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Quá trình điện cực bằng dòng một chiều (DC) cao áp với plasma điện hóa và các ứng dụng công nghệ

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TÓM TẮT

Với điện áp cao một chiều, các phản ứng điện hóa vẫn có thể được thực hiện ngay cả trong nước cất có độ dẫn điện rất thấp. Ion kim loại từ phản ứng hòa tan ở anot có thể phản ứng với khí hiđro được tạo thành từ catot trong môi trường nước để tạo thành kim loại; rồi nguyên tử kim loại tương tác tiếp tục bằng lực Van der Walls để tạo nên các hạt nano kim loại. Các quá trình phản ứng trên các điện cực để chế tạo dung dịch nano kim loại được kiểm soát bằng điện áp cao một chiều, khoảng cách giữa các điện cực anot với catot và độ dẫn của môi trường. Các đặc tính của dung dịch nano bạc kim loại như phổ UV-Vis, hình dạng hạt TEM, phân bố kích thước hạt, thế zeta cũng như khả năng diệt khuẩn đã được xác định và chứng minh. Sản phẩm thu được có độ tinh khiết cao do dung dịch nano không chứa các ion Na^+, NO_3^- cũng như các sản phẩm phản ứng và chất ổn định khác nên có thể ứng dụng cho nhiều đối tượng mà không ảnh hưởng đến sức khỏe con người. Ngoài bạc, các kim loại khác như Au, Cu, Fe,... cũng có thể được chế tạo ở dạng nano bằng công nghệ DC cao áp.

Môi trường khí được tạo ra trên điện cực bằng phản ứng điện hóa cao áp một chiều với điện trường lớn và hiệu điện thế cao cũng như tác dụng đốt nóng của môi chất sẽ là điều kiện thích hợp để chuyển từ trạng thái khí sang trạng thái plasma. Dấu hiệu cho thấy sự hiện diện của plasma điện hóa là sự phát sáng trên điện cực cũng như cường độ dòng điện tăng đột biến theo thời gian. Cũng có thể điều khiển thời gian xuất hiện plasma điện hóa khi thay đổi các thông số công nghệ phản ứng điện hóa cao áp. Trạng thái plasma điện hóa sẽ tạo ra H_2O_2 và các gốc tự do như OH• có khả năng phản ứng mạnh. Điều đó được sử dụng để xử lý các chất gây ô nhiễm nước như 2,4-D hoặc 2,4,5-T thành sản phẩm cuối cùng là CO_2 rất hiệu quả, đặc biệt trên điện cực Fe thêm phản ứng Fenton. Tương tự, nước thải dệt nhuộm có xanh metylen cũng như nước thải sinh hóa bệnh viện có nồng độ cao cũng có thể được xử lý cho kết quả tốt bằng DC cao áp với plasma điện hóa.

Từ khóa: *Dòng điện một chiều DC cao áp, nano kim loại, plasma điện hóa, gốc tự do, xử lý ô nhiễm.*

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Electrode processes by DC high-voltage - electrochemical plasma and technological applications

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ABSTRACT

With high DC voltage, electrochemical reactions can still be carried out even in distilled water with very low conductivity. Metal ions from the dissolution reaction at the anode can react with formed hydrogen gas from the cathode in aqueous medium to form metal and then interact for metal nanoparticles. The reaction processes on the electrodes to make metal nanoparticle solutions are controlled by high DC voltage, distance between anode and cathode electrodes and conductivity of the medium. The properties of metallic silver nanosolutions such as UV-Vis spectrum, TEM particle shape, particle size distribution, zeta potential as well as bactericidal ability have been determined and demonstrated. The obtained product has high purity because the nano solution does not contain Na^+, NO_3^- ions as well as other reaction products and stabilizers, so it can be applied to many objects without affecting human health. In addition to silver, other metals such as Au, Cu, Fe, Al, etc. can also be fabricated in nano form by DC high-voltage technology.

The gaseous environment created on the electrode by a DC high-voltage electrochemical reaction with a large electric field and high potential difference as well as the heating effect of the medium will be the right conditions to switch from the gaseous state to the plasma state. Indications of the presence of electrochemical plasma are the glow on the electrode as well as the amperage that spikes with time. It is also possible to control the electrochemical plasma appearance time when changing the DC high-voltage electrochemical reaction technology parameters. The electrochemical plasma state will generate H_2O_2 and free radicals such as $OH^{\bullet}$ which are highly reactive. That is used to treat water contaminants like 2,4-D or 2,4,5-T into the final product CO_2 very efficiently, especially on Fe electrode adding Fenton reaction. Similarly, methylene blue textile dyeing wastewater as well as high concentration hospital biochemical wastewater can also be treated with good results by high pressure DC with electrochemical plasma.

Keywords: *DC high voltage, metallic nanoparticle, electrochemical plasma, free radicals, water pollution treatment.*

1. INTRODUCTION

Unlike normal electrochemical reactions that occur in electrolyte with low DC voltage, electrodic processes by DC high voltage can also occur in media that are not considered electrolytes like double distilled water.[1-3] For non-conductive media, high voltage is used to heat the medium as a resistor but also potential enough to carry out electrochemical processes on the contact surface between the electrode and the aqueous medium.[4,5] At the positive electrode, the anodic reaction will be the process of dissolving

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the metal of the electrode into ions, but with the inert electrode, oxygen will be released from the water and dispersed into the environment. At the same time, on the negative electrode, the cathode reaction of the water electrolysis process will form hydrogen gas and disperse into the water environment.[6-8] These electrochemical processes also obey Faraday's law. Ions formed from electrochemical processes such as Me^{n+}, H^+, or OH^- will increase the conductivity of the aqueous medium.[1,9] However, because the amount of ions formed is not much, the conductivity increases only slightly with the reaction time. Moreover, in the aqueous environment, substances formed by electrode processes can meet and occur neutralization reactions or redox reactions such as $H^+ + OH^- \rightarrow H_2O$ (1) and $Me^{n+} + n/2H_2\ \ Me^0 + nH^+$ (2). The redox reaction between the metal ion generated from the anode process and the nascent hydrogen gas released from the cathode to form a metal with no valence is the basis for the fabrication of metal nano-sized particles: $nMe^0 \rightarrow MeNPs$ (3).[10-13]

