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Supplementary data

Parameter optimization and degradation mechanism for electrocatalytic degradation of 2,4-diclorophenoxyacetic acid (2,4-D) herbicide by lead dioxide electrodes

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Materials

2,4-Dichlorophenoxyacetic acid (2,4-D, chemical formula: $C_8H_6Cl_2O_3$, 99% purity), Lead nitrate ($Pb(NO_3)_2$, >99% purity) and nitric acid (HNO_3, 95% purity) and Sodium Sulfate (Na_2SO_4, 99% purity) were purchased from Sigma Aldrich (St. Louis, MO, USA). The molecular structure of 2,4-D herbicide is presented in Fig. S1. Other required chemicals such as NaOH and HCl were purchased from Merck CO (Darmstadt, Germany). To adjust the pH solution, 1N HCl and NaOH were applied.

Analytical method

The electro-deposition and constant-current electrolysis were powered by a DC power source (DAZHENG PS-305D, China) with an electric current of 0-5 A and voltage of 0-30 V was used to supply the electrical current.

The concentration of 2,4-D was measured using a UV- Vis spectrophotometer (DR 6000, HACH, USA). Moreover, to estimate the accuracy and validity of the data provided by UV-Vis spectrophotometer, the high-performance liquid chromatography ((HPLC), Agilent 1260 infinity, Agilent Technologies Co. Ltd., USA) was also applied. The mobile phase was a mixture of water and acetonitrile (50:50 v/v, HPLC grade, Merck) with a flow rate of 1mL/min at 25^{o}C and the C_{18} column was used as the stationary phase. The chemical oxygen demand (COD) contents of the 2,4-D herbicide were determined by COD ampoules (HACH Chemical) using a spectrophotometer (DR 6000, HACH, USA). The total organic carbon (TOC) contents of the 2,4-D herbicide were determined by TOC analyzer (Elementar, Germany). Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) measurements were carried out at room temperature by the Autolab PGSTAT-20 instrument monitored using the Electrochemical System Software (Nova). The working electrode used in the cyclic voltammetry experiments was a glassy carbon disc (1.8 mm^2 area). A platinum wire was utilized as the counter electrode and an Ag/AgCl (3M) was employed as the reference electrode. The ICP–OES (Optima-8300) was utilized to measure the leaching of Pb^{2+} and Pb^{4+} after the complete degradation of the 2,4-D in the studied processes. The intermediates analysis carried out using the LC/MS (Shimadzu LCMS 2010 A) system equipped with C18 column (100 mm × 2.1 mm) and an electron spray ionization source.

The surface morphology of the PbO_2 deposited onto the stainless steel 316, lead and graphite beds, was investigated by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX) (model HITACHI S-4160, Japan). The phase structure of the PbO_2 layer was analyzed by X-ray diffraction (XRD pattern) using an X'Pert Pro diffractometer (Rigaku RINT2200, Japan) with a 2θ step width of 0.1° and a scan rate of 1520 s/0.1° at 40 kV and the electron probe current of 40 mA. All of the experiments were carried out at room temperature.

Electrochemical treatments

The electrochemical degradation of 2,4-D herbicide was performed in batch mode and constant-current electrolysis with operation using an electrolytic reactor made of Plexiglas having a working volume of 100 mL. A schematic view of the experimental unit is presented in Fig. S2. 100 mL 2,4-D solution with an initial concentration of 100 mg/L was prepared in 0.6 gr/100 cc Na_2SO_4 as supporting electrolyte (SE). The electrode sets consisted of one cathode and two anodes and the distance between the electrodes was 10 mm. The electrodes were vertically and parallelly installed inside the reactor. It should be noted that the anodes used in this study were SS316/β-PbO_2, Pb/β-PbO_2 and G/β-PbO_2, and the cathode was the SS316. A graphite (Sazeh Morakab Inc., Iran) in dimensions of 60 mm × 25 mm × 4 mm and SS 316 (purchased from a local market) in dimensions of 60 mm × 28 mm × 1 mm and Pb in dimensions of 60 mm × 25 mm × 4 mm were used as the substrate to prepare the anodes. In order to mix and to homogenize the samples, a magnetic stirrer was used at 450 rpm. All batch experiments were performed at room temperature in duplicate.

The measurement of Linear sweep voltammetry (LSV) was performed using different β-PbO_2 electrodes on a classical undivided cell configuration with a platinum wire counter electrode and a glassy carbon disc as the working electrode versus an Ag/AgCl reference electrode during the electrolysis. At different time interval (10 min), the electrolysis process was stopped and the solution was subject to voltammetry to acquire the linear sweep voltammograms. Before each experiment, the glassy carbon electrode was carefully polished using the Struers Water Proof Silicon Carbide Paper (granulometry 2400 and 4000) to gain a stable background voltammogram (Na_2SO_4 0.1 M). The measurement of voltammetric curves was carried out at room temperature. The effectiveness of the electrochemical degradation of 2,4-D was determined at different time intervals (every 10 min) until the complete degradation of herbicide. The use of CV during the electrolysis process is only for monitoring the 2,4-D herbicide degradation process. During the electrolysis process, the peaks related to herbicide in the CV technique is dramatically eliminated and the complete elimination of peaks in this technique indicates the complete degradation of 2,4-D herbicide.

During the electrolysis, the degradation of 2,4-D, formation of the intermediates and removal of COD and TOC was also monitored. In order to analyze the COD, the samples were digested in the COD reactor for 2 h at 150 °C.

The stock solution of 2,4-D (100 mg/L) was prepared in 100 mL buffer (different buffer, c = 0.2 M) solution. In this study, the performance of the process was assessed using different influential parameters, which these parameters and their studied range were as follows: initial pH (3.0-11.0), electrolysis time (20-80 min), initial concentration of 2,4-D (100 mg/L) and current density (1-5 mA/cm^2). It should be mentioned that the optimization of the main parameters was carried out using the central composite design (CCD) method.

After adjusting all components of the daily prepared solution, the samples were collected at predetermined time intervals by passing through the 0.45 μm membrane filter, and the concentration of 2,4-D was determined using a UV- Vis spectrophotometer at a wavelength of 282 nm. To authenticate the accuracy of the measurements, the HPLC was used.

Eq. S1, S2 and S3 were employed to calculate the 2, 4-D degradation, COD (mg/L) and TOC (mg/L) removal efficiency:

$$Degradation\,(\%) = \frac{C_0 - C_t}{C_0} \times 100 \qquad \text{(S1)}$$

$$COD\,removal\,(\%) = \frac{COD_0 - COD_t}{COD_0} \times 100 \qquad \text{(S2)}$$

$$TOC\,removal\,(\%) = \frac{TOC_0 - TOC_t}{TOC_0} \times 100 \qquad \text{(S3)}$$

where C_0 and C_t are representative of the initial of 2, 4-D concentration and the concentration of 2, 4-D at a particular time, during the electrochemical treatment, respectively. COD_0 and COD_t represent the COD before and after electrolysis, respectively. The COD and TOC evolution were measured at the beginning of the electrolysis (0 min) and after 80 min (the end of the electrolysis).

