Supplementary Information

Determination of quercetin by thin film microextraction method using in-situ growth of Co-Al-layered double hydroxide nanosheets on electrochemically anodized aluminum substrate followed by HPLC

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Table S1

Experimental variables and levels of the Plackett–Burman design

Factor	Name	Level	
		Min (-1)	Max (+1)
A	Extraction time (min)	20	40
B	Stirring rate (rpm)	700	1100
C	pH	5	8
D	Desorption time (min)	2	5
E	Ionic strength (% w/v)	0	20
F	Desorption volume (μL)	50	200

Table S2

The matrix of the Plackett–Burman design experiments obtained from MINITAB and the response (peak area).

Experimental number	Factors						Response
	Extraction Time	Stirring rate	pH	Desorption time	Ionic strength	Desorption volume	
1	1	-1	1	1	-1	1	1.29
2	-1	1	1	1	-1	1	0.80
3	1	-1	-1	-1	1	1	1.43
4	1	1	-1	1	-1	-1	0.72
5	-1	1	1	-1	1	-1	0.48
6	-1	-1	-1	-1	-1	-1	0.69
7	1	1	-1	1	1	-1	0.72
8	1	-1	1	-1	-1	-1	0.85
9	-1	-1	1	1	1	-1	0.64
10	-1	-1	-1	1	1	1	1.18
11	1	1	1	-1	1	1	1.14
12	-1	1	-1	-1	-1	1	0.86

Table S3
Analysis of the variance for the fit of the experimental data to Plackett–Burman design

Source	Degree of freedom (D.F)	Sum of squares (seq. SS)	Adjusted sum of squares (adj. SS)	Adjusted mean squares (adj. MS)	*F*-value	*p*-Value
Main Effects	6	0.931167	0.931167	0.155194	160.55	0.000
Extraction Time	1	0.187500	0.187500	0.187500	193.97	0.000
Stirring rate	1	0.154133	0.154133	0.154133	159.45	0.000
pH	1	0.013333	0.013333	0.013333	13.79	0.014
Desorption time	1	0.000833	0.000833	0.000833	0.86	0.396
Ionic strength	1	0.012033	0.012033	0.012033	12.45	0.017
Desorption volume	1	0.563333	0.563333	0.563333	582.76	0.000
Residual Error	5	0.004833	0.004833	0.000967		
Total	11	0.936000				

Table S4

Experimental variables and levels of the Box-Behnken designs design (BBD).

Factor	Name	Level		
		Min (-1)	Central (0)	Max (+1)
A	Desorption volume (μL)	50	125	200
B	Extraction time (min)	20	30	40
C	Stirring rate (rpm)	700	900	1100
D	Ionic strength(% w/v)	0	10	20
E	pH	5	6.5	8

Table S5

The matrix of the Box-Behnken design experiments obtained from MINITAB and the response (peak area for quercetin).

Experimental number	Factors					Response
	Desorption volume	Extraction time	Stirring rate	Ionic strength	pH	
1	1	0	-1	0	0	6.4
2	-1	0	1	0	0	6.2
3	0	-1	0	0	1	5.6
4	-1	0	0	1	0	3.1
5	0	0	1	0	1	3.8
6	0	0	0	1	-1	4.8
7	1	0	0	0	1	4.3
8	0	1	0	0	-1	2.9
9	0	0	0	0	0	6.1
10	-1	0	0	0	-1	4.7
11	1	-1	0	0	0	6.2
12	0	0	1	0	-1	6.8
13	-1	0	0	0	1	6.1
14	0	0	1	-1	0	4
15	0	-1	0	0	-1	6.2
16	-1	1	0	0	0	3.7
17	-1	0	0	-1	0	9.2
18	1	0	1	0	0	7.1
19	0	0	-1	1	0	4.3
20	0	1	1	0	0	5
21	-1	-1	0	0	0	8.5
22	0	0	0	1	1	4.2
23	0	0	-1	0	1	7.3
24	-1	0	-1	0	0	7.9
25	1	0	0	0	-1	5.7

26	0	0	-1	0	-1	4.1
27	0	1	0	1	0	3.9
28	0	0	1	1	0	8.1
29	0	0	0	0	0	6.1
30	0	-1	-1	0	0	8.2
31	0	0	0	0	0	5.9
32	1	1	0	0	0	5.3
33	0	-1	0	-1	0	6.9
34	0	-1	1	0	0	6.8
35	0	1	-1	0	0	4.7
36	0	1	0	-1	0	4.3
37	0	-1	0	1	0	6.7
38	1	0	0	1	0	8.8
39	0	0	-1	-1	0	8.9
40	0	1	0	0	1	3.7
41	1	0	0	-1	0	3.1
42	0	0	0	-1	-1	4.5
43	0	0	0	-1	1	5.3