On the other hand, gases are formed on the electrodes by an electrochemical reaction according to Faraday's law under conditions of continued energy supply due to high voltage, strong electric field and gradually increasing solution temperature according to Joul-Lenz's law will facilitate the appearance of a fourth state, the plasma state.[14,15] With the appearance of plasma state on the electrodes the water dissociation to produce H_2 and O_2 gas on the anode: $4H_2O\rightarrow 3H_2+O_2+H_2O_2$ (4) and on the catode: $2H_2O\rightarrow 2H_2 + O_2$ (5) that will become intense and the amount of gas produced will no longer be calculated according to Faraday's law.[16,17] In the plasma state, the following ionization processes will also occur at the electrodes: $H_2O + e^- \rightarrow H^\bullet + OH^\bullet + e-$ (6); $OH + OH^\bullet \rightarrow H_2O_2$ (7); $2H_2O \rightarrow H_2O_2 + H_2$ (8); $H_2O_2+hv \rightarrow 2OH^\bullet$ (9); $H_2O \rightarrow H + OH^\bullet$ (10).[18-21] Compounds and ions formed from plasma reactions will dissolve and disperse into the aqueous medium, increasing the redox reaction ability for the environment. This is used to treat contaminants present in the aquatic environment. The method of treating water pollution by plasma technology has many advantages such as not using chemicals, only using electricity, thus not causing secondary pollution, low cost, simple equipment and high efficiency because plasma generates very reactive radicals to be able to completely mineralize pollutants.

2. EXPERIMENTAL METHODS

The equipment required to carry out the high-voltage electrochemical reaction as well as the electrochemical plasma generation is a high-voltage DC power source.[22,23] Voltage values are steplessly controlled from 0 to 20 kV with voltage stabilizer and 15 kVA capacity (Figure 1a,b). Values of voltage (kV), current (mA), charge (mAh) and reaction time are shown at control box (1b). The electrochemical reaction vessel is made of heat-resistant glass in the form of a 2-layer tube, the inner tube contains the reaction medium and the outer layer contains cooling water (Figures 1c2, c3). The anode is mounted at the top end (c4) and the cathode (c5) is watertight with the bottom end of the reactor upright. The gas generated from the reaction is collected through valve (c6) and the liquid product is collected through valve (c7).

The evolution of the electrochemical reactions on the electrodes and in the solution such as the formation of bubbles of gas or glow of plasma and color change of liquid were recorded by video. The gaseous high-pressure electrochemical reaction products were collected through valve c6 and determined for volume or qualitatively or quantitatively analyzed using the respective apparatus.

The products of the high-voltage electrochemical reaction dispersed in solution will be characterized or analyzed qualitatively and quantitatively by the respective methods. The loss of anode mass (Δm) due to dissolution by a high voltage direct current electrochemical reaction can be calculated by the gravimetric method according to the formula: $c_{\Delta m} = \Delta m/V$ (mg/L) or by Faraday's law when determination of the charge (*It*) the reaction can be determined according to the formula: $c_{Far.} = kIt/V$ (mg/L). The conductivity and pH variation of the solution were determined using a Conductivity meter HI 8733 and pH meter HI 8314 from Hanna Instrument.

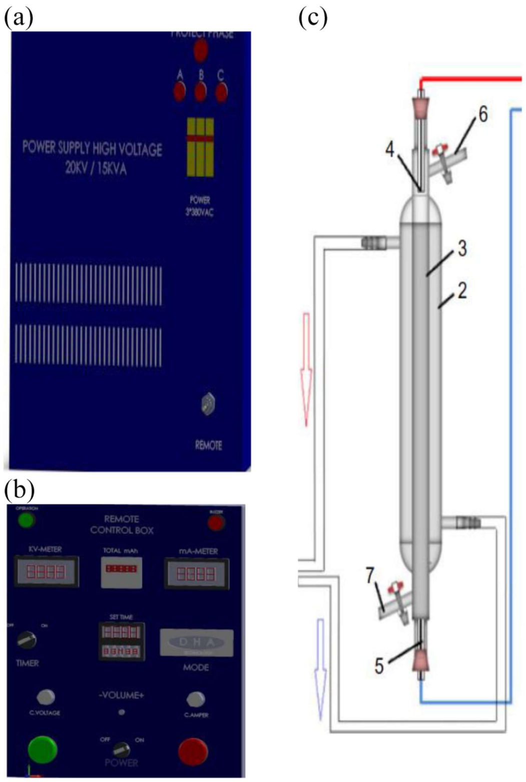


Figure 1. (a) High-voltage rectifiers, (b) Control box, (c) Double layer glass electrochemical reaction vessel. 1. Power supply, 2. Cooling water layer, 3. Reaction medium, 4. Anode, 5 Cathode, 6. Gas escape valve, 7. Reaction product recovery valve.

For products dispersed in solution as nanoparticles, it is possible to characterize UV-Vis spectra on the Hitachi UH-5300 device, the particle size distribution as well as the zeta potential on the SZ-100 device, Horiba, Japan.

For chemical compounds dispersed in solution, gas chromatography-mass spectrometry methods are usually used on the Agilent GC-MS 6890-5975 instrument or atomic mass spectrometry on the ICP-MS 7800/7850 Agilent instrument.

With free radicals such as $OH^\bullet$ or H_2O_2 formed from the plasma reaction and dispersed into the solution, it is determined through the corresponding color complexes with salicylic acid according to the reaction such as: (acid salycylic) $(HO)C_6H_4COOH + OH^\bullet \rightarrow (HO)_2C_6H_3COOH + H^+$ (11) (acid 2,3-dihydroxybenzoic or 2,5-dihydroxybenzoic) and with titanyl according to the following reaction: $Ti^{4+} + H_2O_2 + 2H_2O \rightarrow TiO_2H_2O_2 + 4H^+$ (12) through a suitable UV-Vis spectrum with corresponding quantification curves.

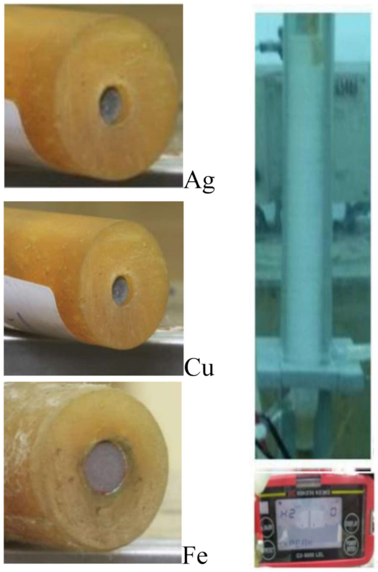
When using high-voltage electrochemical reactions as well as electrochemical plasma to treat environmental pollutants, chemical oxygen demand (COD) methods according to SMEWW 5220C:2017 and determine total organic carbon (TOC) according to TCVN 6634:2000.

Technological factors affecting electrode response as well as electrochemical plasma formation were investigated such as: distance between anode and cathode electrodes, high voltage, conductivity and initial temperature of the medium, the nature of the electrode metals as well as the concentration and nature of the substances dissolved in the aqueous medium. The metals used as electrodes can be Ag, Cu, Fe depending on the purpose of use to prepare metal nano-solutions or to treat contaminated water chemical pollution.