The value of energy consumption as a function of treated solution volume was also calculated by Eq. (S4).

$$E_{EC} = \frac{UIt_{EC}}{V_s} \times 10^{-3} \qquad \text{(S4)}$$

where E_{EC} is the electrical energy in kWh/m^3, U is the cell voltage in volt (V), I is the current in ampere (A), t_{EC} is the electrolysis time of EC process (hr) and V_s is the volume of the electrolyte (L).

Considering that many industrial effluents contain the organics with low conductivity, an SE must be added to increase their conductivity and to reduce the cell potential to simplify the electrochemical process. Therefore, determination of SE concentration was essential to advance the ionic strength, especially for the solutions without enough conductivity[30-31]. To determine the optimum concentration of the SE, which can provide the studied current density (1-5 mA/cm^2), Na_2SO_4 (0-1.0 gr) were dissolved in 100 cc 2,4-D solution, and the corresponding potential was then assessed after applying the currents.

Preparation of the SS316/β-PbO_2 electrode

In order to prepare the SS316/β-PbO2, the SS316 electrodes with dimensions of 60 × 28 × 1 mm were prepared. Then, it was mechanically polished with big-grade rubbers. Furthermore, for decreasing the surface of the SS316 electrodes, they were exposed to diluted nitric acid (HNO3) for 24h. Then, they well washed with distilled water and was sonicated in the water and ethanol solution at 20 KHz for 20 min. Electrodeposition of the lead dioxide on a steel electrode was carried out using 500 ml electrolytic solution including lead nitrate (Pb(NO3)2) and HNO3. The solution was made using 24 g of Pb(NO3)2 in 1 L distilled water and 0.1 molar HNO3. Then, for the electrochemical coating of lead dioxide (PbO2) per cm2, a current of 2 mA was applied for 5 to 8 hours. After the electrochemical coating process, the prepared electrodes were well washed with distilled water[32].

Preparation of the Pb/β-PbO_2 electrode

Preparation of lead bed with the dimensions of 60 × 25 × 4 mm was performed prior to coating to provide good adhesion to lead dioxide (PbO2). First, to increase the PbO2 adhesion, the surface of the lead electrode was mechanically polished using the different grades of sandpaper. Then, to remove the fine particles or any other particle on the metal surface, the lead bed was immersed in a solution of H2SO4 at 65 °C for 30 min to completely clean the surface of the electrode. Formation of PbO2 was carried out using the electrochemical oxidation of lead in H2SO4 (1 M) solution using an anodic current density of 25 mA/cm2 at 25 °C[32-33]

The overall reaction of PbO_2 formation engages two steps[48]. First, Pb is oxidized to PbO and $PbO \cdot PbSO_4$ (Eqs. (S5) and (S6)).

$$Pb + H_2O \rightarrow tet - PbO + 2e^- + 2H^+ \quad \text{(S5)}$$

$$2Pb + SO^{2-}_4 + H_2O \rightarrow PbO.PbSO_4 + 2H^+ + 4e^- \quad \text{(S6)}$$

The second step is the formation of β-PbO_2 that is generated through the oxidation of PbO and $PbSO_4$, respectively. The acidic media has been introduced to be favorable for β-PbO (Eq. S7).

$$PbSO_4 + 2H_2O \rightarrow \beta - PbO_2 + SO^{2-}_4 + 4H^+ + 2e^- \quad \text{(S7)}$$

Preparation of the G/β-PbO_2 electrode

The graphite electrodes with the dimensions of 60 × 25 × 4 mm were used to prepare the G/β-PbO_2. The surface of the electrode was polished by the very soft sandpaper. Afterward, it was washed by distilled water. The G/β-PbO_2 electrode was prepared by electrochemical deposition on graphite. First, the graphite was sonicated with 40% NaOH solution and 1:1 (V/V) HNO_3/H_2SO_4 for 20 min. Finally, the graphite was washed with deionized water and was transferred to an electrochemical deposition cell containing 0.5 M $Pb(NO_3)_2$ in 0.1 M HNO_3 solution. The electrochemical deposition of PbO_2 on graphite was carried out at the current density of 5 mA/cm^2 for 180 to 240 min. All of the experiments were carried out at 25°C[28, 32, 34].

Experimental design

The degradation of 2,4-D herbicide by the electrochemical process was carried out using response surface methodology (RSM). RSM is a set of useful statistical calculation techniques which is utilized to analyze the effects of several independent variables on the response and it is significantly applied to design and to optimize the process. RSM is used to reduce the number of experimental runs, which are necessary to create a mathematical trend in the experimental design region to establish the optimum level of experimental factors required for a given response[35-37]. A central composite design methodology (CCD) was used to optimize the 2,4-D degradation using the electrochemical process. Three major independent variables used in this study based on preliminary experiments include pH, electrolysis time and current intensity. The experimental range and levels of independent variables studied for 2,4-D herbicide degradation at three levels are shown in Table S1. The values of the variables and their variation limits were selected based on preliminary experiments. During these experiments, the 2,4-D herbicide degradation efficiency was used to evaluate the effectiveness of the process. Table 1 shows the experimental conditions according to the factorial design. The measured responses include the degradation of 2,4-D herbicide (100 mg/L) using the anodes electrodes, i.e., SS316/β-PbO_2 (lead oxide coated on stainless steel 316), Pb/β-PbO_2 (lead oxide coated on the Lead bed), G/β-PbO_2 (Graphite coated on graphite). The results obtained based on CCD were analyzed using ANOVA variable analysis and multiple regression analysis. Furthermore, the results can be demonstrated by 3D plot regarding the simultaneous effect of independent variables on the responses. The effectiveness of the fit of the model was represented by the determination coefficient (R^2). Model terms were determined by the p-value and the F-value. The evaluation of the effect of model functions was carried out using the P value (confidence level of 95%). The analysis of variance and other statistical data were calculated and generated using the Design Expert Software version 7.2. The multi-degree coefficients of Eq. S8 were applied to assess the correlations between the responses and the independent variables[38-39].

$$Y= \beta_0+ \beta_i X_i + \beta_j X_j + \beta_{ii} X_i^2 + \beta_{jj} X_j^2 + \beta_{ij} X_i X_j + \ldots \qquad (S8)$$

where Y is the process response, β_0 is the constant coefficient often described as intercept, X_i is the non-coded variable, β_i is the linear, and β_{ii} is the quadratic, and β_{ij} is the second order interaction coefficients.

