is structured consisting of two layers, the inside layer contains the reaction  
98 solution, the outside layer contains cooling water that is pumped cyclically. The reaction  
99 vessel has a valve to get the reaction solution on below and a valve to release gases at the  
100 top, the reaction process is observed by camera. The description of the reaction diagram in  
101 Fig1: 1.High voltage DC: 0÷20 kV; 2.Control box; 3.Anode electrode; 4.Cathode electrode;  
102 5.Solution in; 6.Solution out; 7.Exhaust gases; 8.Cooling water out; 9.Cooling water in;  
103 10.Glass layer; 11.Camera; 12.Air flow pump.

104 The 2,4-D and 2,4,5-T herbicide are pure from Merck, Germany. The double distilled  
105 water has electric conductivity of 1.3  $\mu\text{S}/\text{cm}$  and pH of 7. The concentration of 2,4-D and  
106 2,4,5-T is dissolved in double distilled water was 30 mg/L for each one. BSTFA is used to  
107 silylate organic acids in solution and analyzing by gas chromatograph mass spectrometer  
108 GC-MS 6890-5975 Agilent.

## 109 **2.2. Methods**

110 The using high performance liquid chromatography HPLC 1100 Agilent to analyze  
111 degradable ability of 2,4-D and 2,4,5-T. The sample is injected direct into the HPLC system  
112 with analytical conditions as: hypersil column  $\text{C}_{18}$  (200 x 4mm),  $\lambda = 285$  nm, the mobile  
113 phase with component of acetonitril and  $\text{H}_2\text{O} = 70:30$  (v/v), the flow rate 0.5 mL/min,  
114 pressure 60 bar. The qualitative determination of intermediate products is formed in  
115 reaction solution from 2,4-D and 2,4,5-T decomposition by how to analyze on GC-MS  
116 6890-5975 Agilent system. The analytical process with the water sample is extracted by  
117 diethyl ether and is derived with BSTFA to form volatile compounds . After that, the  
118 sample is analyzed on the HP-5MS column with the conditions as: scan parameter 35÷550  
119 au, initial flow He 1.3 mL/min, average velocity: 41 cm/sec, energy: 70 keV, temperature  
120 program: initial temperature 40 °C, rate 10 °C/minute, final temperature 280 °C, hold time

121 5 minutes, injection volume 1  $\mu$ L. Measuring the conductivity of a solution by how to use  
122 Hanna HI 8314 machine. The amount of chemicals is weighed on the Shimadzu ATX 224  
123 analytical balance with an accuracy of  $\pm 0.1$  mg.

### 124 **3. Results and discussion**

#### 125 ***3.1. The degradable process of 2,4-D and 2,4,5-T depends on reaction factors***

126 Studing the degradable effect of the 2,4-D and 2,4,5-T depend on time. The  
127 experiment was carried out under the condition following: the distance between two  
128 electrodes was 300 mm, the initial concentration of the 2,4-D and 2,4,5-T solutions were  
129 the same, with value was 30 mg / L, the input voltage was 5 kV. Research results show that  
130 degradable efficiency achieved for 2,4-D was 47.93%; 67.13%; 79.70%; 86.60%.  
131 Similarly, the degradable efficiency for 2,4,5-T was 36.97%; 50.80%; 61.83%; 71.17%  
132 corresponds to a reaction duration time of 30 minutes; 60 minutes; 90 minutes; 120  
133 minutes, respectively. As such, it can be seen that degradable efficiency increases over time  
134 (Fig 2a). For this reason, when increases reaction time leading to OH $\bullet$  free radicals content  
135 and amount of active species such as H<sub>2</sub>O<sub>2</sub> went up. Thus, the oxidative ability and decay  
136 of 2,4-D and 2,4,5-T also grow. The results also indicated that the degradable efficiency of  
137 2,4-D was higher than that of 2,4,5-T at the same time. For this cause, its can be due to the  
138 2,4,5-T molecule had Cl content in benzene ring higher than 2,4-D leading to molecular  
139 structure of 2,4,5-T was more sustainable and therefore degradable efficiency was lower  
140 than 2,4-D.