3. ELECTRODE PROCESSES AT DC HIGH VOLTAGE AND APPLICATION FOR METAL NANOFABRICATION

The anodic electrochemical reaction to dissolve the metal of the electrode material has created oxidizing substances in the aqueous medium in the form of metal ions: $Me \rightarrow Me^{n+} + ne^-$ (13).

The metals that have been tested for anodic dissolution by DC high voltage are Ag, Cu, and Fe. Figure 2 shows that the Ag and Cu anots are dissolved after the reaction (Figure 2a) and the gas is released simultaneously on the cathode (Figure 2b).



(a) **(b)**

Figure 2. (a) The anodes of Ag, Cu, Fe are dissolved due to the DC high voltage electrochemical reaction and (b) The H_2 gas released on the cathode simultaneously with the metal dissolution at the anode is determined by the instrument corresponding.

Table 1 presents the concentrations calculated by determining the weight loss of the dissolved anode during the electrochemical reaction in distilled water at different voltage conditions and distances of the cathode and anode.[6,9,10]

Table 1. Metal concentration values calculated by gravimetric method of Ag, Cu, Fe anode materials at electrochemical reaction conditions such as high voltage, electrode distance and reaction time different.

Anode	UDC, kV	DAC, mm	cMe, mg/L
Ag	16	350	700
	15	650	194
	14	1000	104
Cu	16	425	1.82
	16	470	1.90
	16	550	3.21
Fe	16	605	4.87
	15	515	4.50
	14	425	3.96

From Table 1, it can be seen that the amount of metal dissolved by the anode depends not only on the high voltage and time, but also on the distance between the anode and the cathode. When voltage (U_{DC}) is applied to an electrochemical system consisting of two electrodes and an electrolyte medium, the value of electrical energy is distributed to the electrode reactions (E_A, E_C) and ion transport in the medium ($IR_{Elec.}$) according to the equation: $U_{DC} = E_A + IR_{Elec.} + E_C$. Thus, at the value of voltage (U_{DC}), electrochemical reactions occur in time (t) and with current (I), as well as the temperature change (ΔT) of the reaction medium and the cooling water is determined, it will be calculated energy distribution for electrode reaction processes with DC high voltage according to the formula: $H_{DC} = H_E + H_W + H_V$, where $H_{DC} = UIt$ (Wh) is the energy supplied from the power source; H_E is the energy to carry out the electrode reaction; $H_W = mC.\Delta T$ (Wh) is the heating energy of the reaction medium and cooling water and $H_V = m_V\lambda$ is the water evaporation energy which is assumed to be zero at temperatures lower than 100^{o}C.

Table 2 presents the results of determining the energy distribution for the DC high-voltage electrochemical reaction of silver electrodes in distilled water at different electrode distances (D_{A-C}), times (t) and temperatures (T).

Table 2. Value and ratio of energy distribution for high voltage DC electrochemical reaction of silver electrode in distilled water at different electrode distances, time and temperature.

		H_{DC}	H_W		H_E	
		Wh	Wh	%	Wh	%
D_{A-C}	500 mm	615.4	608.9	98.94	6.5	1.06
	750 mm	761.3	688.2	87.67	96.8	12.33
	1000 mm	1044.7	860.6	82.38	184.1	17.62
t	15 min	424.1	350.7	82.69	73.4	17,31
	50 min	718.0	693.9	96.64	24.1	3.36
	80 min	866.8	823.4	94.99	43.4	5.01
T	288 K (15^{o}C)	408.2	350.8	85.94	57.4	14.06
	318 K (20^{o}C)	348.7	332.6	95.38	16.1	4.62
	328 K (55^{o}C)	336.4	332.6	98.87	3.8	1.13

From the results of Table 2, it can be seen that the proportion of electrical energy distributed to the electrochemical reaction at the electrodes is smaller than the energy converted to heat.[4] The highest percentage accounts for nearly a quarter of the total energy supplied and fluctuates depending on reaction conditions such as voltage, electrode distance, ambient temperature as well as reaction time. However, it indicates the possiblity of controlling the rate of electrochemical reactions at high voltage by reaction technology parameters. Thus, the electrochemical reactions on the anode dissolve the metal into ions and generate hydrogen gas on the cathode to form a reducing agent that is dispersed into the aqueous medium. In the heart of the aqueous environment, an oxidation-reduction reaction between metal ions and hydrogen gas will occur to form metal atoms and at the same time create metal nanoparticles through the Van de Wall interaction according to the equations: $Me^{n+} + nH_2 \rightarrow Me^0 + 2nH^+$ (14); $xMe^0 \rightarrow MeNPs$ (15).[29]

Figure 3 shows a video image of the color change process of the solution over time from colorless (Figures 3a, b) to (Figures 3c, d) brown and dark brown (Figure 3e) due to the reaction to form metal nanoparticles.

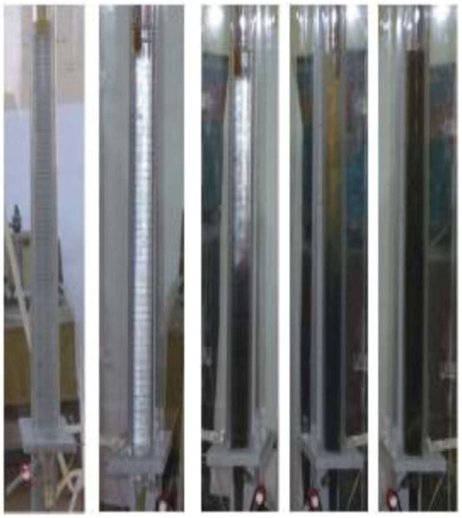

(a) (b) (c) (d) (e)

Figure 3. Color change of aqueous medium at high voltage electrochemical reaction times of Ag electrode from (a) 0 min to (b) 5 min, (c) 10 min, (d) 20 min and (e) 30 min.

The process of forming metal nanoparticle occurs from the cathode region and spreads upward to the anode region. The process occurs not only for metallic silver but also for other metals such as copper, iron, gold and aluminum. Of course, the color of the solution depends on the concentration and nature of the metal in which the high-voltage electrochemical reaction is performed.

The basic properties of metallic silver nanoparticles prepared by high-voltage electrochemical methods similar to other methods such as chemical, physical or biological reduction are the UV-Vis spectral region (Figure 4a), shape (Figure 4b) and particle size distribution (Figure 4c) as well as the ability to kill various bacteria (Figure 4d, e, f).[12] Because the reaction to create silver nanoparticles by H_2 gas generated on the cathode dispersed into the solution meets silver ions due to the dissolved anode, the higher the water temperature increases, the faster the gas escapes from the solution, so the concentration of silver nanoparticles is obtained smaller, and the lower the UV-Vis spectral peak (Figure 4a).