The effect of supporting electrolyte

Supporting electrolyte (SE) is one of the most important parameters, which is effective on the electro-catalytic degradation process. In the present study, Na_2SO_4 was selected as an SE. When Na_2SO_4 is used as an auxiliary electrolyte to increase the electrical conductivity of the solution (it increases the current density), the pollutant is indirectly oxidized by hydroxyl radicals and sulfate radicals during the electrolysis process[17]. The results of the study conducted by Souza et al. (2013) showed that Na_2SO_4 had the greatest effect on the phenol removal efficiency among the supporting electrolytes studied[40]. Moreover, Jafarzadeh et al. (2018) introduced the Na_2SO_4 as a best supporting electrolyte, among the three supported electrolytes (Na_2SO_4, NaCl and $NaNO_3$), to degrade the 2,4-Dichlorophenoxyacetic acid (2,4-D) herbicide[41], which it confirms the results of the present study. Determination of the optimum amount of Na_2SO_4 (used as supporting electrolyte, SE) was performed based on the appropriate applied voltage. As seen from Table S5, all concentrations can provide the required current densities, but the higher potentials need to be applied at low SE dosages. Considering the proximity of the voltage produced at both SE dosage (0.6 and 1 g/100 cc), the SE dosage of 0.6 g/100 cc was selected as the optimum value for the present study (Table S5). The rest of the 2,4-D herbicide electro-catalytic degradation experiments were performed by three anodes electrodes (SS316/β-PbO_2, Pb/β-PbO_2 and G/β-PbO_2) using the determined SE dosage.

Table S1. Examined levels of independent variables

Symbol	Factors	Unit	Range and levels		
			-1	0	+1
A	pH	-	3	7	11
B	Current density (*j*)	mA/cm^2	1	3	5
C	Electrolysis time	min	20	50	80

Table S2. Statistical models obtained from the analysis of variance for response surface reduced quadratic model for optimization of 2,4-D degradation. (SS316/β-PbO_2 electrode anode)

Source	Sum of Squares	Df	Mean Square	F- Value	p-value	Prob > F
Model	2560.17	6	426.69	45.46	< 0.0001	significant
A-pH	400.69	1	400.69	42.69	< 0.0001	
B-*j*	557.41	1	557.41	59.39	< 0.0001	
C-Time	1158.42	1	1158.42	123.42	< 0.0001	
AC	155.85	1	155.85	16.60	0.0013	
BC	65.15	1	65.15	6.94	0.0206	
C^2	222.64	1	222.64	23.72	0.0003	
Residual	122.02	13	9.39			
Lack of Fit	90.49	8	11.31	1.79	0.2695	not significant
Pure Error	31.54	5	6.31			
Cor Total	2682.19	19				

Table S3. Statistical models obtained from the analysis of variance for response surface reduced quadratic model for optimization of 2,4-D degradation. (Pb/β-PbO_2 electrode anode)

Source	Sum of Squares	Df	Mean Square	F- Value	p-value	Prob > F
Model	3726.30	6	621.05	44.12	< 0.0001	significant
A-pH	658.69	1	658.69	46.79	< 0.0001	
B- *j*	595.06	1	595.06	42.27	< 0.0001	
C-Time	1567.50	1	1567.50	111.36	< 0.0001	
AC	160.56	1	160.56	11.41	0.0050	
BC	119.97	1	119.97	8.52	0.0120	
C^2	624.51	1	624.51	44.37	< 0.0001	
Residual	182.99	13	14.08			
Lack of Fit	140.80	8	17.60	2.09	0.2171	not significant

Pure Error	42.19	5	8.44			
Cor Total	3909.30	19				

Table S4. Statistical models obtained from the analysis of variance for response surface reduced quadratic model for optimization of 2,4-D degradation. (G/β-PbO_2 electrode anode)

Source	**Sum of Squares**	**Df**	**Mean Square**	**F- Value**	**p-value**	**Prob > F**
Model	3538.89	6	589.82	47.08	< 0.0001	significant
A-pH	690.56	1	690.56	55.12	< 0.0001	
B- *j*	509.08	1	509.08	40.63	< 0.0001	
C-Time	1510.69	1	1510.69	120.58	< 0.0001	
AC	182.02	1	182.02	14.53	0.0022	
BC	88.45	1	88.45	7.06	0.0197	
C^2	558.10	1	558.10	44.55	< 0.0001	
Residual	162.87	13	12.53			
Lack of Fit	131.84	8	16.48	2.66	0.1485	not significant
Pure Error	31.03	5	6.21			
Cor Total	3701.77	19				

Table S5. Supporting electrolyte (SE) dose providing desired currents and the corresponding potentials

Na_2SO_4 dose (gr/100 cc)	**Current (A)**	**Voltage (V)**		
		SS316/β-PbO_2	**Pb/β-PbO_2**	**G/β-PbO_2**
0	0.07	8.9	8.5	6.7
	0.19	18.2	17.1	12.5
	0.32	28.5	25.7	18.2
0.1	0.07	4.5	4.3	3.8
	0.19	7.3	6.9	5.5
	0.32	10.4	9.6	7.2
0.2	0.07	3.8	3.7	3.5
	0.19	5.5	5.3	4.5
	0.32	7.2	6.9	5.5
0.3	0.07	3.6	3.4	3.3
	0.19	4.9	4.6	4.1
	0.32	6.3	5.8	4.9
0.6	0.07	3.3	3.1	3.1
	0.19	4.1	3.9	3.6
	0.32	5	4.6	4.2
1	0.07	3.1	2.9	2.9
	0.19	3.7	3.5	3.3
	0.32	4.3	4	3.7

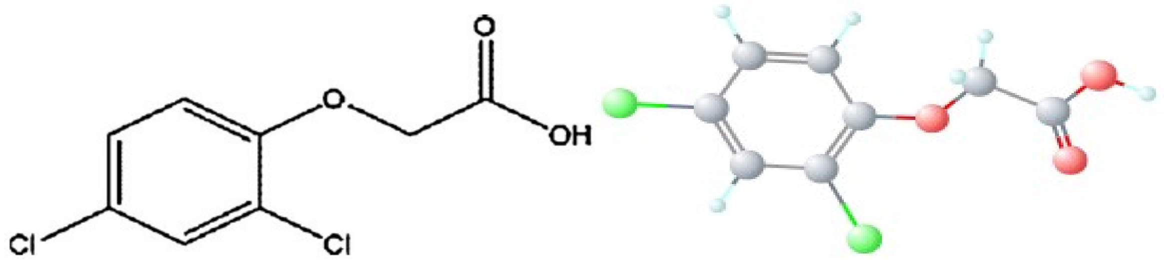


Fig. S1. Molecular structure of 2, 4- diclorophenoxy acetic acid herbicide.