Table S6

Analysis of the variance for the fit of the experimental data to response surface model

Source	Degree of freedom (D.F)	Sum of squares (seq. SS)	Adjusted sum of squares (adj. SS)	Adjusted mean squares (adj. MS)	*F*-value	*p*-Value
Regression	19	122.627	122.627	6.4541	922.96	0.000
Linear	5	30.904	30.904	6.1807	883.88	0.000
Desorption volume	1	0.391	0.391	0.3906	55.86	0.000
Extraction time	1	29.160	29.160	29.1600	4170.03	0.000
Stirring rate	1	1.000	1.000	1.0000	143.01	0.000
Ionic strength	1	0.331	0.331	0.3306	47.28	0.000
pH	1	0.022	0.022	0.0225	3.22	0.086
Square	5	19.476	19.476	3.8952	557.03	0.000
Desorption volume* Desorption volume	1	2.477	0.477	0.4767	68.17	0.000
Extraction time* Extraction time	1	0.314	0.870	0.8703	124.45	0.000
Stirring rate* Stirring rate	1	8.580	1.921	1.9214	274.76	0.000
Ionic strength* Ionic strength	1	0.565	0.380	0.3803	54.38	0.000
pH* pH	1	7.540	7.540	7.5400	1078.26	0.000
Interaction	9	72.247	72.248	8.0275	1147.97	0.000
Desorption volume * Extraction time	1	3.803	3.802	3.8025	543.78	0.000
Desorption volume * Stirring rate	1	1.440	1.440	1.4400	205.93	0.000
Desorption volume * Ionic strength	1	34.810	34.810	34.8100	497.101	0.000
Desorption volume * pH	1	1.960	1.960	1.9600	280.29	0.000
Extraction time * Stirring rate	1	0.722	0.722	0.7225	103.32	0.000
Extraction time * pH	1	0.490	0.490	0.4900	70.07	0.000
Stirring rate * Ionic strength	1	18.922	18.922	18.9225	2706.02	0.000
Stirring rate * pH	1	9.610	9.610	9.6100	1374.28	0.000
Ionic strength * pH	1	0.490	0.490	0.4900	70.07	0.000
Residual Error	23	0.161	0.161	0.0070		
Lack-of-Fit	21	0.134	0.134	0.0064	0.48	0.851
Pure Error	2	0.027	0.027	0.0133		
Total	42	122.788				

Table S7

Estimated regression coefficients of Y (peak area) for the proposed model of BBD design together with standard error and *t*-value

Term	Coefficient	Standard error of coefficient	*t*-value
Constant	6.03333	0.04828	124.967
Desorption volume(A)	-0.15625	0.02091	-7.474
Extraction time(B)	-1.35000	0.02091	-64.576
Stirring rate(C)	-0.25000	0.02091	-11.958
Ionic strength(D)	-0.14375	0.02091	-6.876
pH (E)	0.03750	0.02091	1.794
Desorption volume*Desorption volume	0.27292	0.03305	8.256
Extraction time*Extraction time	-0.36875	0.03305	-11.156
Stirring rate*Stirring rate	0.54792	0.03305	16.576
Ionic strength*Ionic strength	-0.24375	0.03305	-7.374
pH*pH	-1.08542	0.03305	-32.837
Desorption volume*Extraction time	0.97500	0.04181	23.319
Desorption volume*Stirring rate	0.60000	0.04181	14.350
Desorption volume*Ionic strength	2.95000	0.04181	70.555
Desorption volume*pH	-0.70000	0.04181	-16.742
Extraction time*Stirring rate	0.42500	0.04181	10.165
Extraction time*pH	0.35000	0.04181	8.371
Stirring*Ionic strength	2.17500	0.04181	52.019
Stirring*pH	-1.55000	0.04181	-37.071
Ionic strength*pH	-0.35000	0.04181	-8.371

Table S8

Estimated determination coefficient of the BBD design

R^2	R^2 (pred)	R^2 (adj)
0.9987	0.9954	0.9976

Table S9
Optimized value of the factors obtained from BBD design (coded and un-coded values).

Factor	**Desorption volume**	**Extraction time**	**Stirring rate**	**Ionic strength**	**pH**
Coded value	-1	-1	-1	-1	1
un-coded values	50 µL	20 min	700 rpm	0%	8