The distinctive feature of metal nanoparticles prepared by DC high-voltage electrochemical method and other methods of $AgNO_3$ salt reduction is that only AgNPS products are obtained without other ions such as Na^+, NO_3, products of reducing agents as well as stabilizers. Therefore, the conductivity of the metal nanoparticle solution prepared by DC high-voltage electrochemical method is very small compared to that of the product prepared by the method from $AgNO_3$ salt.[5,13,15]

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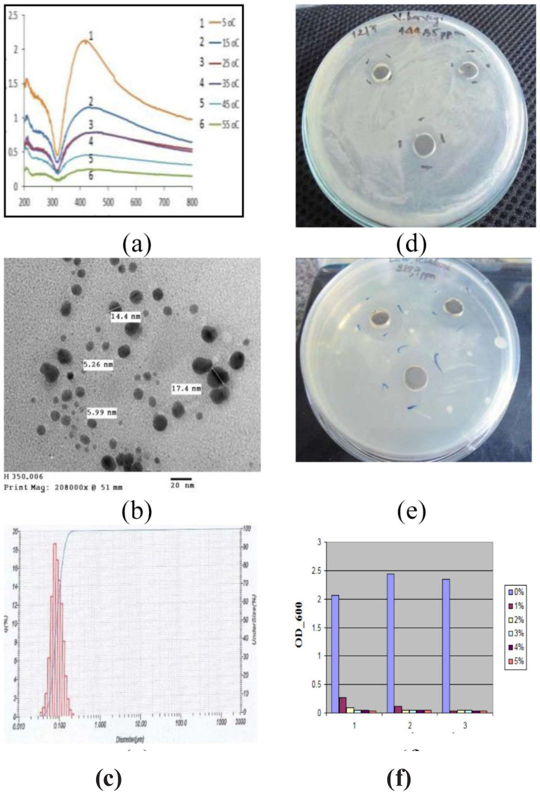

Figure 4. Basic properties of nanosilver solution prepared by DC high voltage method; (a) UV-Vis spectrum, (b) Nanoparticle shape, (c) Nanoparticle size distribution, (d) Antibacterial ring of *Vibrio harveyi*, (e) Antibacterial ring of *Edwardsiella ictaluri*, (f) Bactericidal performance of *E. Coli*.

Another feature of the metal nano-solutions prepared by DC high-voltage is that no stabilizer is needed, but the determined zeta potential value is still greater than 40 mV and has a different sign from the nano-solutions prepared from the reduction process of salt (Figure 5).

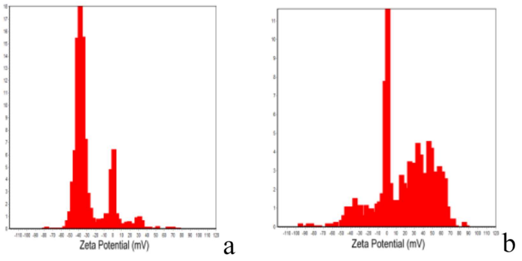

Figure 5. Comparison of zeta potential distribution of colloidal silver solution prepared by DC high-voltage electrochemical method (5a) with chemical reduction method from $AgNO_3$ salt.

From Figure 5, it can be seen that the colloidal solution of nano silver solution prepared by chemical method is a colloidal system with many distributions because in the solution there are many ions such as Na^+, NO_3^-, products of reducing agents and stabilizers determined. Therefore, the outstanding advantage of metallic silver nano-solutions prepared by DC high-voltage method is the purity of only metal nanoparticles without other ions as well as stabilizers. That could eliminate the effect of foreign substances in the solution, such as NO_3^- when applied specifically to areas related to human health.[30-32]

Similar to silver nano, nano-metals of other metals such as copper, iron, gold, aluminum, etc. have also been prepared by high-voltage DC current, but have not been tested as much as AgNPs.[3,6,8,10,33]

4. ELECTROCHEMICAL PLASMA FORMATION AND APPLICATION TO ENVIRONMENTAL POLLUTION TREAMENT OF WASTE WATER

As mentioned above, the electrochemical reaction by high voltage DC current still occurs in non-conductive distilled water and produces hydrogen gas on the cathode and dissolved metal or oxygen on the anode. The gaseous state on the electrodes with high voltage, strong electric field and suitable increase in ambient temperature due to the conversion of electrical energy into heat will convert to the plasma state.[14,28,34,35] A sign of the transition to the plasma state at the electrodes is the observed appearance of glow on the electrodes (Figure 6a). A sign of the simultaneous appearance of the plasma state is the electrochemical reaction rate represented by a rapidly increasing current (Figure 6b).

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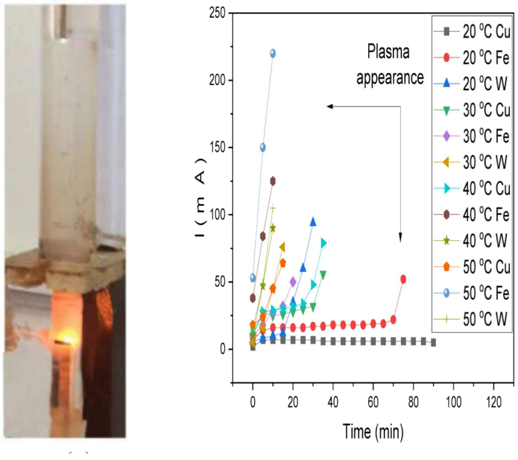

(a) (b)

Figure 6. (a) The appearance of electrochemical plasma on the electrodes, (b) The time-dependent electrochemical reaction rate when plasma appears on the W, Cu, Fe electrodes at different initial temperatures of the aqueous medium. The reaction was carried out at high voltage of 15 kV, pH 7, cathode-anode distance 200 mm and water conductivity 1.4 µS/cm.

From Figure 6a it can be seen that the plasma on the cathode with hydrogen gas is yellow-orange and larger than the plasma on the anode with oxygen gas which is blue due to less gas. In Figure 6b, it can also be seen that the plasma current spikes at different times with the metals W, Cu, Fe and the initial temperature of the different aqueous medium. At the initial temperature of the water environment at 20 ^{o}C with a potential of 15 kV, the electrochemical plasma appeared on the W electrode at 30 minutes, on the Fe electrode at 70 minutes and on the Cu electrode until 90 minutes, there was still no plasma. As the initial temperature of the aqueous medium increases, the time electrochemical plasma appears gradually accelerates, in which the fastest on the W electrode and the slowest on the Cu electrode. That has to do with the rate and amount of gas escaping on the electrode from DC high voltage DC electrochemical reactions.