141 Besides, the decay of 2,4-D and 2,4,5-T also depends on the input voltage, the  
142 experimental results descripted that the degradable efficiency achieved for 2,4-D was  
143 18.5%; 40.97%; 63.17%; 76.5%; 85.9%. Simultaneously, the decomposition rate for  
144 2,4,5-T was 14.3%; 34.2%; 55.10%; 70.17%; 81.77% corresponds to the input voltage of 2  
145 kV; 4 kV; 6 kV; 8 kV and 10 kV. The reason for the increase in decomposition efficiency  
146 was due to increasing input voltage. Thus, the leading to the plasma formation was earlier.  
147 In addition, the area of the plasma that was formed be larger. There fore, the formation of  
148 free radicals and active species were more than. It means that oxidative ability was higher  
149 according to formulas (1) to (10) that was cited above. Because of this, the degradable  
150 efficiency of 2,4-D and 2,4,5-T pollutants will increase with voltage (Fig 2b).

151 Fig 3a illustrated the influence of electrode distance and Fig 3b described the effect of  
152 the initial concentration on the decay ability of the 2,4-D and 2,4,5-T compounds. The  
153 experimental results showed that when electric discharging at 5kV input voltage, with the  
154 initial concentration of 30 mg/L, after 30 minutes, decomposition performance of 2,4-D  
155 decreased according to distance between two electrode was 56.22%; 47.93%; 36.19%;  
156 27.68%; 10.05%; for 2,4,5-T, decomposition efficiency achieved under the same conditions  
157 was 45.56%; 36.97%; 28.56%; 20.47%; 4.69% corresponds to the value increase of the  
158 electrode distance was 250 mm; 300 mm; 350 mm; 400 mm to 500 mm, respectively.  
159 From the results it can be seen that when distance was larger, the degradative efficiency of  
160 the 2,4-D and 2,4,5-T was lower. The cause of the degradative decrease can be due to the  
161 increase in the distance between the two electrodes leading to the reduction of the kinetic  
162 energy of the electrons in the solution as well as the process of plasma formation occurred  
163 slower and the area of plasma is formed smaller. Therefore, the ability to form OH• free  
164 radicals and active species as H<sub>2</sub>O<sub>2</sub> were lower, their content was also decline. Because of  
165 this cause, the result leading to reduce the decay ability of 2,4-D and 2,4,5-T when the  
166 distance between the two electrodes rised.

167 The degradation efficiency depends on the initial concentration. When 2,4-D and  
168 2,4,5-T concentration increased from 30 mg/L to 50 mg/L. The scale of the oxidative agent  
169 compared with the pollutant compounds was reduction due to the formation of OH• and  
170 H<sub>2</sub>O<sub>2</sub> under the same conditions was not changed, for this reason, leading to reduced  
171 degradation efficiency (Fig 3b). The analytical results presented that the 2,4-D degradation  
172 efficiency at 30 mg/L concentration was 47.93%; 67.13%; 79.70%; 86.60%, meanwhile,  
173 the decomposition efficiency of 2,4-D at 50 mg / L concentration was only achieved  
174 36.23%; 51.98%; 60.75%; 65.38%. The similar results also showed that when the initial  
175 concentration of 2,4,5-T was 30 mg/L, the degradation efficiency was 36.97%; 50.80%;  
176 61.83%; 71.17%, when increasing the initial concentration of 2,4,5-T to 50 mg/L, the  
177 degradation efficiency achieved at 21.35%; 39.46%; 53.95%; 62.81% corresponds to the  
178 electrolysis reaction time and plasma appearance time was 30 minutes, 60 minutes, 90  
179 minutes and 120 minutes, respectively. It was clear that the initial concentration of 2,4-D

180 and 2,4,5-T affected to the decay efficiency. It means that when the initial concentration  
181 was high leading to the degradation efficiency went down.