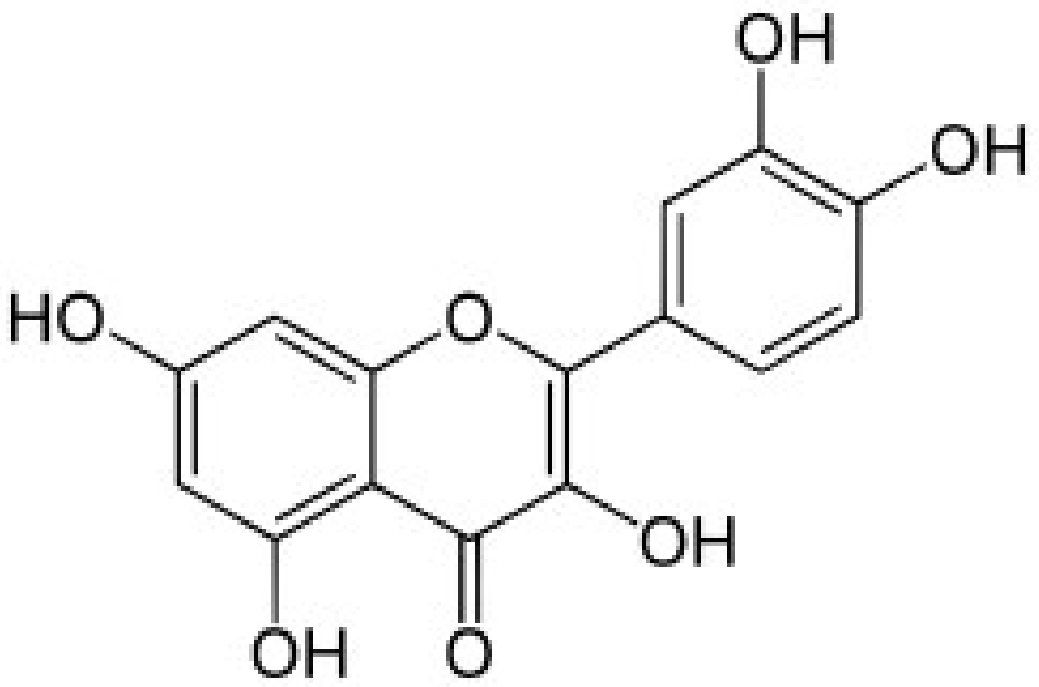


Figure S1. The structure of the quercetin [1]

[1] J. M. Herrero-Martínez, M. Sanmartin, M. Rosés, E. Bosch, C. Ràfols, Determination of dissociation constants of flavonoids by capillary electrophoresis, Electrophoresis 26 (2005) 1886–1895.