The results from Figure 6 show that it is possible to control the electrochemical plasma appearance time by changing the conditions of the high-voltage electrochemical reaction such as: voltage (U_{DC}), distance between anode-cathode ($D_{A\text{-}C}$), initial temperature of aqueous medium (T), pH, electrical conductivity (λ) of the medium as well as the nature (Cu, Fe, W,…) and size ($\varnothing$) of the electrodes.

Table 3. Effect of factors with DC high voltage electrochemical reaction on plasma appearance time on Cu, Fe, W electrodes.

U_{DC}, kV	T, ^{o}C	$D_{A\text{-}C}$, mm	pH	$\varnothing$, mm	λ, µS/cm	t_{pl}, min		
						Cu	Fe	W
5	30	200	7	3	1,	No	No	No
10	30	200	7	3	1,4	6		
15	30	200	7	3	1,4	30	20	5
15	30	220	7	3	1,4	No	35	10
15	30	230	7	3	1,	No	40	12
15	30	300	7	3	1,4	No	No	15
15	30	200	7	3	20	No	No	9
15	30	200	7	3	50	No	3	2
15	30	200	7	3	100			
15	30	200	7	3	150	< 1	< 1	< 1
15	30	200	7	3	200	< 1	< 1	< 1
15	20	200	7	3	1,	No	70	14
15	40	200	7	3	1,4	25	5	4,5
15	50	200	7	3	1,4	5	< 1	< 1
15	30	200	4	3	120	1	< 1	< 1
15	30	200	5	3	69	4	2	
15	30	200	6	3	52	No	3	2
15	30	200	8	3	40	No	8	7
15	30	200	9	3	60	4	2	1,5
15	30	200	10	3	110	1	< 1	< 1
15	30	200	11	3	150	< 1	< 1	< 1
15	30	200	7	6	1,4	22	15	2

The results presented in Table 3 show that the electrochemical plasma appearance time (t_{pl}) on the electrode has different values, from less than 1 minute to more than 70 minutes or no plasma depending on the conditions of the DC high-voltage electrochemical reaction such

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as high-voltage, distance between electrodes, temperature, pH and conductivity of the aqueous medium as well as metal nature and size of the electrodes. That allows to master the process using electrochemical plasma. The ionized state has many advantages for different application purposes.

The first advantage is that the amount of gas generated when electrolysis of water by plasma reaction will be more than that of electrochemical reaction calculated according to Faraday's law. Table 4 presents the value of total gas volume (V_{Ex}) performed with DC high-pressure current with plasma at different reaction conditions compared with the value calculated (V_F) according to Faraday's law.

Table 4. Gases volume of the high DC voltage electrochemical process in comparison with the calculation from Faraday law.

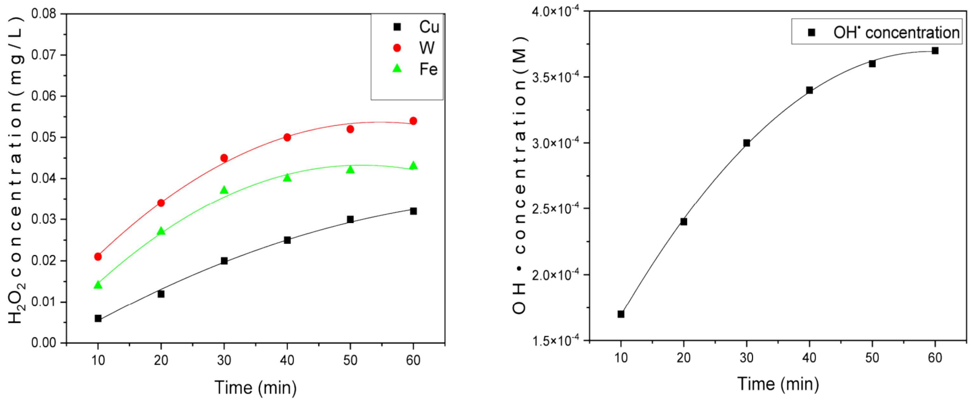
Ø, mm	D_{A-C}, mm	*t*, min	*I*, mA	V_F, mL	V_{Ex}, mL	V_{Ex}/V_F
3	500	15	93.6	14.7	63	4.3
4	500	25	83.5	21.9	75	3.4
4	500	20	88	18.4	80	4.3
5	500	25	91.2	23.9	110	4.
5	500	20	87.7	18.4	73	4.0
7	500	25	80.9	21.2	80	3.8
7	500	20	87.5	18.3	61	3.
4	850	30	115.7	36.4	150	4.
4	850	18	119.3	22.5	80	3.
4	850	35	106.7	39.1	250	6.4
4	700	15	112.1	17.6	110	6.3

The results from Table 4 show that the amount of gas contributing to plasma electrolysis is 3.3 to 6.4 times higher depending on the reaction conditions compared to the electrochemical process alone.

The more important advantage of plasma reactions is the generation of active substances such as H_2O_2 and especially $OH^•$ radicals (according to Equations 6 to 10).

Figure 7 presents the formation of H_2O_2 with time having electrochemical plasma on the Cu, W, Fe electrodes (Figure 7a) as well as the OH radical on the Fe electrode (Figure 7b).

From Figure 7 it can be seen that both the concentration of H_2O_2 and the free radical $OH^•$ increase rapidly during the first 30 minutes, but they then increase slowly because these very active agents are both unstable. Especially with the Fe electrode in an aqueous environment with H_2O_2 will also form a Fenton system (H_2O_2/Fe^{2+}) which also contributes to the formation of $OH^•$ free radicals according to the following reaction: $Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O$ (16) and $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^• + OH^-$ (17).[36-38] Therefore, when using Fe electrode to perform DC high-voltage electrochemical reaction to form plasma, it will be very practical to handle pollutants in water environment because Fe is cheap and can combine advantages of the electrochemical plasma with the Fenton reaction.



(a) (b)

Figure 7. The dependence of the electrochemical plasma lifetime of the H_2O_2 concentration formed at 15 kV, 30 °C, D_{A-C} 200 mm on the W, Cu, Fe (a) electrodes as well as the $OH^•$ free radical concentration on the Fe electrode (b).

Table 5. Variation with reaction time of chemical oxygen demand (COD) and total organic carbon (TOC) of 2,4-D and 2,4,5-T polluted treatment by DC high voltage and electrochemical plasma at Fe electrode, with U_{DC}: 5 kV, $D_{A\text{-}C}$: 300 mm, T: 30 ^{o}C, λ: 38,8 µS/cm.