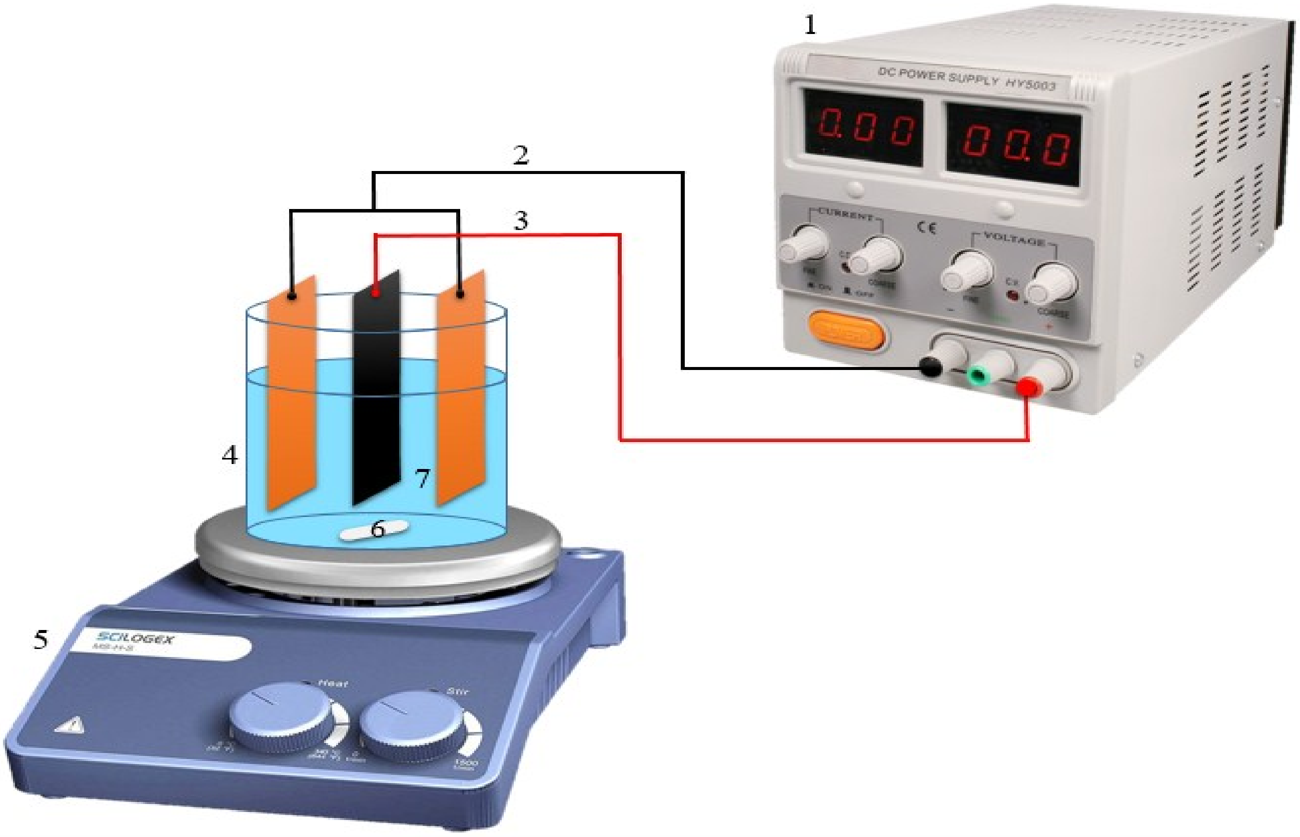


Fig. S2. The batch electrochemical reactor, 1. DC Power supply, 2. Anode electrode, 3. Cathode electrode, 4. Electrochemical cell, 5. Magnetic stirrer controlled, 6. Magnetic stirrer bar, 7. Simulated 2,4-D herbicide solution.

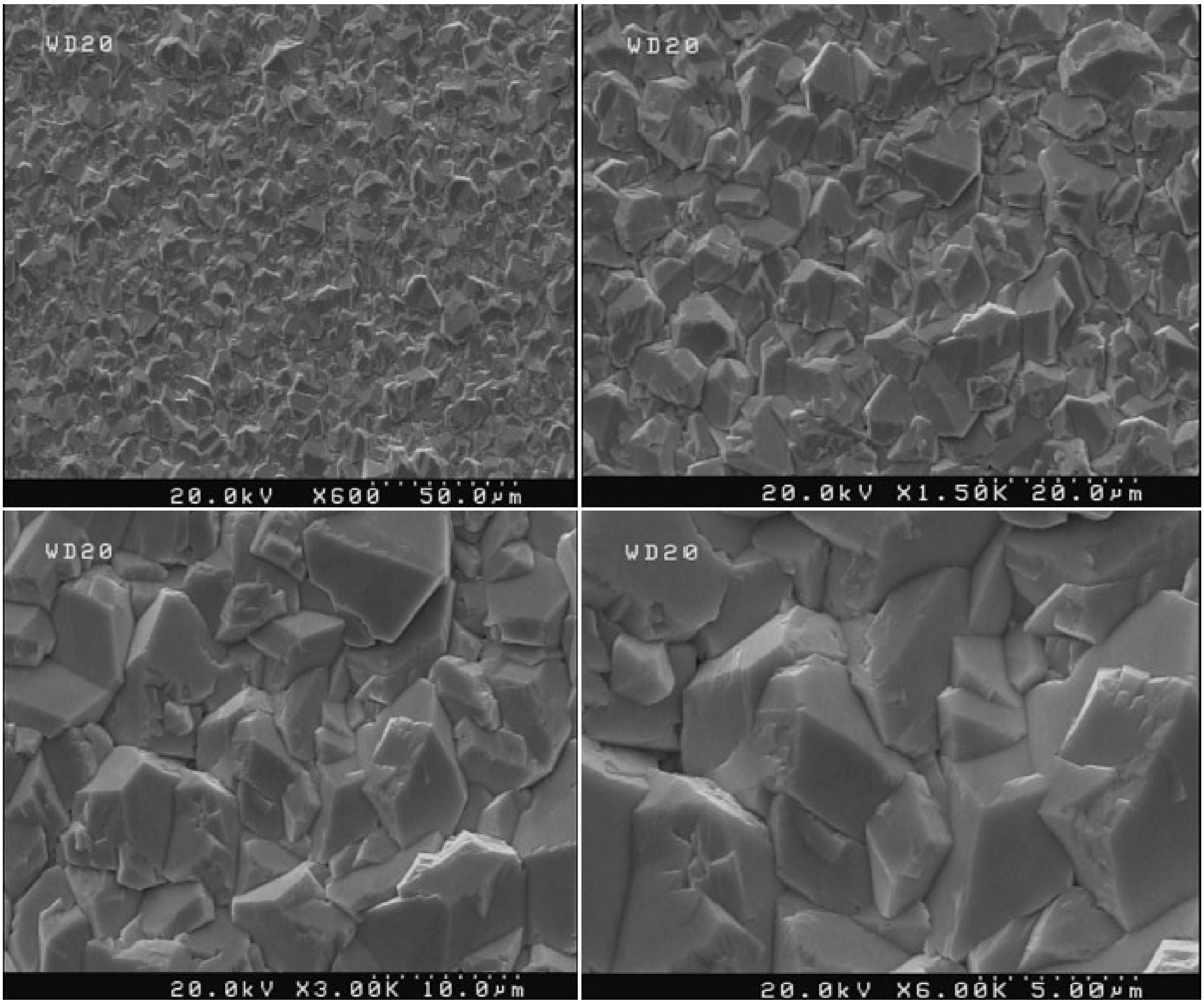


Fig. S3. Part I (a)

