Supplementary material

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A simple design of new recyclable magnetic carbon graphite adsorbent by 2-amino-5-mercapto-1, 3, 4-thiadiazole for fast extraction of two anti-depressant drugs

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Method optimization by experimental design methodology

The Effective parameters in the adsorption step are the solution pH (A), adsorbent dosage (B), and ultrasonic time (C). The levels –α and +α (α is the number of axial points) were applied for the parameters A, B, and C, and the results were tabulated in Table 1S. Also the analysis of variance (ANOVA) results were presented and showed in Table 2S and Fig 1S.

According to the second degree models that include linear, interactive, and quadratic terms, this model can be expressed as follows:

$$Y = \beta_0 + \Sigma_{i=1}^{K} \beta_i \mathrm{X}_i + \Sigma_{i=1}^{k} \beta_{ii} \mathrm{X}_i^2 + \Sigma_i \Sigma_{j=i+1}^{k} \beta_{ij} \mathrm{X}_i \mathrm{X}_j \quad (4)$$

In this equation, the recovery percentage (response) is Y; the independent variables are X_i and X_j; and β_0, β_i, β_{ii}, and β_{ij}, are a constant, linear, quadratic, and interaction coefficients respectively.

Therefore, the obtained models are as follows.

$$R_{(\text{Amitriptiline})} = -2468.45 + 426.41(A) + 8.89(B) - 26.60(C) + 0.58(A)(B) + 4.0(A)(C) + 0.4(B)(C) - 19.14(A)^2 - 0.60(B)^2 - 1.91(C)^2 \quad (5)$$

$$R_{(\text{Imipramine})} = -2918.61 + 457.45(A) + 39.60(B) - 2.03(C) - 1.75(A)(B) + 2.24(A)(C) - 0.56(B)(C) - 18.75(A)^2 - 0.47(B)^2 - 1.27(C)^2 \quad (6)$$

The analysis of variance (ANOVA) results, the P-value for regression, and the P-value for lack-of-fit (LOF) for the two responses are shown in Table 2. According to the results obtained, a P-value < 0.05 (for regression) and the P-value > 0.05 (for LOF) show a high accuracy and reliability of the proposed models in the determination of the response values. Also the values for R-Squared and Adj R-Squared were found to be 0.996 and 0.992 for ATP, and 0.994 and 0.990 for IMP, which confirm the high validity of the model. To illustrate the correlation between the

experimental results and the values calculated, the normal distribution diagram was examined. According to Fig. 7, the uniform distribution of points show that the experimental results are in good agreement with the calculated values.

Table 1s. Experimental variables and their levels in CCD for the adsorption step.

Factors	Levels				
	–α	Low (–1)	Center (0)	High (+1)	+α
A: Solution pH	10	11	12	13	14
B: Adsorbent dosage (mg)	5	9	13	17	21
C: Ultrasonic time (min)	2	4	6	8	10