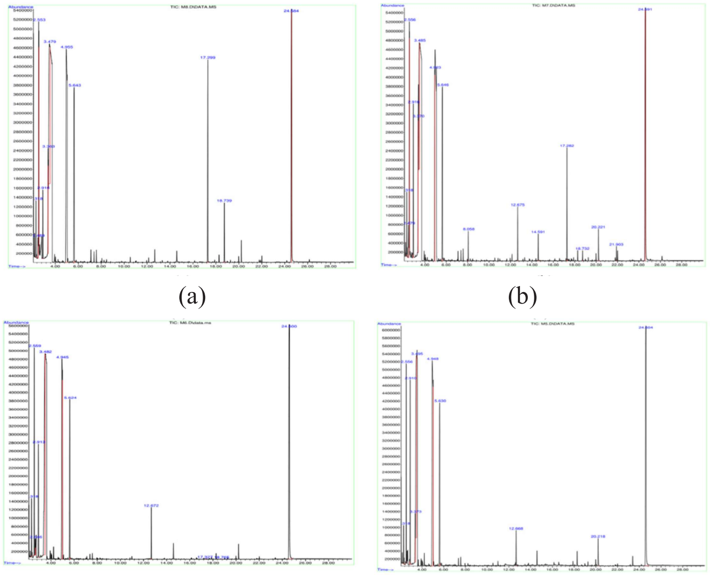
t, min	COD				TOC			
	2,4-D		2,4,5-T		2,4-D		2,4,5-T	
	mg/L	Eff., %	mg/L	Eff., %	mg/L	Eff., %	mg/L	Eff., %
0	106	0	57	0	6.1	0	4.6	
30	40	62	30.2	47	4.7	22.9	3.7	19.5
60	15.9	85	12.4	78				
90	6.8	93.6	8.9	84.3	2.8	54.1	2.4	47.8
120	2.1	98	4.1	92.8	2.1	65.6	1.8	60.6

Table 5 presents the results of treatment of polluted water by 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic (2,4,5-T) which are aromatic cyclic compounds by electrochemical technique of DC high voltage with plasma on Fe electrode at 5 kV and electrode distance 300 mm.

Very high COD as well as TOC efficiency values show that 2,4-D and 2,4,5-T are well and thoroughly treated to CO_2 and H_2O. Table 6 presents parameters of water polluted by 2,4-D and 2,4,5-T after high voltage DC electrochemical treatment with plasma compared with national standard QCVN 40:2011 and shows that the treated water is grade A and can be discharged directly into the environment.

Table 6. Values of water parameters polluted by 2,4-D and 2,4,5-T treated with high voltage DC and electrochemical plasma on Fe electrode at UDC; 5 kV, DA-C: 300 mm, T: 30 ^{0}C, λ: 38,8 µS/cm and national standard QCVN 40:2011.

No.	Parameter	Value after pollution treatment		National standard QCVN 40:2011	
		2,4-D	2,4,5-T	A	B
1	$c_{Polu.}$, mg/L	< 0,005	< 0,05	0,05	0,1
2	pH	5,7	5,5	6÷9	5,5÷9
3	COD, mg/L	6,8	8,9	75	150
4	c_{Fe}, mg/L	3,1	4,5	1	5
5	c_{Cl^-}, mg/L	7,6	10,7	500	1000
6	TDS, mg/L	14,2	15,8	50	100



(a) (b)

(c) (d)

Figure 8. GC-MS spectrum of 2,4-D degradation products after 30 min (b), 90 min (c) and 120 min (d) of reaction with DC high voltage and electrochemical plasma on Fe electrode at U_{DC}: 5 kV, $D_{A\text{-}C}$: 300 mm, T: 30 ^{o}C and λ: 38,8 µS/cm.

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Figure 8 presents the GC-MS spectrum of intermediate products formed by the reaction of 2,4-D or 2,4,5-T pollutants with agents formed from high pressure DC reaction and electrochemical plasma on the Fe electrode at U_{DC}: 5 kV, $D_{A\text{-}C}$: 300 mm, T: 30^{o}C and λ: 38,8 µS/cm.

From the results of GC-MS analysis, it can be seen that the aromatic ring of 2,4-D or 2,4,5-T is oxidized to phenol compounds and then continued to form a straight-chain acid and finally to CO_2 and H_2O, which is represented as a schematic diagram in Figure 9.

2,4-D	2,4,5-T

↓+ $OH^{\bullet}$

Phenol$_{(6.839)}$
4-chlorophenol$_{(10.223)}$
1-chlorophenol$_{(10.387)}$
2,3-dichlorophenol$_{(9.925)}$
3,4-dichlorophenol$_{(13.925)}$
2,4-dichlorophenol$_{(9.844)}$
2,4,5-dichlorophenol$_{(12.498)}$
2,4,6-dichlorophenol$_{(12.580)}$
2,3,5-dichlorophenol$_{(12.432)}$

↓+ $OH^{\bullet}$

Acid formic$_{(2.198)}$
Acid acetic$_{(2.911)}$
Acid propanoic$_{(4.051)}$
Acid pentanoic$_{(6.842)}$
Acid hexanoic$_{(8.355)}$
Acid succinic$_{(11.958)}$
Acid oxalic$_{(12.038)}$

↓+ $OH^{\bullet}$

CO_2+H_2O

Figure 9. Model of 2,4-D or 2,4,5-T decomposition by DC high voltage with electrochemical plasma

Results of treatment of water contaminated with 300 mg/L methylene blue dye ($C_{16}H_{18}ClN_3S$) by DC high pressure with electrochemical plasma on Fe electrode at U_{DC} 2.5 kV, $D_{A\text{-}C}$: 300 mm, pH: 6.06 and λ: 156 µS/cm presented in Table 7.

Table 7. Time variation of TOC value and treatment efficiency of methylene blue polluted water by DC high pressure with plasma on Fe electrode at U_{DC}: 2.5 kV, $D_{A\text{-}C}$: 300 mm, pH: 6.06 and λ: 156 µS/cm

t, min	0	2	5	10	
TOC, mg/L	68	40	35	25	12
Eff., %	0	40.2	52.3	88.4	99

From the results of Table 7, it can be seen that the treatment efficiency of water contaminated with methylene blue dye is also very high, and the mineralization capacity is determined to 81.9%. This proves that the reaction of the radicals generated by the electrochemical plasma oxidizes methylene blue to CO_2 and water.[39]

By using of DC high-voltage with plasma, it can also be applied to treat liquid waste from hospital biochemical tests with very high concentrations and unknown composition. Figure 10 presents the treatment of wastewater from a hospital biochemical test by DC high-voltage with plasma on iron electrodes with different anode area ratios.