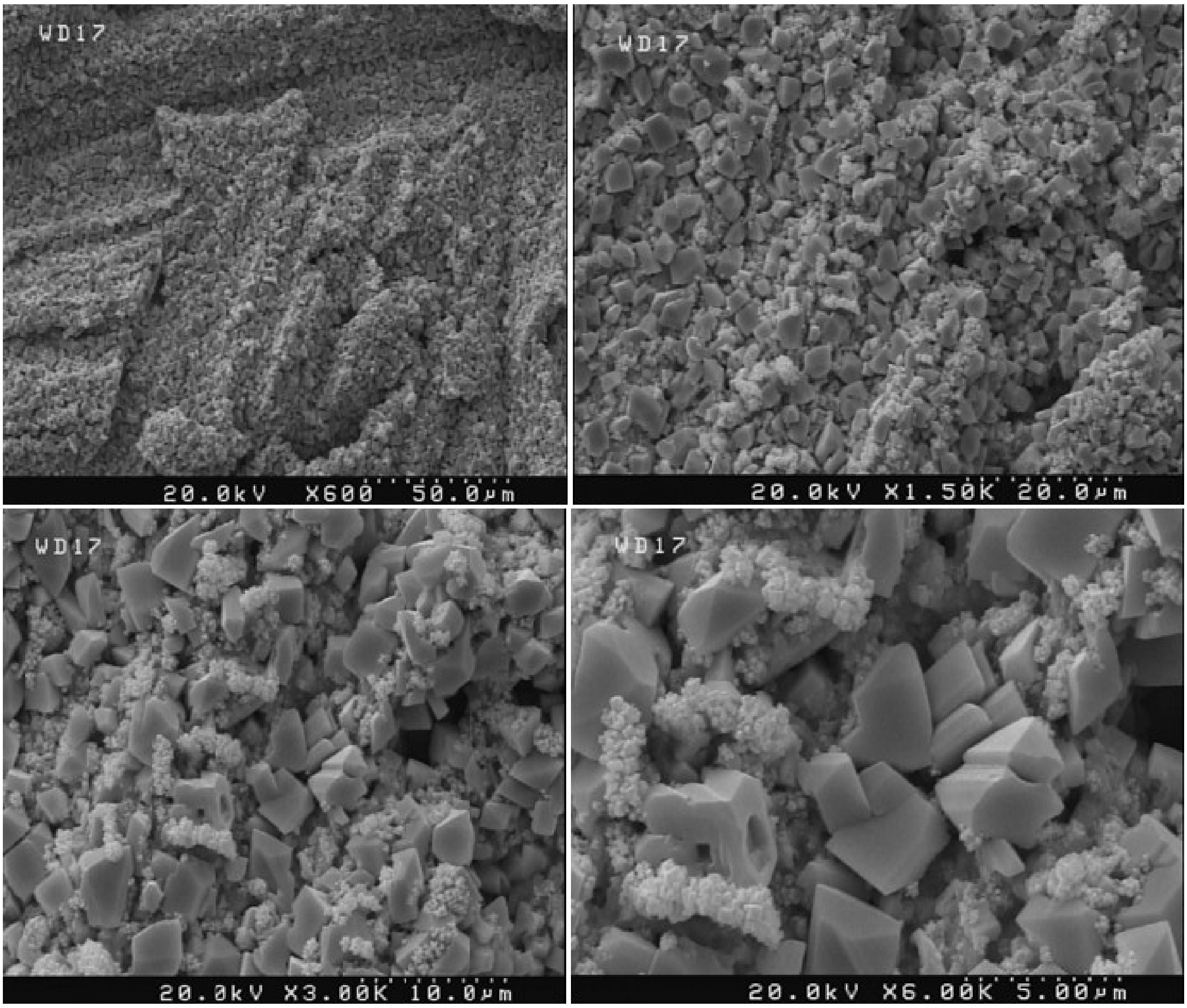


Fig. S3. Part I (b)