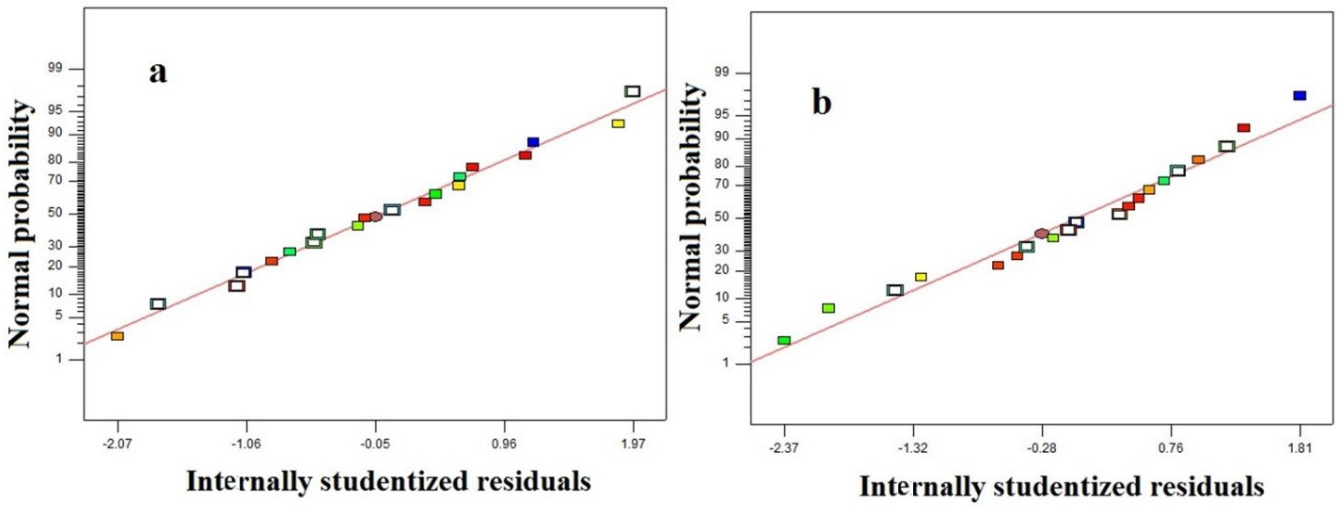

Fig 1S. Plots of normal probability vs. internally studentized residuals for a) ATP and b) IMP.

Table 2S. ANOVA results for CCD for extraction percentages of drugs in the adsorption step.

Source	Sum of squares	Df	Mean square	F-value	P-value	
ATP						
Model	13221.52	9	1469.06	276.41	< 0.0001	significant
Residual	53.15	10	5.31			
Lack-of-fit	35.61	5	7.12	2.03	0.2277	not significant
Pure error	17.53	5	3.51			
IMP						
Model	12440.97	9	1382.33	214.34	< 0.0001	significant
Residual	64.49	10	6.45			-
Lack-of-fit	49.86	5	9.97	3.41	0.1023	not significant
Pure error	14.64	5	2.93			-

Optimization conditions for extraction in desorption step

A suitable eluting agent with no adverse effect on the adsorbent structure is very important in the desorption step. The type of organic solvent, used as the eluent, was investigated using acetonitrile, ethanol, methanol, and acetone. The results obtained (Fig. 2S a) showed that the recovery percentage using acetonitrile in optimal conditions was higher than that for the other solvents. This is likely to be due to the higher affinity of the target analytes in their molecular form to a non-polar solvent. As a result, acetonitrile was chosen as the appropriate eluting agent for the next experiments [9]. To investigate the effect of the volume of the organic solvent, the volumes of 100, 200, 300, and 400.0 µL were investigated. The results obtained (Fig. 2S b) showed that the extraction percentages increased with increase in the volume of the organic solvent up to 300.0 µL and then they decreased. Therefore, the volume of 300 µL was selected for the next experiments. The effect of ultrasonic time (2, 3, 4, and 5 min) on the extraction percentages was then studied. By comparing the extraction percentages at different times (Fig. 2S c), it was observed that by increasing the time to 3 min, the extraction percentages increased, and then by increasing the time to 4 and 5 min, they decreased. According to the results obtained, the best experimental conditions are as follows.

Type of organic solvent, acetonitrile; volume of the solvent, 300.0 µL; ultrasonic time, 3 min.

Effect of salt

The presence of a salt in the sample solution can lead to different results for the extraction percentages; it can lead to significant or non-significant effects. Generally, the presence of a salt can decrease the solubility of the hydrophilic compounds in aqueous samples and increase their penetration into the organic solvent. On the other hand, with increase in the salt content, the migration of the analytes to the organic solvent may be reduced. Also, in some cases, it can be effectless [25]. As a result, the effect of the presence of a salt on the extraction percentages is important. The effect of the presence of NaCl on the extraction of the understudied drugs was evaluated in the concentration range of 0-15% (w/v). The results shown in Fig. 2S d indicate that the amount of NaCl has a decreasing effect on the extraction percentages. According to these results, the method were done in the absence of a salt.