182 Especially, the electric discharge process had plasma appearance, simultaneously,  
183 combined with process flowing air via the solution with the flow was about 500 mL per  
184 minute to make increasing the decay efficiency of 2,4-D and 2,4,5-T (Fig 4a). The  
185 experimental results at time of 30 minutes; 60 minutes; 90 minutes and 120 minutes  
186 indicated that when 2,4-D concentration was 30 mg/L then the treatment efficiency  
187 reached 49.61%; 72.24%; 89.18%; 99.98%, respectively. Besides, at a concentration of  
188 2,4,5-T of 30 mg/L, the treatment efficiency was lower and the values only reached  
189 38.72%; 67.52%; 85.26%; 99.83%, respectively. It can be seen that the decomposition  
190 efficiency achieved the highest when had a process of the flowing air through the solution.  
191 This can be explained by the facts that when the air flowing through the solution, it would  
192 contact with plasma and therefore, would do increasing the concentration of free radicals  
193 leading to rised oxidative ability and increased the destruction ability of 2,4-D and 2,4,5-T  
194 pollutant compounds (Anpilov et al. 2001; Burlicaa et al. 2004). In general, from the  
195 research results, it can be seen that when the air is flowed through the solution, the  
196 treatmental process efficiency reached the highest.

197 The intermediate products of the reaction were straight chain organic acids. Oxidative  
198 process leads to opened of the benzene ring and next step was oxidative process of long  
199 chain acids and cut them into shorter chain acids and the final, these acids is oxidized  
200 completely to generate product CO<sub>2</sub> and H<sub>2</sub>O. In the electric discharging process of the  
201 reaction in the solution leading to form the organic acids that did changing and increasing  
202 of electrical conductivity (Fig 4b).

### 203 ***3.2. Kinetic of decomposition process 2,4-D and 2,4,5-T***

204 The Fig 5a showed the concentration of 2,4-D and 2,4,5-T contaminant compounds  
205 that is degraded depending on the duration time of reaction. The Fig 5b shows the  
206 dependency on the time between the scale of 2,4-D concentration in solution (c) comparing  
207 to the initial concentration (c<sub>0</sub>) and which is presented as the formula type  $\ln(c/c_0)$ .

208 From the graph in Fig 5a, it can be seen clearly that hyperbolic curve that characterize  
209 for the differential equation of the 2,4-D and 2,4,5-T decomposition kinetic reaction , it is