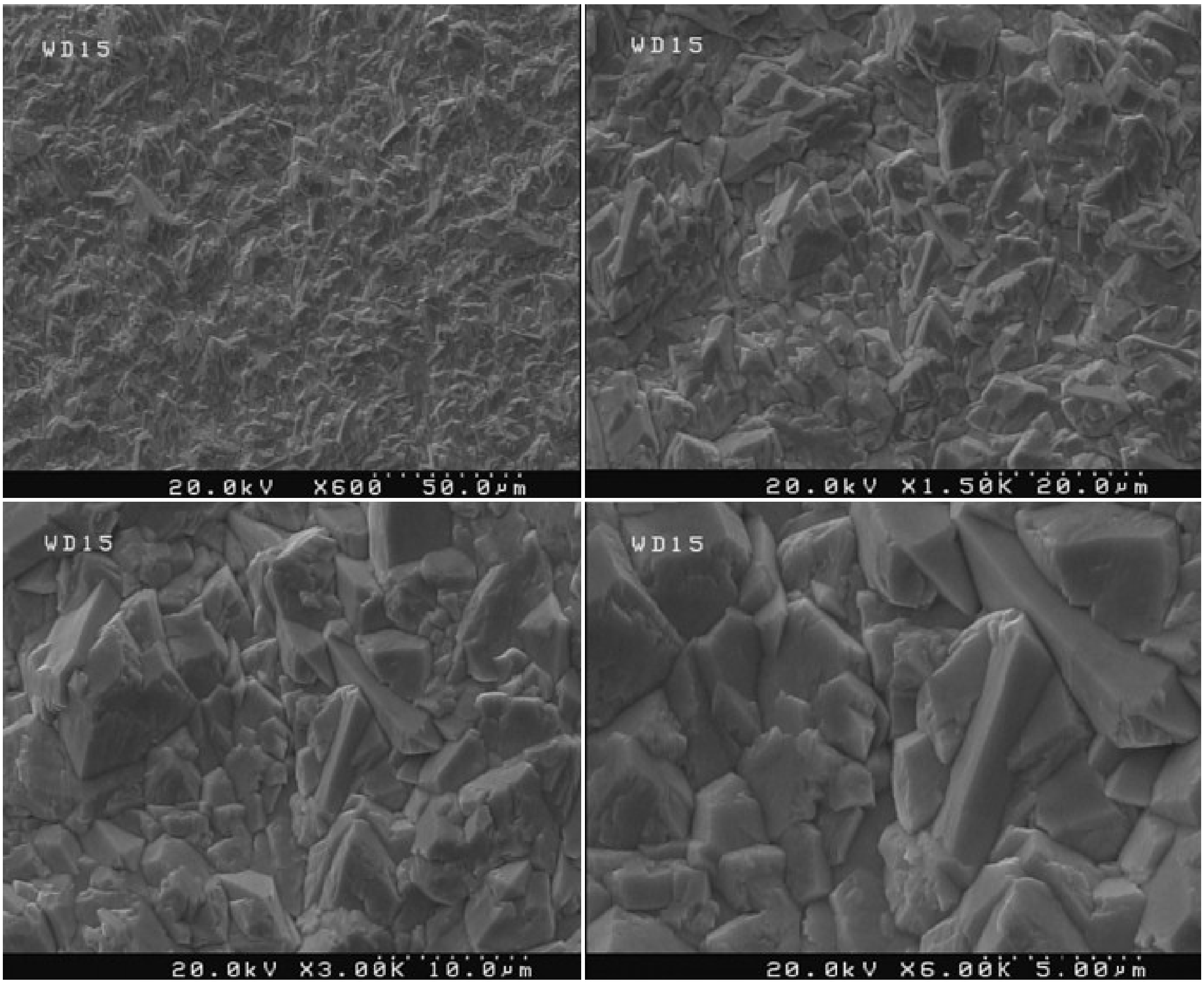
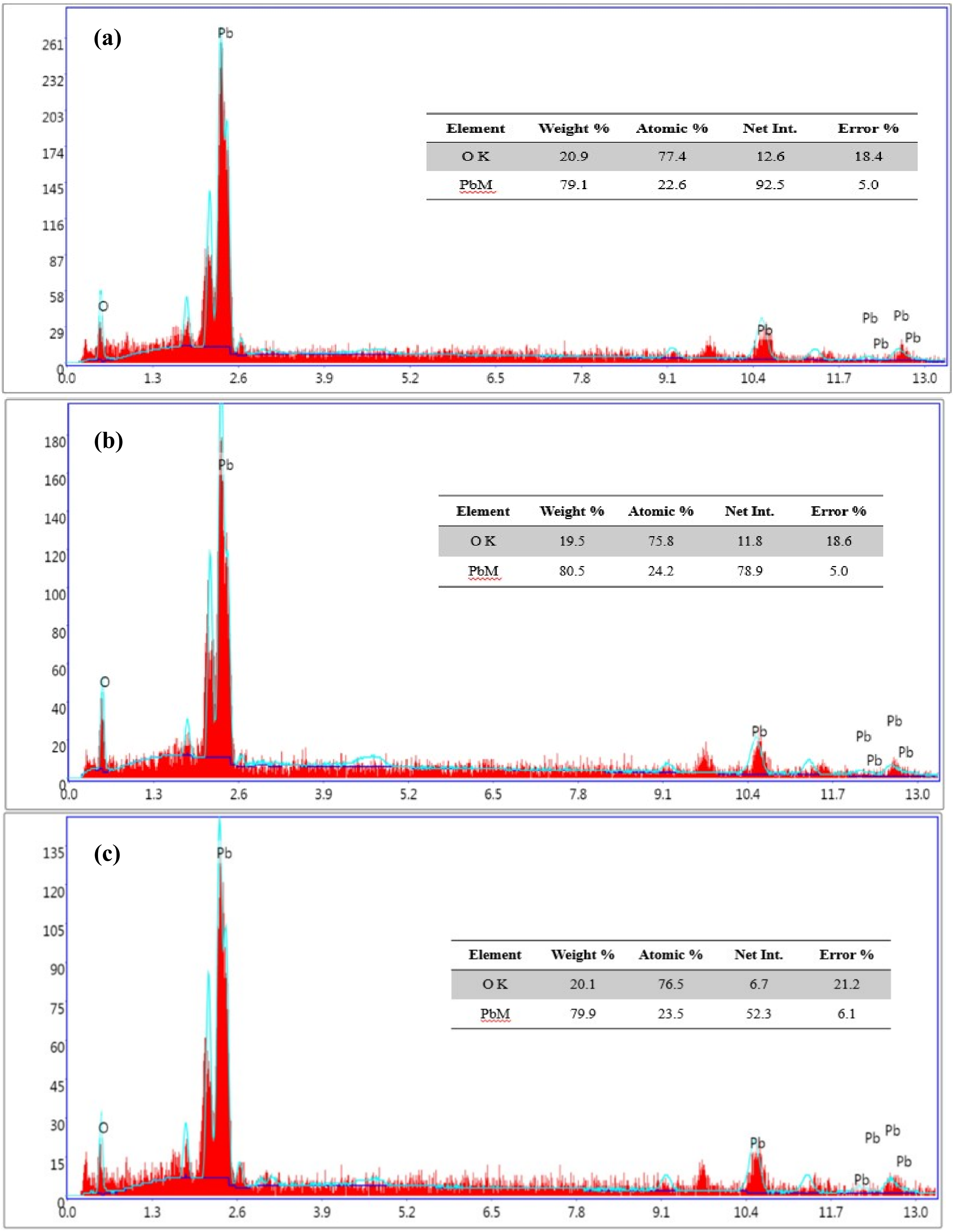


Fig. S3. Part I (c)



(a)

Element	Weight %	Atomic %	Net Int.	Error %
O K	20.9	77.4	12.6	18.4
PbM	79.1	22.6	92.5	5.0

(b)

Element	Weight %	Atomic %	Net Int.	Error %
O K	19.5	75.8	11.8	18.6
PbM	80.5	24.2	78.9	5.0

(c)

Element	Weight %	Atomic %	Net Int.	Error %
O K	20.1	76.5	6.7	21.2
PbM	79.9	23.5	52.3	6.1