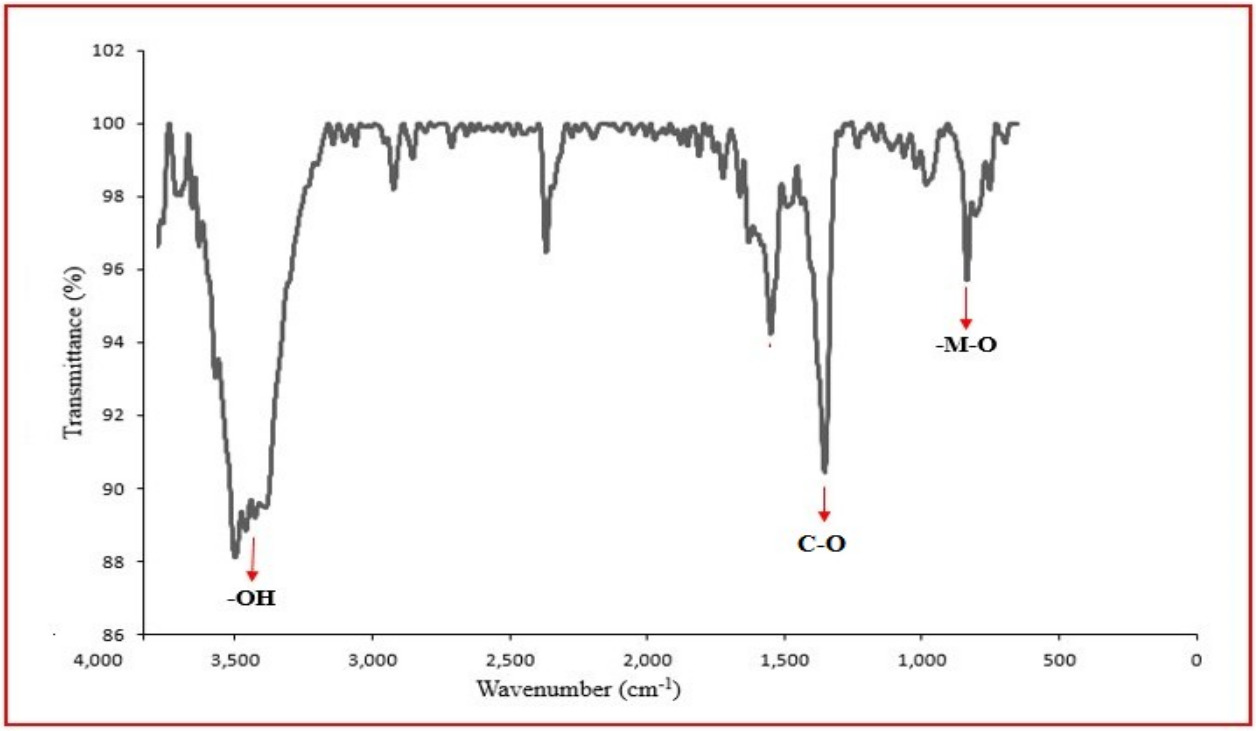


Figure S2. FT-IR of the prepared Co-Ni LDH film

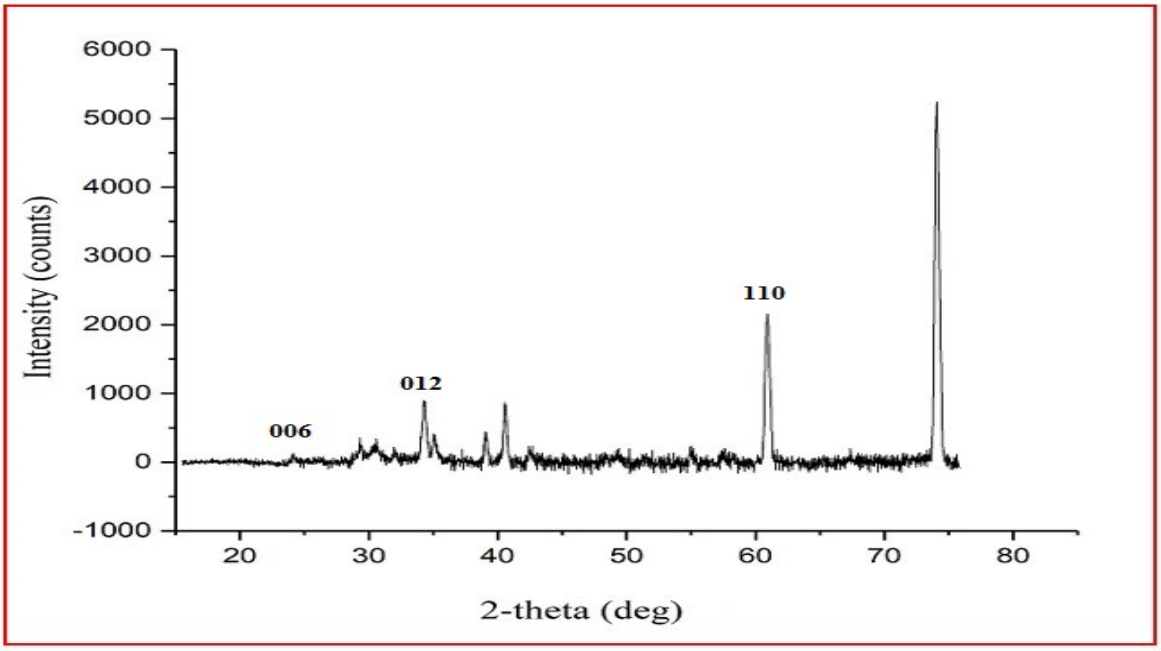


Figure S3. XRD of the prepared Co-Ni LDH film

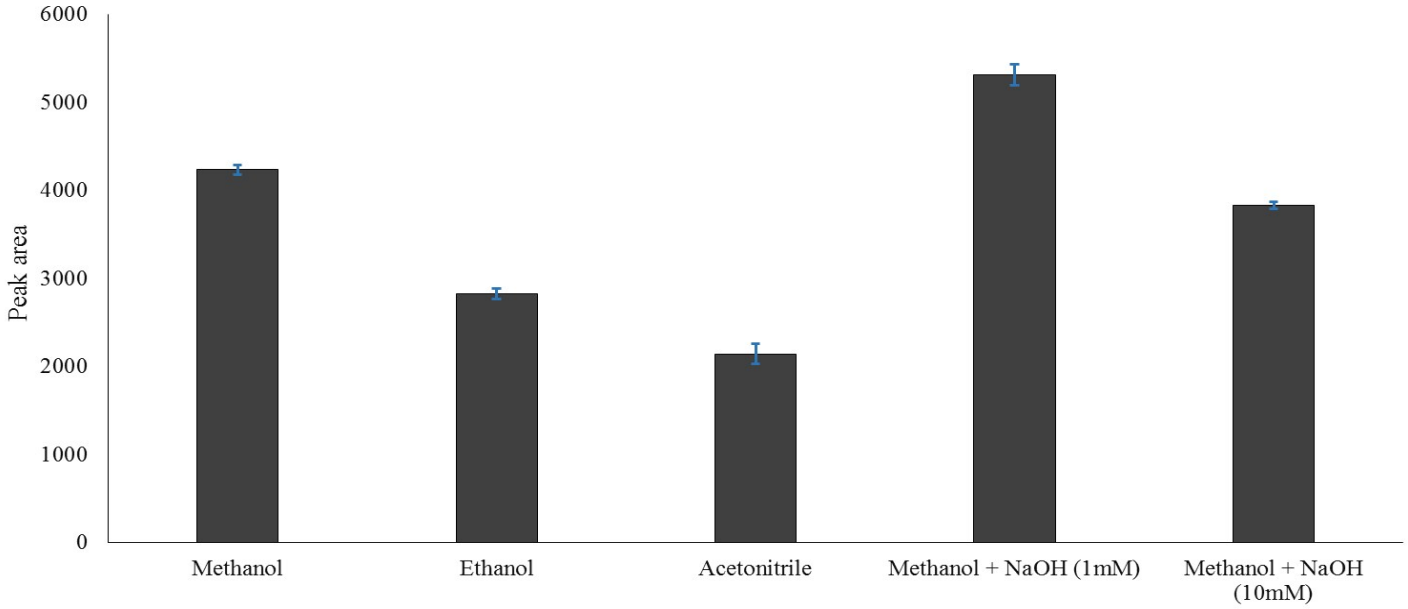


Figure S4. Optimization of desorption solvent. Three