In-situ growth of zeolitic imidazolate framework-8 on *GO-PVDF* membrane as a sorbent for thin-film microextraction of caffeine followed by quantitation through high-performance liquid chromatography

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Synthesis of graphene oxide

Concentrated H_2SO_4 (23 mL) was affixed to a mix of graphite powder (1.0 g) and sodium nitrate (0.5 g) in an ice bath and stirred. Then potassium permanganate (3.0 g) was added gradually to this mix for 20 min. After 5 h, the mix was removed from the ice-bath and extra 3 g of potassium permanganate was affixed to the mix. After 12 h, 140 mL of deionized water was poured into the mix. Then,1 mL of H_2O_2 (30% v/v)) was added dropwise to the mixture subsequently until the color of the mixture changed from brownish into bright yellow. The mix was centrifuged. The obtained results were then washed with 30% HCl and water until the pH reached to neutral. The finally obtained product was vacuum-dried at 50 °C.

Synthesis of Zn-Al-LDH/graphene oxide

For preparation of Al-Zn/LDH-GO, first 0.070 g of GO was dispersed in an aqueous solution (2.06 mL) containing 9.9 mmol NaOH. Subsequently, 1.4 mL of a mixture solution of 2.80 mmol of Zn(NO3)2.6H2O and 1.40 mmol Al(NO3)3.9H2O was added to the above mixture. The resulting black suspension was stirred at 60 °C for 2 h under nitrogen atmosphere. The mixture was sonicated for 2 h under nitrogen atmosphere. The solid was recovered and washed with double distilled water several times and finally dried under vacuum at 80 °C for 12 h.

Preparation of Zif 8/ LDH/ GO/PVDF film

In order to prepare Zif -8/LDH/GO/PVDF, 5 mg of prepared Zif -8/LDH/GO composite and 5 mg of PVDF were dispersed in 1 mL of DMF by sonicating for 10 min. This final dispersion (Zif-8/LDH/GO/PVDF) was cast onto a circular glass Petri Dish (50 mm diameter). The solvent was removed and the resulting Zif-8/LDH/GO/PVDF was delaminated from the glass substrate by

immersion in methanol. Finally, the film was thoroughly washed with methanol and allowed to dry at room temperature. The GO/PVDF, LDH/GO/PVDF, Zif 8/GO/PVDF and blank PVDF film were also prepared following the same procedure. Finally, the prepared Zif-8/LDH/GO/PVDF thin film was cut into a particular shape and used for further experiments.

Calculation of enrichment factor

The enrichment factor (EF) is defined as the ratio between the analyte concentration in eluent (C_{elu}) and the initial concentration of analyte (C_0) within the aqueous sample solution, as follows:

$$EF = \left(\frac{C_{elu}}{C_0}\right) \times 100$$

BBD and RSM studies

The numeral of total experimental points (Y) is obtained from equation S1.

$$Y=2X(X-1)+y_0$$
 S1

where X is the number of parameters and y_0 is the number of central points.

The established polynomial model to predict the extraction performance in terms of original factors and interaction of the variable is in accordance with equation S2:

$$Y = 64721 - 2213 A + 8472 B - 35463 C + 25041 D + 41189 A^{2} - 15776 C2 + 21023 D^{2} - 11460 AB + 53996 AC + 11544 AD - 3984 BC - 11694 CD$$

Where Y was the extraction responses (peaks area of diclofenac), A, B, C and D are desorption time, stirring rate, salt effect and solvent volume, respectively.

The spiking recovery (SR) was calculated by the followed equation

Spiking recovery (%) =
$$\frac{C_{found} - C_{real}}{C_{added}} \times 100$$
 S3

 C_{real} and C_{found} are the concentration of analyte in the real sample, before and after spiking. C_{added} is the analyte amount which is spiked to the real sample.

Relative recoveries were calculated as the ratio of the analytical signal in the real sample to the water sampl espiked with the same amount of the analytes.

Fig S1. FT-IR pattern of GO(a), GO-LDH(b) and GO /LDH/ZIF8 (c).

Figure S2. Effect of desorption solvent type on the extraction efficiency.

Figure S3. Pareto chart of the standardized effects obtained from a Plackett-Burman design.

Figure S4. Profiles for predicted values and desirability function for the extraction target analyte.

Figure S5. Response surface plots of each pair of the independent factors: (A)desorption time vs stirring rate., (B) stirring rate vs solvent volume, (C) desorption time vs. salt effect, (D) desorption time vs solvent volume, (E) stirring rate vs salt effect, (F) solvent volume vs salt effect.

Figure S6. The calibration curve and the linear equation for A) Water, and B) Urine.