Fig.S3. Part II

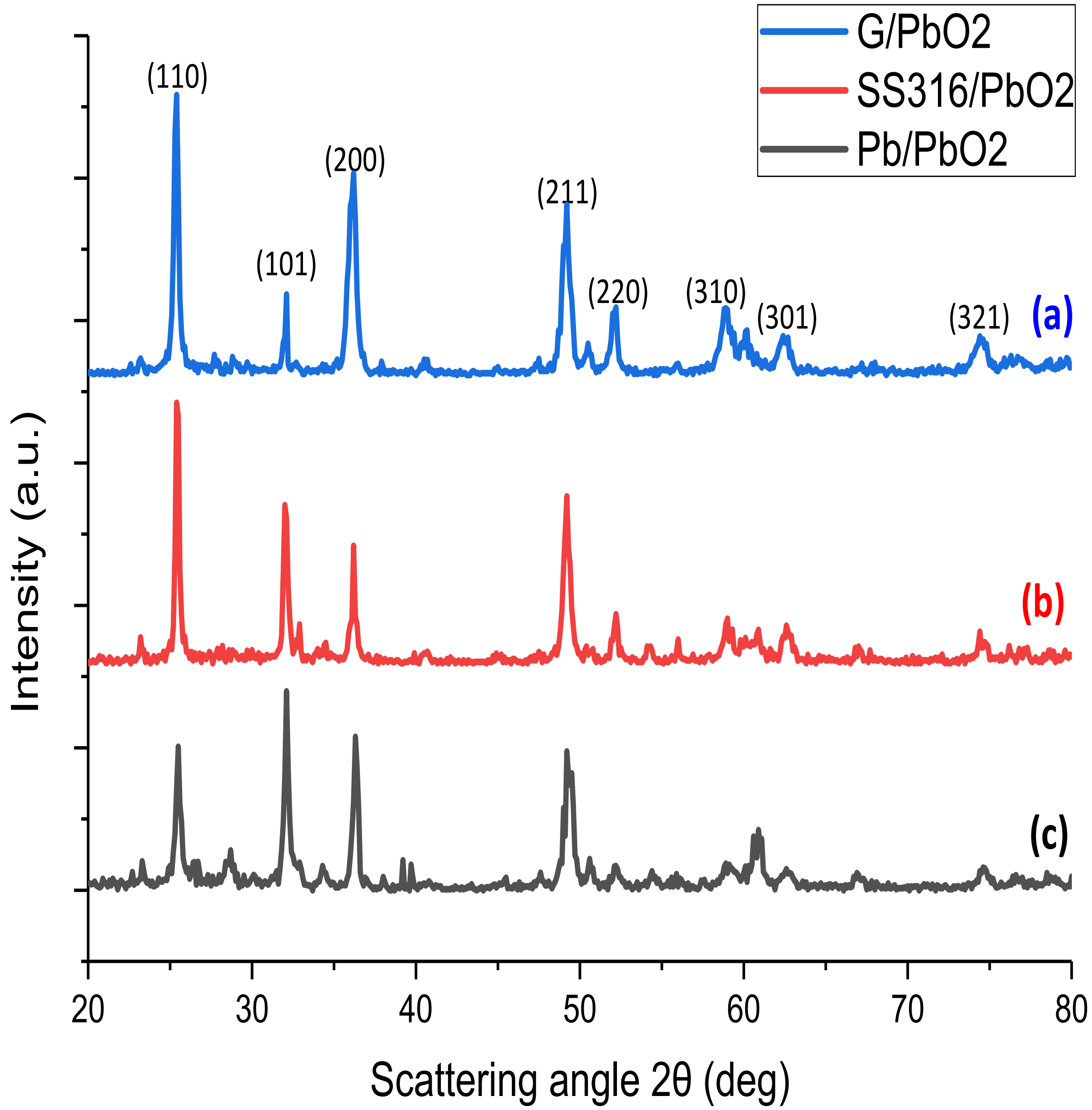


Fig.S3. (Part III)

Fig.S3. SEM images of the surface morphology at different magnifications (Part I), EDX analysis (Part II), and XRD diffractograms (Part III) of the β-PbO_2 electrodeposited on different substrates. (a) G/β-PbO_2, (b) Pb/β-PbO_2 and (c) SS316/β-PbO_2.

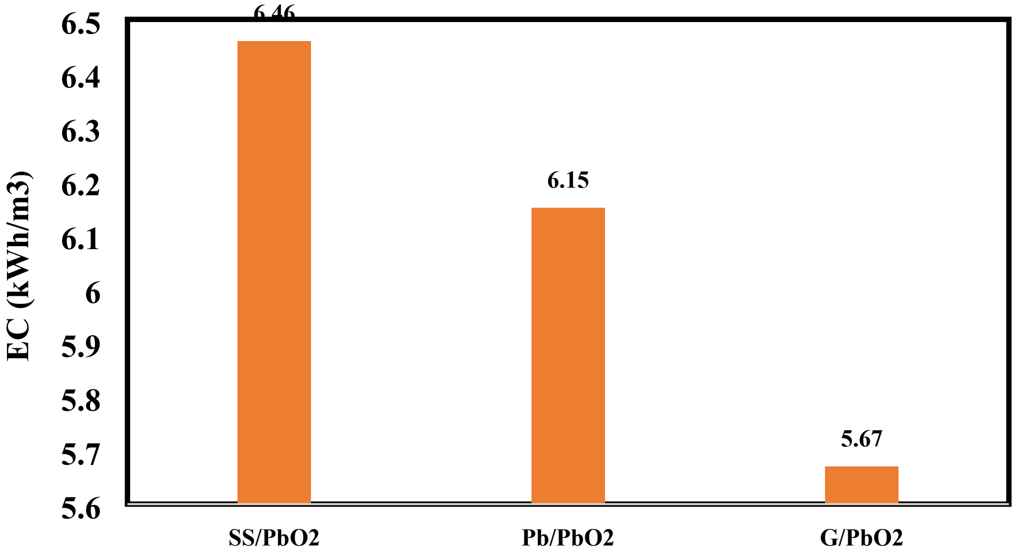


Fig. S4. The Energy consumption to 2,4-D herbicide removal at optimum conditions by EC. pH: 7, *j*: 3 mA/cm^2 and Time 50 min)