replicated experiments were performed under the following conditions: stirring rate of 500 rpm, desorption time of 2 min and extraction time of 25 min. Desorption was occurred using an ultrasonic bath for 5 min

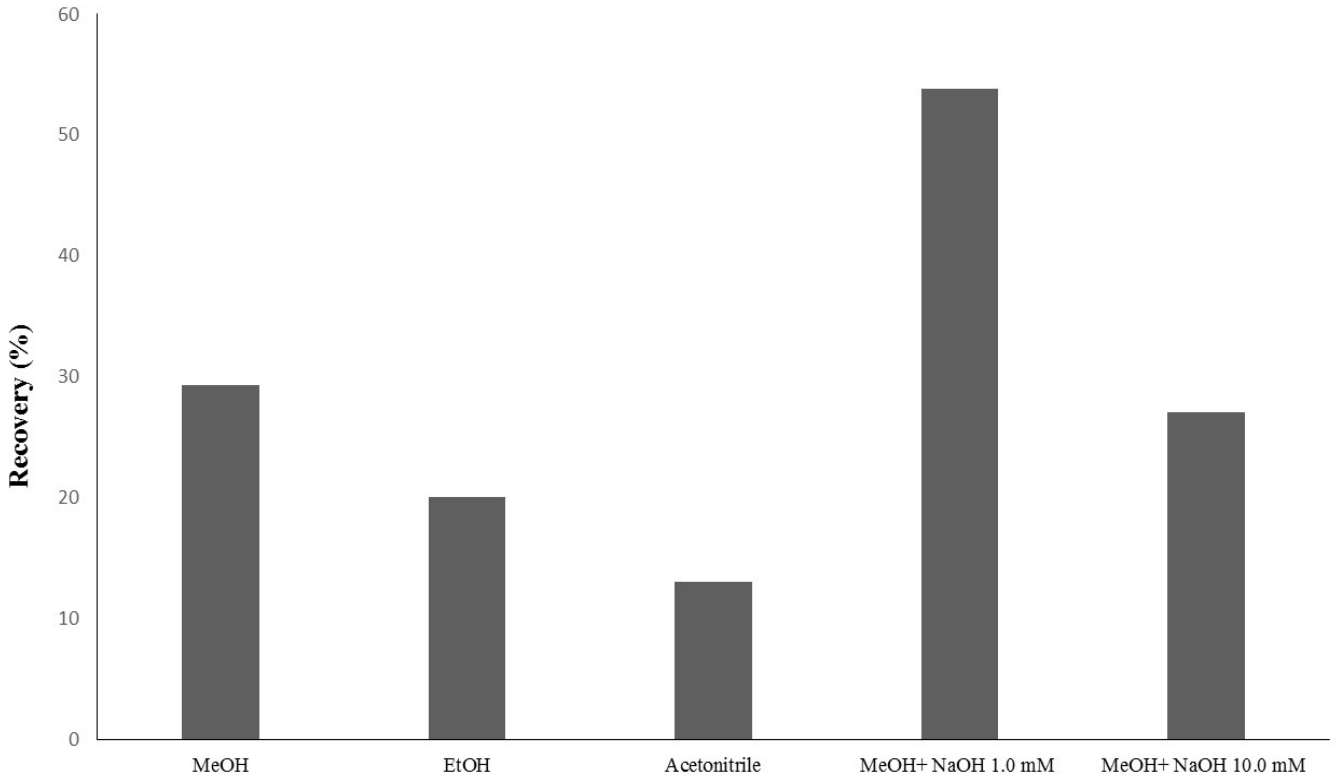


Figure S5. Optimization of desorption solvent (based on the recovery). Three replicated experiments were performed under the following conditions: stirring rate of 500 rpm, desorption time of 2 min and extraction time of 25 min. Desorption was occurred using an ultrasonic bath for 5 min.