(a) (b) (c) (d)

Figure 10. The color change of treated wastewater from the hospital's biochemical analytical process by DC high voltage reaction with plasma on iron electrode: (a) S_A/S_C = 1; (b,c,d) S_A/S_C = 4; (a) the pink color of initial solution; (c) turning dark brown color; (b,d) turning blue-black color.

From Figure 10 it can be seen that the color of the solution with biochemical test waste changes color very quickly when treated with a high-pressure DC current with plasma from orange to blue-black. This color change is related to the formation of compounds with iron ions dissolved from the anode to coagulate and separate from the system.

Table 8. Variation of concentrations of NH_4^+, NO_2^-, NO_3^- as well as COD and TDS at different treatment times with DC high-voltage with plasma on Fe electrode.

t, min	0	78	2
NH_4^+, mg/L	1600	650	490
NO_2^-, mg/L	0.30	3.50	0.25
NO_3^-, mg/L	0	520	250
COD, mg/L	19000	8500	1020
TDS, mg/L	-	4050	3220

Table 8 presents the variation of important values of wastewater such as NH_4^+, NO_2^-, NO_3, COD and TDS depending on the time of wastewater treatment from biochemical tests by DC high-voltage plasma technology. From the results of Table 8, it can be seen that the COD decreases very strongly, demonstrating high treatment efficiency. Interestingly, ammonium is also treated, so its concentration decreases with time while the evolution of NO_2^- and NO_3^- concentrations increases initially and then decreases.[40] That proves that ammonium is oxidized to form NO_2^- and then further into NO_3^-.

5. CONCLUSION

When using high voltage DC, electrochemical reactions can still be performed even in low conductivity water with the anodic dissolution of the metal electrode and the release of hydrogen on the cathode. The rate of electrical energy distribution for electrochemical processes is usually smaller than for the heating of the medium. However, it is possible to control this ratio by reaction parameters such as voltage, distance between the two electrodes, pH and conductivity as well as the temperature of the medium. The products of electrode processes such as metal ions from the anode and hydrogen gas from the cathode disperse into the environment and carry out an oxidation-reduction reaction to form metal and then metal nanoparticle. The nanofabrication process by this method does not use silver salts and reducing agents, so the resulting product is different from other methods in that it has high purity that can be applied to health-related fields because there is no influence of ions such as NO_3^- as well as stabilizers. In addition to metallic silver nano, other metal nanoparticles such as gold, copper, iron, aluminum, tungsten,... can also be prepared by high voltage DC.

With the gaseous environment created on the electrodes in a strong magnetic and electric field as well as an appropriate increase in ambient temperature, a cold plasma state will appear at the electrodes, an ionized state. The hallmark of the electrochemical plasma is the electrode glow and the characteristic amperage of the electrochemical reaction rate that spikes with time. The time of appearance of the electrochemical plasma state can be controlled by electrochemical reaction parameters such as: high voltage DC, distance between electrodes, conductivity or initial temperature of the aqueous medium and the nature of the electrode metals. In the electrochemical plasma state, besides the process of forming metal nanoparticles, it also forms substances with proven strong activators such as H_2O_2 and especially $OH^\bullet$ radicals. The strong reactants of the electrochemical plasma state on the iron electrode with the formation of H_2O_2, the stability of the $OH^\bullet$ radical is supported by the Fenton reaction. The treatment of environmental pollutants with difficult-to-handle aromatic rings such as 2,4-D or 2,4,5-T by high voltage DC with electrochemical plasma on the iron electrode will achieve efficiencies as high as 98% and 92.8% and form the final products CO_2 and H_2O with mineralization up to 65,6% and 60,6%. Similarly, blue methylene dyes are also treated with high yield 99,6% and mineralization 81,9%. Waste from hospital biochemistry tests with very high concentrations of pollutants can also be treated by DC high-voltage with plasma on iron electrodes with high efficiency, especially for contaminant as ammonium NH_4^+.

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REFERENCES

1. N. D. Hung. Electrochemical technology and metal protection, *Vietnam Journal of Science and Technology*, **2012**, *50*(6), 767-793.
2. N. D. Hung, N. T. Dung. Fabrication of metallic silver nano-solutions using electrochemical method, *Journal of Military Science and Technology*, **2009**, *02*(08), 67-71.
3. N. D. Hung, N. M. Thuy, D. T. Tuan. Nano aluminum solution prepared by high voltage anodic dissolution process, *Journal of Military Science and Technology*, **2011**, *08*(14), 97 -101.
4. N. D. Hung, M. V. Phuoc, N. M. Thuy. Energy balance in the process of creating silver nanoparticles by high voltage electrochemical technology, *Vietnam Journal of Chemistry*, **2014**, *2*(6B), 326-333.
5. N. M. Thuy. *Research on dissolution reaction of anode (anodic) to create silver nano solution by high voltage*, Doctoral thesis in Chemistry, Academy of Military Science and Technology - Ministry of National Defense, 2015.
6. N. D. Hung, N. M. Thuy, D. T. Tuan. *Nano copper solution formed by anodic disoved process under high voltage*, International Workshop on Nanotechnology and Application – IWNA, Vung Tau, 2011.
7. N. M. Thuy, N. D. Hung, N. T. Dung, M. V. Phuoc. Preparation of metallic silver nano-solutions by ultra-high voltage electrochemical technology to kill bacteria, *Journal of Technique and Equipment*, **2012**, *05*, 43-46.
8. V. T. Vinh, N. D. Hung, N. T. Hai. Formation process of copper nanoparticles from high voltage electrode reaction, *Vietnam Journal of Chemistry*, **2014**, *52*(6B), 1-6.
9. N. D. Hung, M. V. Phuoc, N. M. Thuy. Conductivity of silver nano-solutions, *Journal of Military Science and Technology*, **2012**, *17*, 96-101.
10. N. D. Hung, D. T. Tuan. Preparation of nano iron solution by high voltage anode dissolving process, *Vietnam Journal of Chemistry*, **2012**, *50*(04), 425-428.
11. N. D. Hung, N. M. Thuy, M. V. Phuoc, N. N. Tru. Preparation of nanosilver colloidal solution by anodic disolution under high DC voltage, *Electrochemistry*, **2013**, *81*(6), 453-459.
12. N. M. Thuy, N. D. Hung, N. T. N. Tinh, N. N. Tru. Silver nano solution prepared by high-voltage electrochemical method: bactericidal ability and application in medicine, *Vietnam Journal of Chemistry*, **2012**, *50*(5A), 134-138.
13. N. N. Tru, N. M. Thuy, N. D. Hung, M. V. Phuoc. Characterization of particles size distribution for nano silver solution prepared by high DC voltage electrochemical technique, *Vietnam Journal of Chemistry*, **2012**, *52*(05), 543-547.
14. N. D. Hung. Electrochemical reaction at high voltage with electrode plasma, *Vietnam Journal of Chemistry*, **2012**, *50*(DB), 103-111.
15. N. M. Thuy, N. D. Hung, N. N. Tru. The contribution of electrode plasma to nano silver formation in aqueous solution by DC high voltage electrolysis, *Vietnam Journal of Chemistry*, **2015**, *53*(5E1), 119-123.
16. A. K. Susanta, K. Sengupta, R. Singh. A study on the origin of nonfaradaic behavior of anodic contact glow discharge electrolysis – The relationship between power dissipated in glow discharges and nofaradaiic yields, *Journal of the Electrochemical Society*, **1998**, *145*(7), 2209-2213.
17. T. Mizuno, T. Akimoto, K. Azumi, T. Ohmori, Y. Aoki and A. Takahashi. Hydrogen evolution by plasma electrolysis in aqueous solution, *Japanese Journal of Applied Physics*, **2005**, *44*(1A), 396-401.
18. C. Chiuderi, M. Velli. *Basics of plasma astrophysics*, Milano: Springer Milan, 2015.