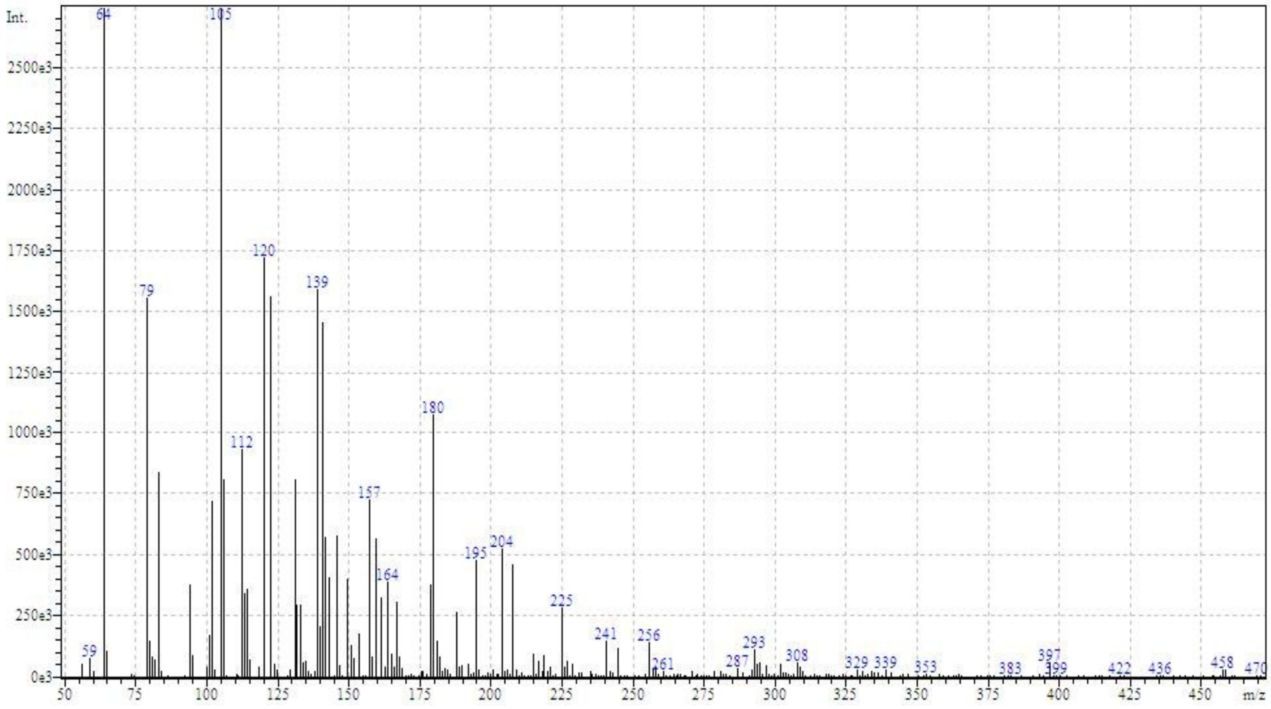


Fig. S5. LC/MS chromatographs after degradation of 2,4-D herbicide at the optimum conditions.

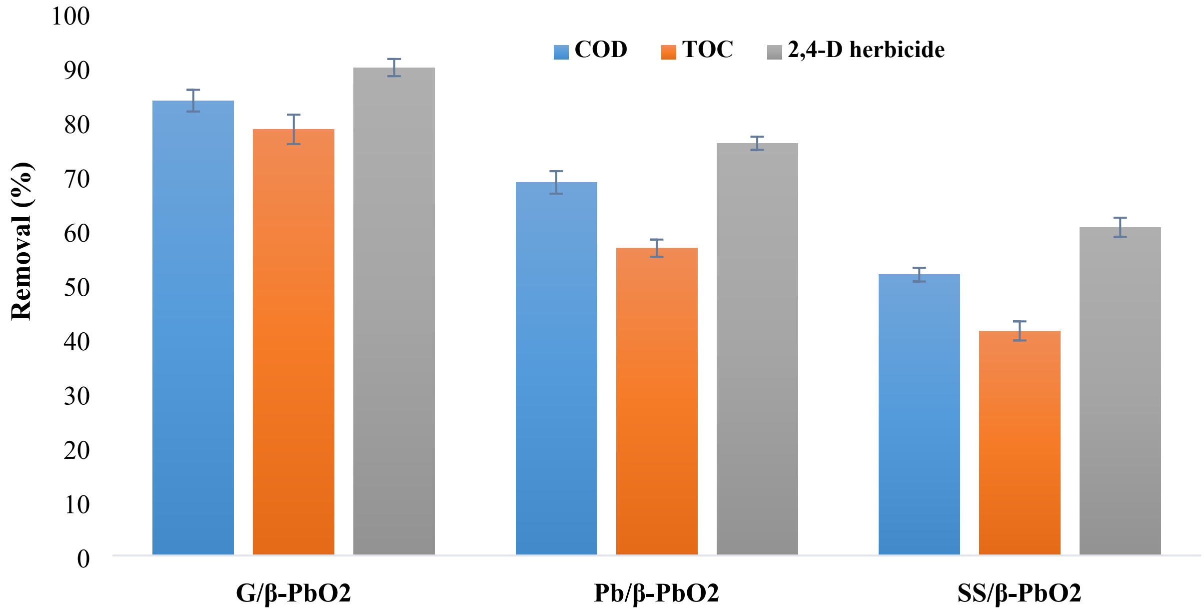


Fig. S6. Performance comparison of anode electrodes in the removal of 2,4-D herbicide and COD (pH: 3, Time: 80 min, Current density: 5 mA/cm^2, COD$_0$=108 mg/L, TOC$_0$= 57 mg/L, Supporting electrolyte: 0.6 gr/100cc Na_2SO_4 and initial 2,4-D herbicide: 100 mg/L).

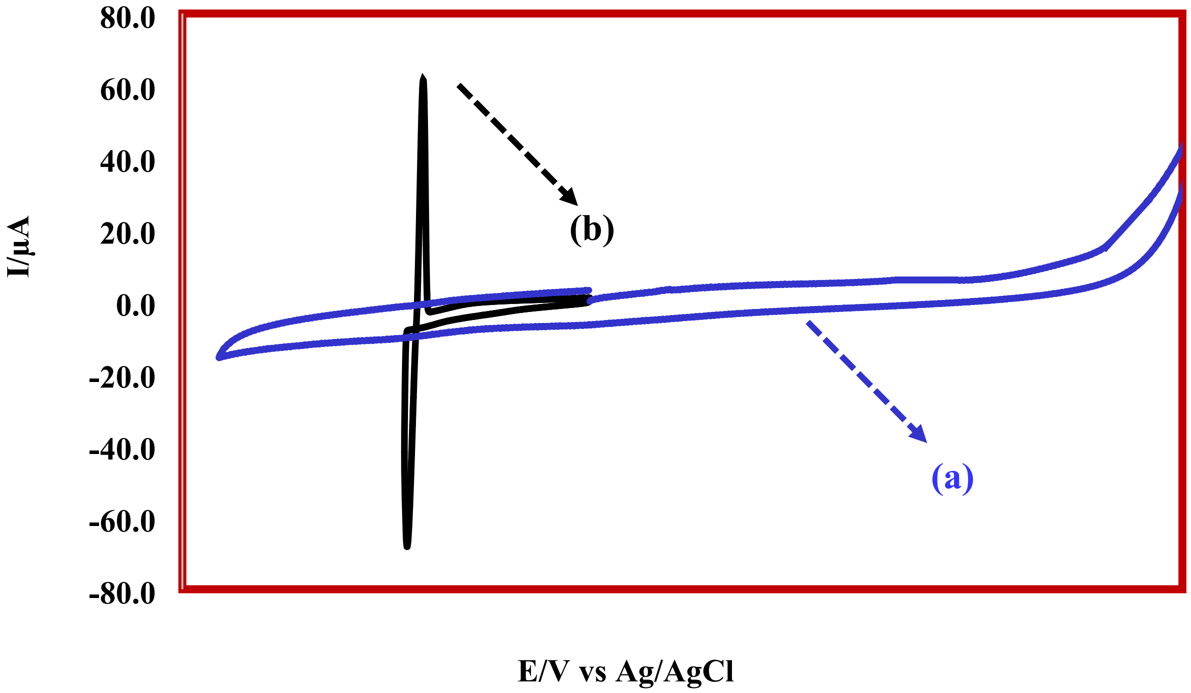


Fig. S7. Cyclic voltammogram of the electrolyzed solution containing 2,4-D herbicide + Na_2SO_4. (a) before spiked with $Pb(NO_3)2$ and (b) after spiked with $Pb(NO_3)2$ (1.5 x 10^{-6} M), at glassy carbon electrode, in aqueous solution, pH = 5.0. Scan rate: 100 mV/s at room temperature.