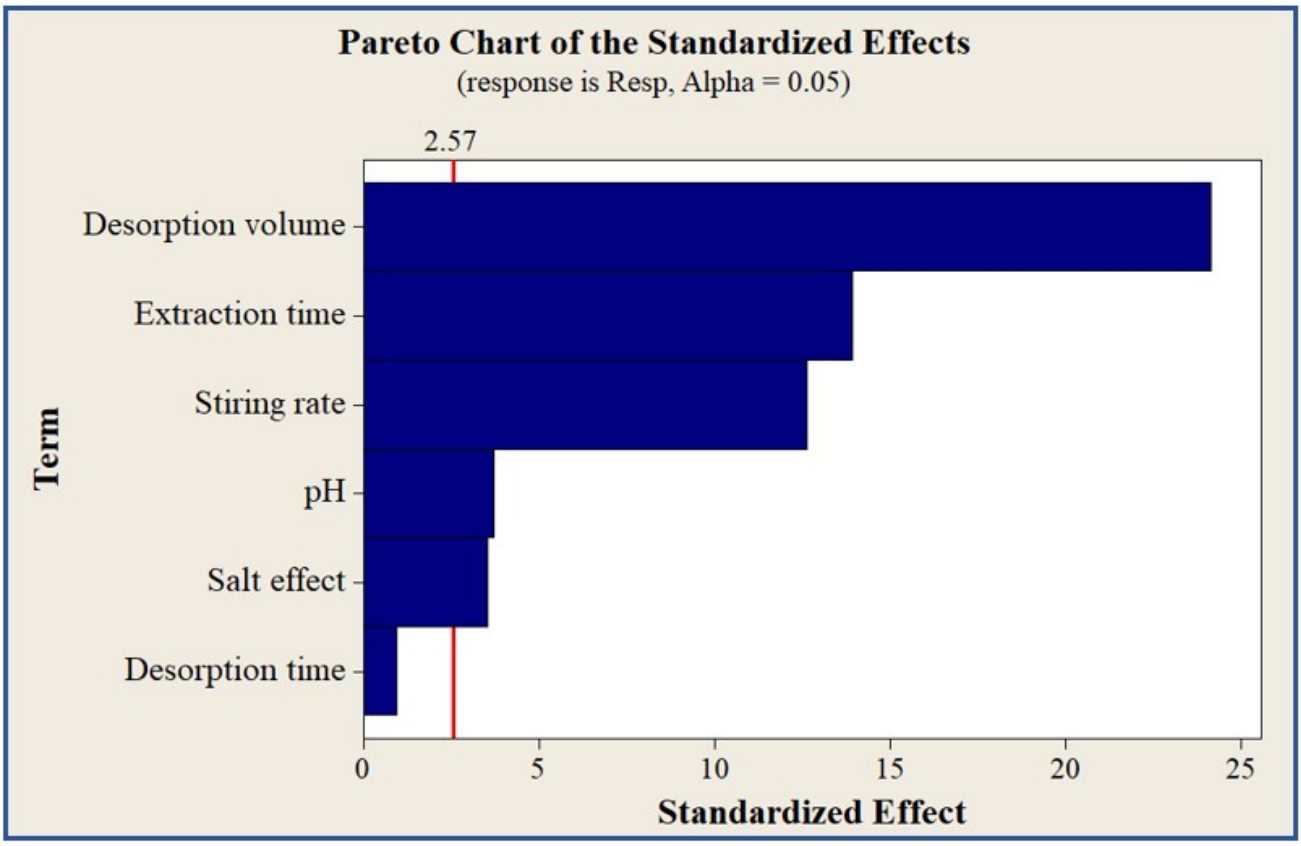
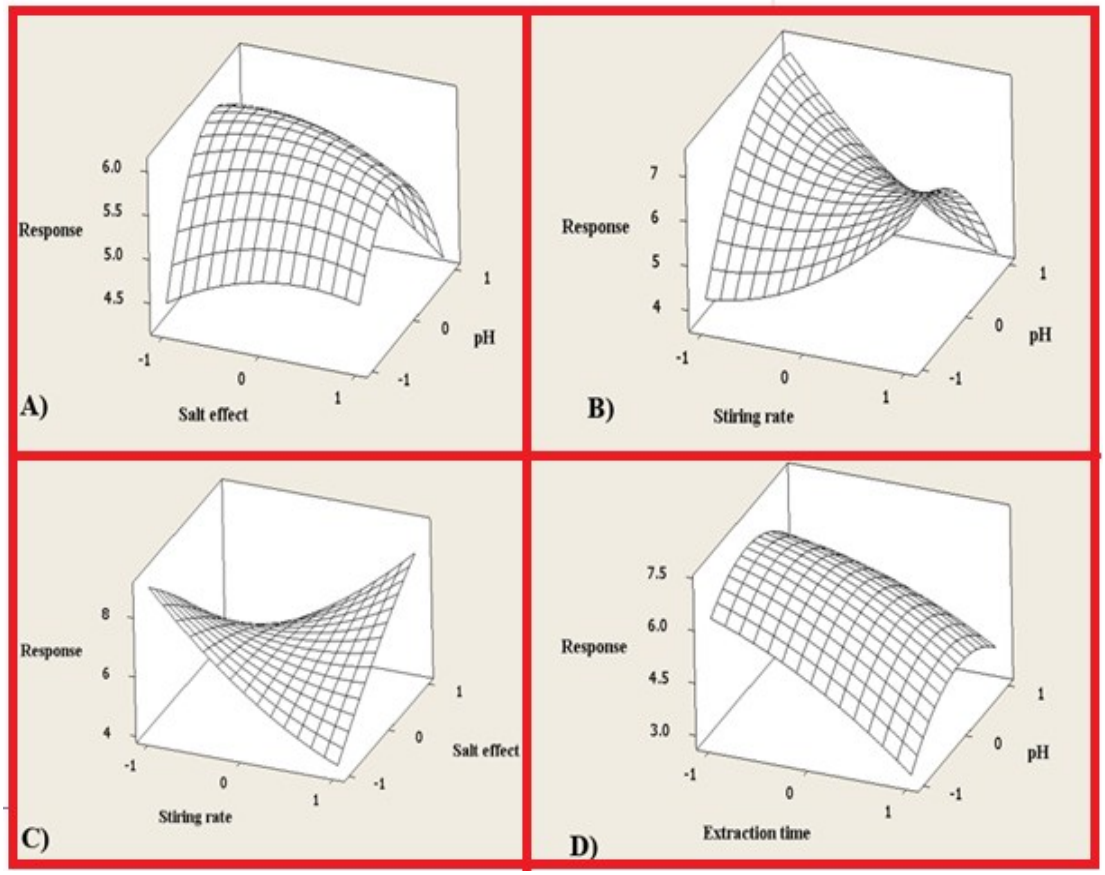