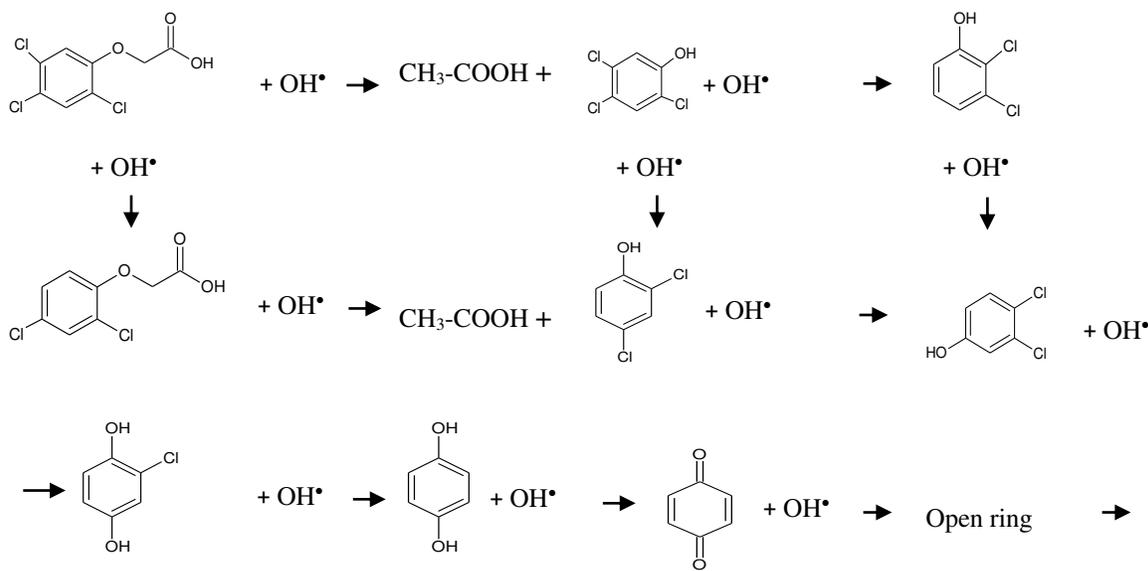
210 presented by math equation:  $v = dc/dt = k(c_0 - c)$ . The Fig 5b described the differential  
211 equation  $\ln(c/c_0) = kt$  that has a straight line kind corresponding to reflecting the model of  
212 pseudo first order kinetic for the 2,4 -D; 2,4,5-T decomposition process by the current of  
213 the high voltage DC with plasma appearance on the iron electrode:  $y = ax + b$ . For 2,4-D,  
214 the value of the slope coefficient is calculated as:  $a_{2,4-D} = - 0.016$ ; the value of the intercept  
215 coefficient is calculated as:  $b_{2,4-D} = - 0.070$ ; the value of R square correlation coefficient is  
216 calculated as:  $R^2_{2,4-D} = 0.992$ ; the reaction rate constant is calculated be:  $k_{2,4-D} = 0.016$   
217  $\text{min}^{-1}$ . For 2,4,5-T, the value of the slope coefficient is calculated as:  $a_{2,4,5-T} = - 0.010$ ; the  
218 value of the intercept coefficient is calculated as:  $b_{2,4,5-T} = - 0.084$ ; the value of R square  
219 correlation coefficient is calculated as:  $R^2_{2,4,5-T} = 0.974$ ; the reaction rate constant is  
220 calculated as:  $k_{2,4,5-T} = 0.010 \text{ min}^{-1}$ . Thus, it can be seen that the 2,4-D decomposition  
221 reaction rate was greater than the decomposition reaction rate of 2,4,5-T under the same  
222 conditions.

### 223 ***3.3. Propose the mechanism for 2,4-D and 2,4,5-T decomposition process***

224 The 2,4-D; 2,4,5-T pollutant decomposition reaction is performed under conditions:  
225 2,4-D; 2,4,5-T concentrations were the same and reach 30 mg/L; electrode distance of 300  
226 mm, input voltage of 5 kV. The intermediate products after decomposition process is  
227 extracted and transformed into a volatile compounds form by how to silylate with BSTFA.  
228 After that, analyze on GC-MS Agilent 6890-5975 system. The analysis spectrum of the  
229 degradable products from 2,4-D and 2,4,5-T is illustrated in the Fig 6.

230 The analytical results showed that 2,4,5-T and 2,4-D decomposed into intermediate  
231 organic compounds as 2,4,5-TCP; 2,4-DCP; 3,4-DCP; 2,3-DCP. These clophenol  
232 compounds are oxidized by free radicals  $\text{OH}\cdot$  to reduce chlorine atom in the aromatic ring  
233 and continue to create hydroquinone. Hydroquinone is oxidized and open ring into the  
234 straight chain organic acids. These organic acids had different chain length and can be  
235 oxidized to carboxylic acid at one or both ends of the carbon chain. The hexanoic acid had  
236 carbon chain was the longest and the acid formic had carbon chain was the shortest.  
237 Finally, these organic acids are oxidized to carbon dioxide and water.

238 From the analytical results mentioned above. It can be assumed that the decomposition  
239 process of 2,4-D and 2,4,5-T according to mechanism as follows:



Pentanoic acid, 4-on  
 Hexanoic acid  
 Propanoic acid, 2-ol  
 Pentanoic acid  
 Succinic acid  
 Propanoic acid, 2-methyl + OH• → CO<sub>2</sub> + H<sub>2</sub>O  
 Propanoic acid  
 Oxalic acid  
 Acetic acid  
 Formic acid

240 Thus, it can be seen that the degradable mechanism of 2,4-D and 2,4,5-T were almost  
 241 the similar, the decomposition process of 2,4,5-T was longer because it went through more  
 242 than the intermediate steps to reduce chlorine atom because the 2,4,5-T aromatic ring had  
 243 more chlorine atom than 2,4-D aromatic ring. The analysis results of decomposition  
 244 efficiency also showed that under the same conditions, the decomposition efficiency of  
 245 2,4,5-T was always smaller than the decomposition efficiency of 2,4-D.