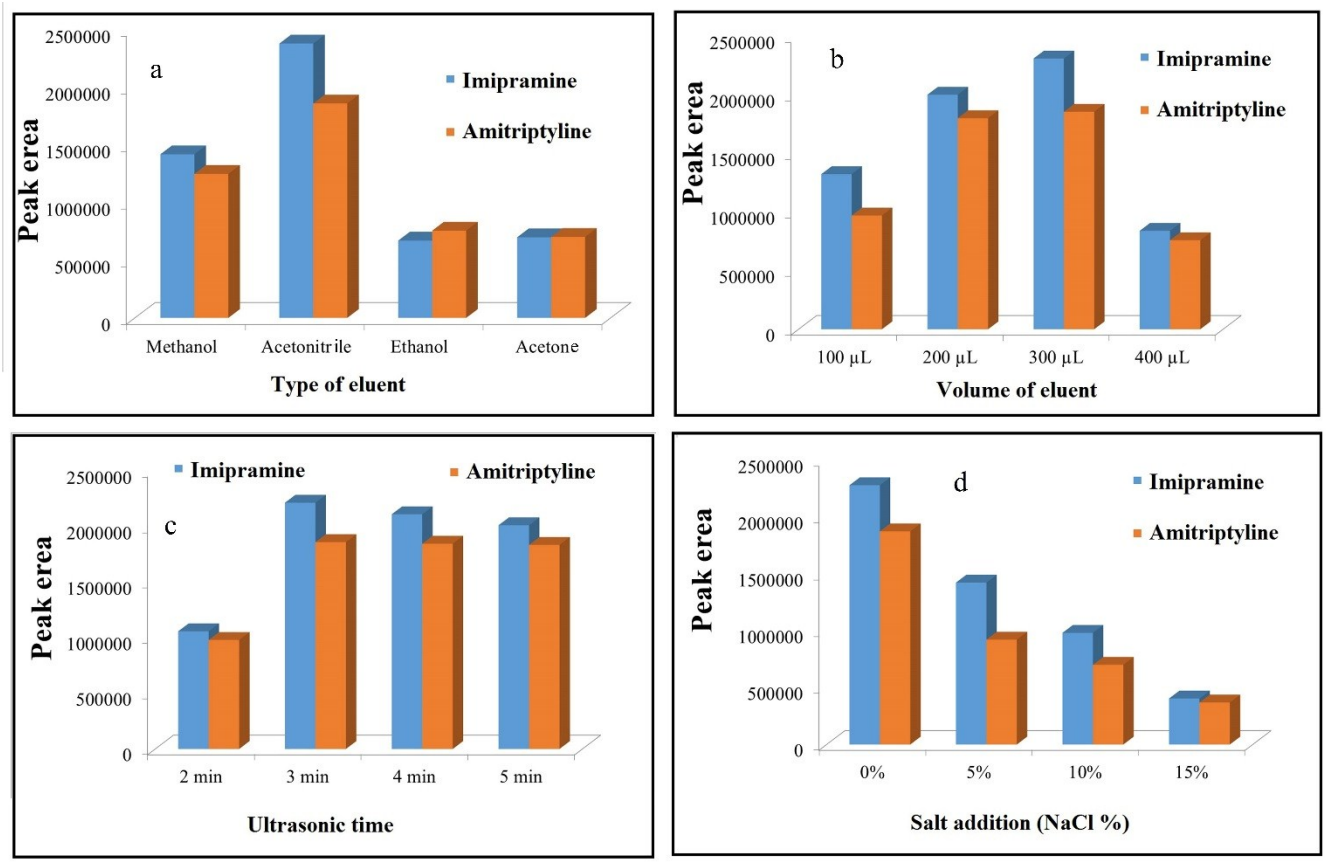

Fig 2S. The effect of the parameters on the recovery percentages of analytes in desorption step: (a) the effect of eluent type; (b) the effect of eluent volume; (c) the effect of ultrasonic time and (c) the effect of salt addition.