https://doi.org/10.52111/qnjs.2022.16501

19. B. Jiang, J. Zheng, S. Qui, M. Wu, Q. Zhang, Z. Yan, Q. Xue. Review on electrical discharge plasma technology for wasterwater remediation, *Chemical Engineering Journal*, **2014**, *236*, 348-368.
20. P. K. Chu, X. P. Lu. *Low temperature plasma technology: Methods and applications*, CRC Press-Taylor & Francis Group, 2013.
21. J. Szalatkiewicz. Metals recovery from artificial ore in case of printed circuit boards, using plasmatron plasma reactor, *Materials (Basel)*, **2016**, *9*(8), 683.
22. N. D. Hung. The method of manufactoring of nano-silver solution and the equipment to implement this method, the Vietnam patents, VN 1-0012229, 2013.
23. Y. Cui, J. Cheng, Q. Chen, Z. Yin. The types of plasma reactors in wastewater treatment, *Earth and Environmental Science*, **2018**, *208*, 012002.
24. N. D. Hung, N. M. Thuy, N. N. Tru. Characteristics and electrochemical mechanisms of a nanosilver solution formed by anodic dissolution with high DC voltage, *Journal of Applied Physics*, **2013**, *63*, 20402.
25. N. D. Hung, V. N. Nam, T. T. Nhan, T. T. Ngoc Dung. Quantitative concentration determination of silver nanoparticles prepared by DC high voltage electrochemical methothod, *Vietnam Journal of Chemistry*, **2018**, *56*(5), 553-558.
26. N. D. Hung, L. V. Hung, N. M. Thuy. UV-Vis application to research silver nanosolutions prepared by super high voltage anode dissolving method, *Journal of Military Science and Technology*, **2012**, *19*(06), 94–99.
27. N. D. Hung, M. V. Phuoc, N. M. Thuy. Effect of electrode-electrode spacing on the process of creating silver nanoparticles by super-high voltage anodic dissolution method, *Journal of Science and Technique, University of Military Technique*, **2012**, *149*, 109 –117.
28. T. V. Cong, N. D. Hung, L. X. Bach, T. V. Hung, N. N. Dang. Factors efecting the formation of plasma on Fe, Cu and W electrodes using an electrochemical reaction in an aqueous environment with high-voltage DC, *Journal of Materials Research and Technology*, **2021**, *10*, 1462-1470.
29. N. D. Hung, M. V. Phuoc, N. M. Thuy. Manufactoring of nano silver solution using electrochemical technology, *Vietnam Jounal of Chemistry*, **2012**, *50*(2), 261–263.
30. N. D. Hung, T. B. Loc, T. T. N. Dung. Manufactoring of electrochemical and chemical silver nano solution for prevention and treatment of diarrhea in piglets, *Quy Nhon University Journal of Science*, **2018**, *12*(1), 55-62.
31. N. D. Hung, N. T. T. Ha, T. T. N. Dung. Fabrication of porous ceramic carried silver nano of antibacterials for water treatment from Thi Nai swamp - Binh Dinh, *Quy Nhon University Journal of Science*, **2016**, *10*(4), 139-145.
32. N. D. Hung, N. T. Linh, T. T. N. Dung. Research on creating antibacterial nano silver films on glass and porcelain surfaces, *VNU Journal of Science - Natural Sciences and Technology*, **2016**, *32*(4), 53-57.
33. N. D. Hung, T. V. Cong, H. N. Trang. Synthesis of bimetallic Cu-Ag nanoparticles prepared by DC high voltage electrochemical method, *Vietnam Journal of Chemistry*, **2019**, *57*(5), 609-614.
34. N. D. Hung, N. M. Thuy, N. T. Hai, P. T. Trang. Plasma electrolysis effects by the preparation of silver nanoparticles with DC high voltage, *Vietnam Journal of Chemistry*, **2014**, *52*(3), 326–333.
35. N. D. Hung, V. N. Nam, L. V. Trung, T. T. N. Dung. Electrochemical preparation of nano silver by combining high DC voltage with anodic plasma, *Vietnam Journal of Science and Technology,* **2019**, *57*(2), 186-198.
36. N. V. Hoang, T. V. Cong, T. T. N. Dung, N. D. Hung. Research on the influence of electrode materials on the ability to form plasma and decompose 2,4 dichlorophenynoxy acetic acid in water environment, *Journal of Military Science and Technology*, **2021**, *72* (04), 53-59.

https://doi.org/10.52111/qnjs.2022.16501

37. T. V. Cong, N. D. Hung, T. T. N. Dung, N. V. Hoang. S. V. P. Vattikuti, N. N. Dang. Electrochemical Plasma for Treating 2,4,5-Trichlorophenoxyacetic Acid in Water Environment Using Iron Electrodes, *ACS Omega*, **2016**, *6*, 26329-26337.

38. T. V. Cong, N. V. Hoang, T. T. N. Dung, N. D. Hung Decomposition of 2,4-D Dichlorophenoxyacetic acid in water environment by the DC high voltage electrochemical reaction with the plasma appearance on iron electrode, *Vietnam Journal of Chemistry*, **2020**, *58*(5E12), 302-308.

39. N. D. Hung, P. H. Long, T. V. Cong. Electrochemical plasma application on iron electrodes for wastewater treatment from hospital biochemistry assays, *Journal of Tropical Science and Technology*, **2019**, *18*(07), 46-51.

40. N. D. Hung, V. N. Nam, T. T. N. Dung. Applicability of high-voltage electrochemical methods to treat environmental pollution, *Journal of Military Science & Technology*, **2019**, *60*(4), 126-131.