#### 246 4. Conclusions

247 The high voltage electric discharge process occur on iron electrode that is immersed in  
 248 an aqueous solution. It caused plasma formation and created free radicals. In particularly,  
 249 the OH• free radicals with a high oxidation potential caused oxidative and degradable  
 250 process of 2,4-D; 2,4,5-T pollutant organic compounds. The oxidation process depended on  
 251 the factors such as the electric discharge time; input voltage; initial concentration; distance  
 252 between two electrodes, and the process of the flowing air through the solution. The

253 experimental results also showed that the treatment ability of 2,4-D; 2,4,5-T reached up to  
254 99.98%; 99.83% , respectively, when discharging electric with plasma appearance and  
255 combining with the process flowing air via the solution. The studying the kinetic of 2,4-D,  
256 2,4,5-T oxidative reaction obey the model of pseudo first order with the reaction rate  
257 constant  $k_{2,4-D} = 0.016 \text{ min}^{-1}$ ,  $k_{2,4,5-T} = 0.010 \text{ min}^{-1}$ . From the reaction rate constant of  
258 2,4-D and 2,4,5-T showed that the oxidative rate of 2,4,5-T was lower than 2,4-D.

259 The analyzing of the intermediate products by GC-MS 6890-5975 Agilent system  
260 showed that the degradable reaction and oxidative process of 2,4-D; 2,4,5-T were  
261 performed by  $\text{OH}^\bullet$  free radicals. The intermediate product was straight chain organic acids,  
262 which do increasing the electric conductivity of the reaction solution and the oxidative  
263 process always was happened leading to results was cutting long chain organic acids into  
264 short chain organic acids until the final product was carbon dioxide and water. Therefore,  
265 it can be seen that the high voltage electrochemical reaction with the electric discharge and  
266 combining with the plasma formation could decompose almost completely the pollutant  
267 compounds in the water environment of 2,4-D; 2,4,5-T that was difficult to treat by other  
268 methods.

#### 269 **Note:**

270 - Ethical Approval: Not applicable

271 - Consent to Participate: Not applicable

272 - Consent to Publish: Not applicable

273 - Authors Contributions: Cong Van Tran, MSc conducted researching and experiment.

274 Hung Duc Nguyen, Ph.D designed for high voltage power sources and reactors. Dung Thi Ngoc  
275 Tran, Dr and Hoang Van Nguyen, Dr analyzed the data and contributed equally to this  
276 work.

277 - Funding: Not applicable

278 - Competing Interests: Not applicable

279 - Availability of data and materials: The datasets used and analysed during the current study are  
280 available from the corresponding author on reasonable request.