Figure S6. Pareto Chart of the standardized effect for Placket-Burman design.


Response
6.0
5.5
5.0
4.5
-1
0
1
Salt effect
-1
0
1
pH
A)
Response
7
6
5
4
-1
0
1
Stiring rate
-1
0
1
pH
B)
Response
8
6
4
-1
0
1
Stiring rate
-1
0
1
Salt effect
C)
Response
7.5
6.0
4.5
3.0
-1
0
1
Extraction time
-1
0
1
pH
D)

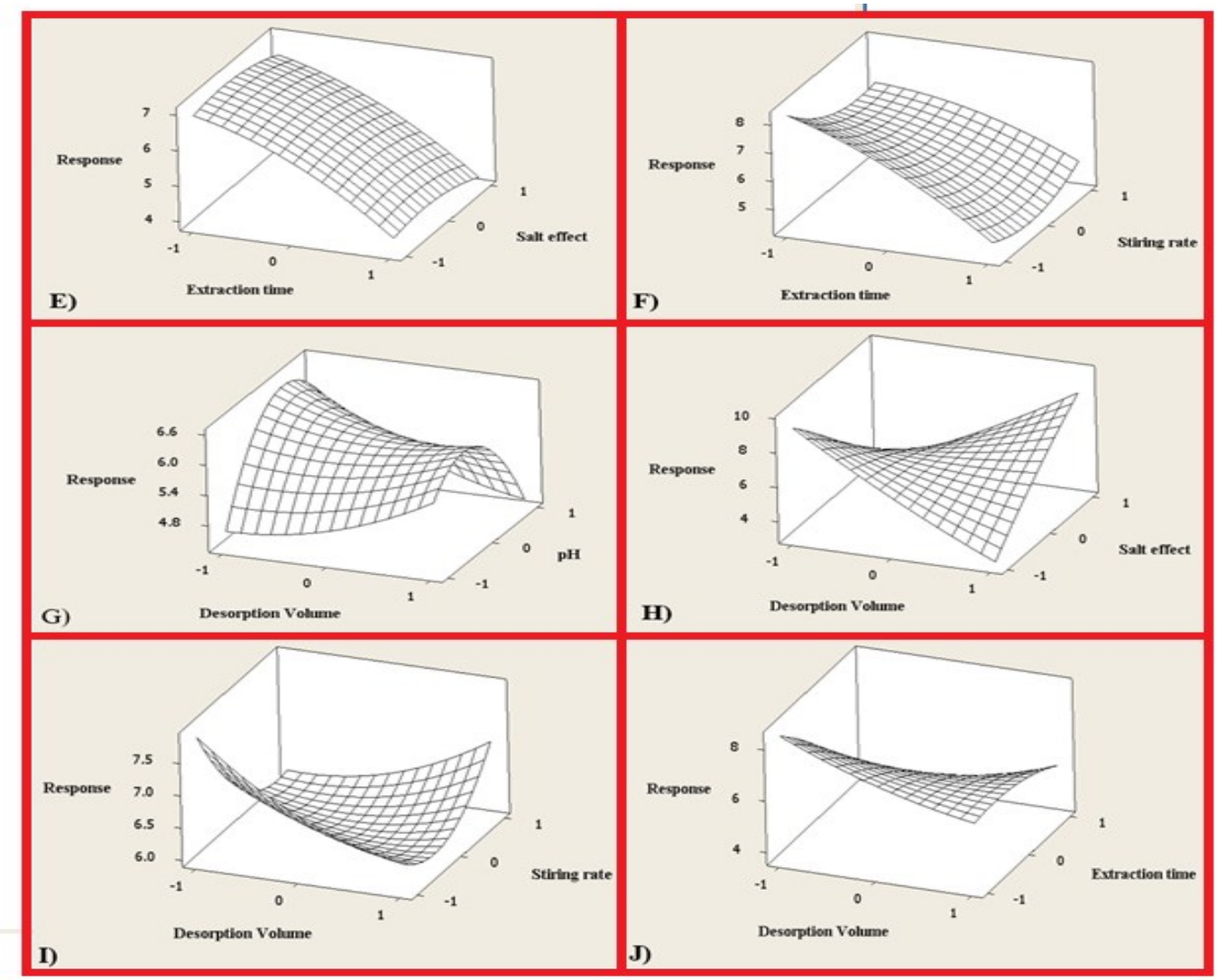


Figure S7. The response surface plots of selected variables, (A) salt effect & pH, (B), Stirring rate & pH, (C), Stirring rate & salt effect, (D), Extraction time & pH, (E), Extraction time & salt effect, (F), Extraction time & stirring rate, (G), Desorption time & pH, (H), Desorption volume and salt effect, (I) Desorption volume and stirring rate and (J), Desorption volume and extraction time.

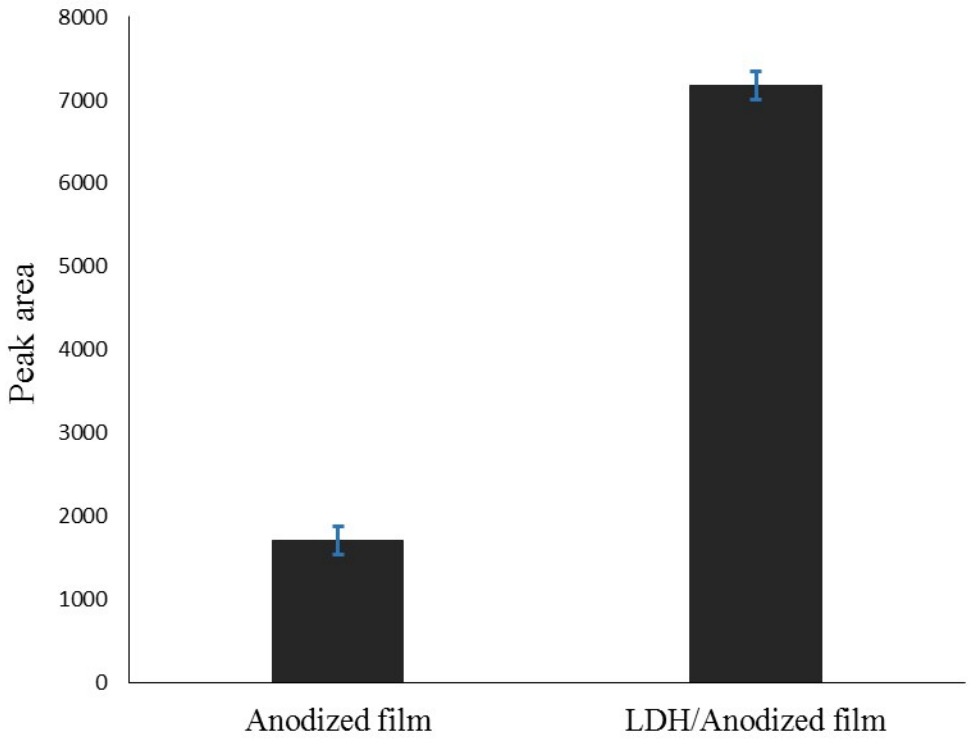


Figure S8. The comparison between the anodized aluminum film and Co-Al LDH film under the optimum condition