1		Level			
Factor	Name	Min	Max		
		(-1)	(+1)		
А	Extraction time (min)	5	20		
В	Desorption Time (min)	2	10		
С	Stirring rate (rpm)	100	800		
D	Solvent volume (µL)	100	500		
Е	Salt effect (w/v%)	0	20		

 Table S1

 Experimental variables and levels of the Plackett–Burman design

Source	Degree of freedom (D.F)	Sum of squares (seq. SS)	Adjusted mean squares (adj. MS)	F-value	p-Value
Main Effects	5	2.80031E+11	56006204000	34.53	0.000
Extraction Time	1	1206208008	1206208008	0.74	0.422
Desorption Time	1	10162302008	10162302008	6.27	0.046
Stirring rate (rpm)	1	76713944120	76713944120	47.30	0.000
Solvent volume (µL)	1	27681033861	27681033861	17.07	0.006
Salt effect (w/v%)	1	1.64268E+11	1.64268E+11	101.29	0.000
Residual Error	6	9730697816	1621782969		
Total	11	2.89762E+11			

Table S2. Analysis of the variance for the fit of the experimental data to Plackett-Burman design

Table S3

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Experimental	nental Factors				
number -	Equilibrium time	Stirring time	Solvent volume	Salt effect	Response
1	0	0	0	0	67110
2	0	0	1	1	60058
3	-1	0	0	1	119920
4	1	-1	0	0	86714
5	1	0	1	0	144264
6	1	0	-1	0	108900
7	0	1	0	1	75479
8	-1	1	0	0	114297
9	0	1	-1	0	114439
10	0	1	1	0	44225
11	0	-1	-1	0	96075
12	0	-1	0	1	68005
13	-1	-1	0	0	74105
14	-1	0	0	-1	89189
15	0	0	0	0	62175
16	1	0	0	-1	65409
17	0	-1	0	-1	11998
18	-1	0	-1	0	219164
19	1	1	0	0	81066
20	0	1	0	-1	35409
21	0	0	1	-1	35054
22	0	0	-1	1	153629
23	1	0	0	1	142314
24	0	-1	1	0	26350
25	-1	0	1	0	38544
26	0	0	-1	-1	81849
27	0	0	0	0	64879

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Table S4 Analysis of	the variance for	or the fit of the e	experimental data to	response surface i	nodel	
Source	Degree of freedom (D.F)	Sum of squares (seq. SS)	Adjusted sum of squares (adj. SS)	Adjusted mean squares (adj. MS)	<i>F</i> -value	<i>p</i> -Value
Regression	14	533675568	3811968116	417.07	0.000	53367553628
Linear	4	235368335	5884208389	643.80	0.000	23536833555
А	1	58750725	58750725	6.43	0.026	58750725
В	1	861365185	861365185	94.24	0.000	861365185
С	1	150918470	15091847060	1651.22	0.000	15091847060
D	1	752487054	7524870584	823.31	0.000	7524870584
Square	4	164995564	4124889181	451.31	0.000	16499556724
ÂA	1	904836298	9048362908	989.99	0.000	9048362908
BB	1	132738568	1327385628	145.23	0.000	1327385628
CC	1	235705203	2357052043	257.89	0.000	2357052043
DD	1	21487388	21487388	2.35	0.151	21487388
Interaction	6	133311639	2221860558	243.10	0.000	13331163349
AB	1	525326400	525326400	57.48	0.000	525326400
AC	1	116622724	11662272064	1275.98	0.000	11662272064
AD	1	533009569	533009569	58.32	0.000	533009569
BC	1	59780	59780	0.01	0.937	59780
BD	1	63496992	63496992	6.95	0.022	63496992
	1	546998544	546998544	59.85	0.000	546998544
Residual Error	12	109677912	9139826			109677912
Lack-of-Fit	10	97463512	9746351	1.60	0.446	97463512
Pure Error	2	12214401	6107200			12214401
Total	26	534772314 1				53477231541

	1401	• 50 : 1 2000 000	periorinali	••••••					
				Precision (%) ^a					Film-to-film
Analyte Lin ran (µg	Linear range	Determination n coefficient (r^2)	Inter-day		Intra-day		– LOD	LOQ	reproducibility
	(µg L- 1)		10	100	10	100	(μg L ⁻¹)	(µg L ⁻¹)	D
			μg L ^{-1c}	μg L ⁻¹	μg L ⁻¹	μg L-1			
Caffeine (Water matrix)	0.1-200	0.9985	4.0	1.5	4.8	3.5	0.03	0.099	3.2
Caffeine (Urine matrix)	0.2-200	0.9968	4.2	1.9	5.1	3.8	0.08	0.266	-

Table S5. Analytical performance characteristics of the method.

^a Relative standard deviation (n = 3).

^b Film-to-film reproducibility was calculated by analyzing water samples spiked at 50-100μg L⁻¹ using three different films prepared under the same conditions. ^c Spiking level.



Fig S1



Fig S2



Fig S3



Fig S4



Fig S5



Fig S6