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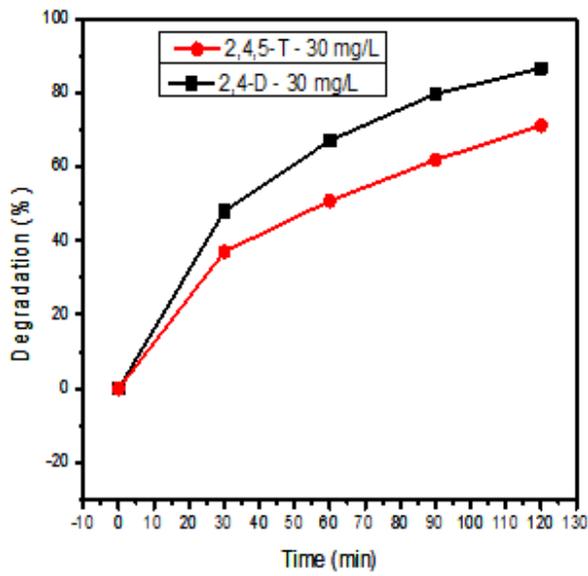
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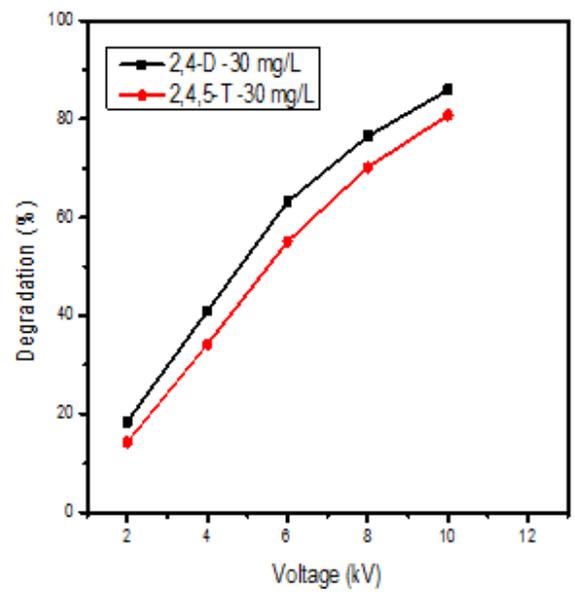
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# Figures



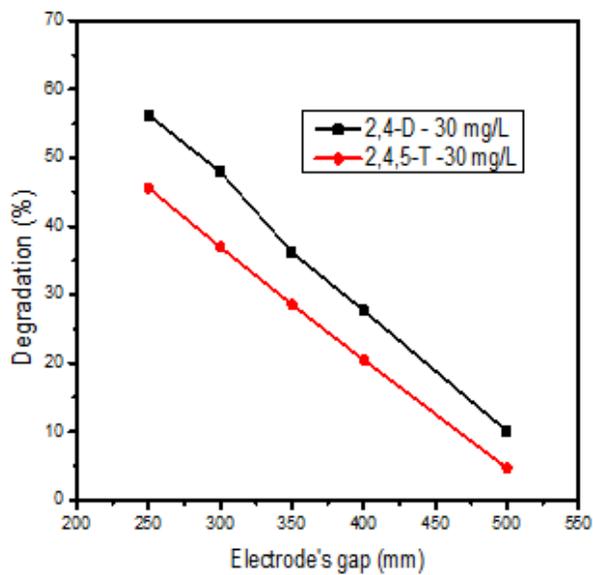
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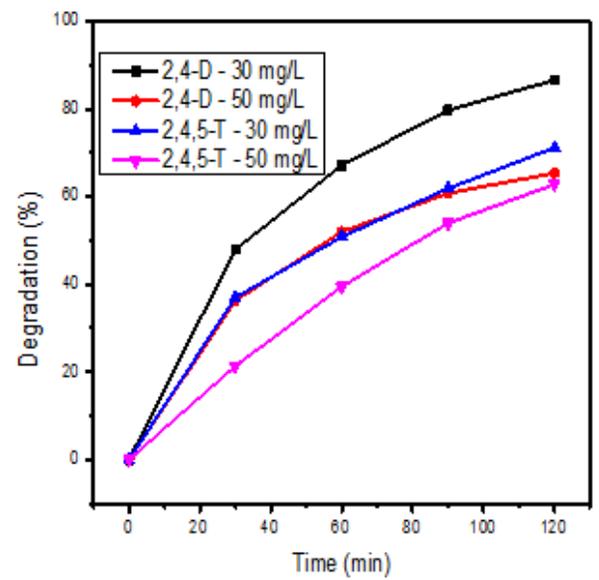
b

## Figure 1

Diagram of the high voltage DC power source



a



b

## Figure 2

Effect of reaction time (a) and voltage (b) on treatment efficiency of 2,4-D and 2,4,5-T with initial concentrations of 30 mg/L and electrode's gap of 300 mm

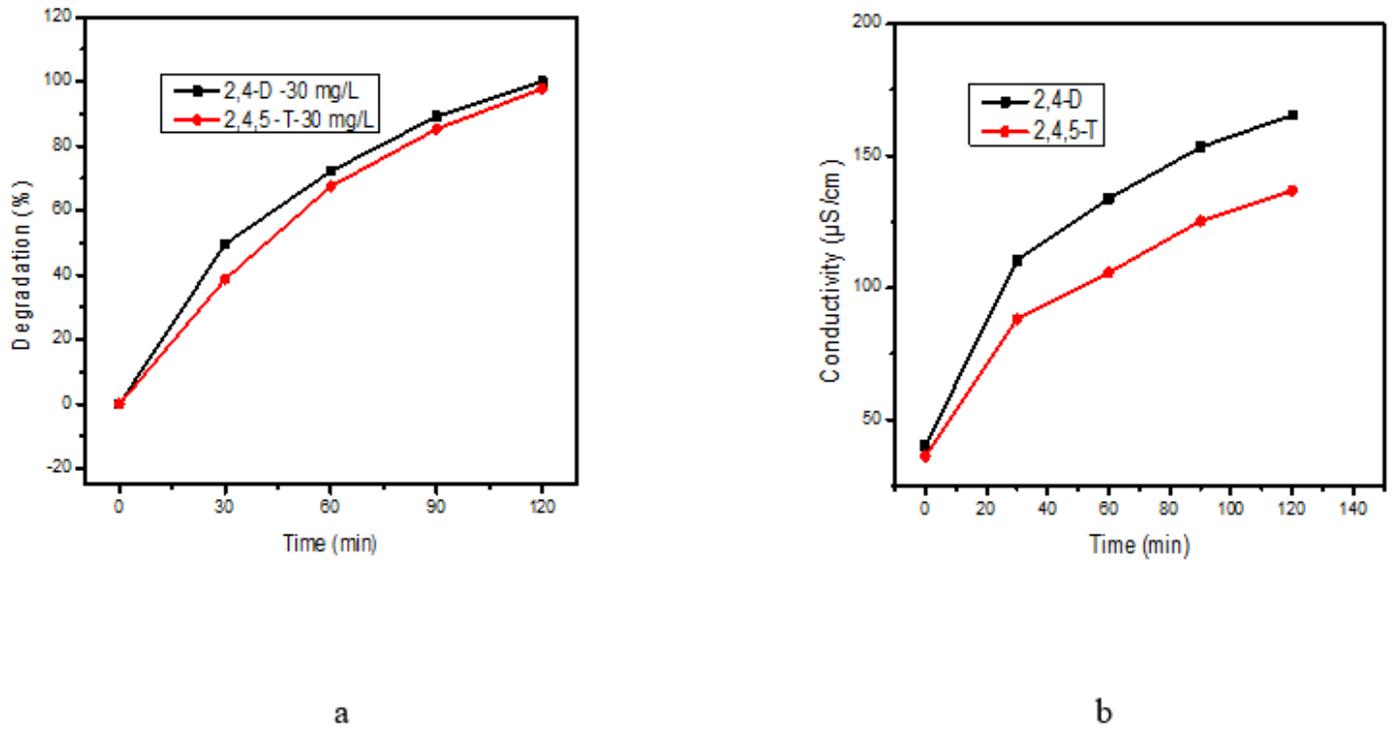


Figure 3

Influence of electrode distance (a) and initial concentration (b) on the decay efficiency of 2,4-D and 2,4,5-T at 5 kV input voltage, electrode distance of 300 mm

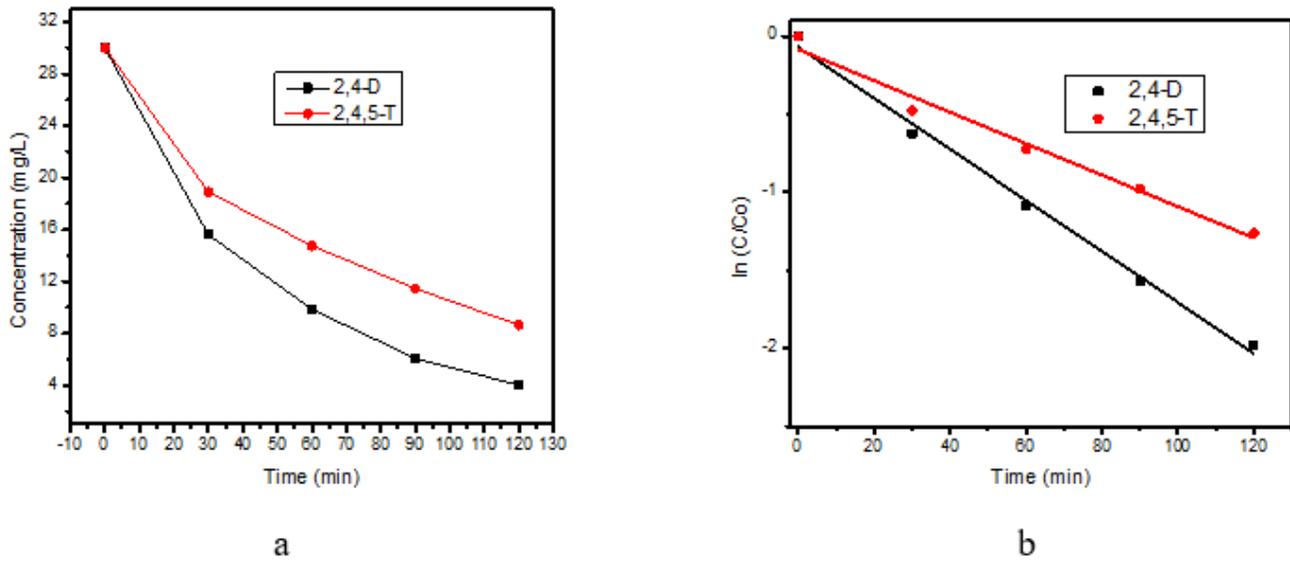
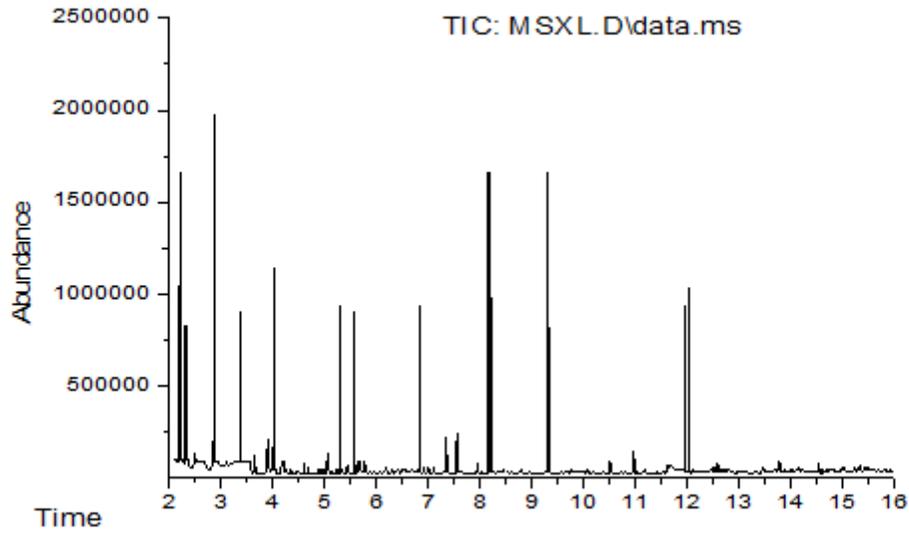


Figure 4

Effect of flowing air through solution on 2,4-D and 2,4,5-T treatment performance (a) and change in the conductivity of the treatment solution (b)



**Figure 5**

The concentration of 2,4-D; 2,4,5-T depend on the reaction time (a) as well as the ratio  $\ln(c/c_0)$  (b) input voltage of 5 kV, electrode's gap of 300 mm and at 30 °C

