**Electronic Supplementary Material**

**Combination of ultrasonic assisted dispersive liquid phase micro-extraction with magnetic dispersive solid phase extraction for the pre-concentration of trace amounts of atrazine in various water samples**

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*2.2. Apparatus*

Atrazine concentration was measured by a high-performance liquid chromatography (HPLC, CECIL 4100, USA) equipped with a UV–Visible Detector. The pH was measured at room temperature with a digital HQ40D Portable Multi Meter pH(Hach HQ-USA). Separation was made using a Nucleodur Sphinx RP (25.0 cm × 4.6 mM) column (MZ-1 PerfectSil, Germany) at a flow rate of 1 ml/min. The mobile phase consisted of a mixed solvent of A (water) and B (methanol). A gradient elution program was employed for the separation which was as follows: 20:80 (A: B) was held for 2 min and changed to 90:10 (A: B) in 15 min and 215 nm was chosen as the best wavelength for the detection and quantification.

*3.1. Characterization of N-Octadecyltriethoxysilane functionalized magnetic nanoparticles*

The morphological of Fe3O4 nanoparticles and N-Octadecyltriethoxysilane functionalized magnetic nanoparticles was performed by scanning electron microscopy. According to the Figure 2 (a), the size of synthesized Fe3O4 and N-Octadecyltriethoxysilane functionalized magnetic nanoparticles were in the nano-scale. The XRD analysis of Fe3O4 nanoparticles and N-Octadecyltriethoxysilane functionalized magnetic nanoparticles was shown in Figure 2 (b). The observed diffraction peaks in the range of 20-70° for magnetic nanoparticles and N-Octadecyltriethoxysilane functionalized magnetic nanoparticles confirm the magnetic structure of synthesized sorbent. The FT-IR spectra pattern of Fe3O4 and N-Octadecyltriethoxysilane functionalized magnetic nanoparticles was evaluated in the range of 400-3000 cm-1. There was observed a broad peak in the range of 700-500 cm-1, which is assigned to the Metal-O functional group vibration. The detected peak around 560 cm-1 is ascribed to the oscillation of Fe-O functional group. The absorption peak of Si-OH and Si-O-Si was approximately appeared in 955 and 1100 cm-1, respectively. According to the FT-IR sepctrum, the observed peak in the mentioned region is rather broader for Fe3O4@SiO2, and the observation is related to the overlapping of Si-O and Fe-O peaks. The H-O-H bending vibration bands at 1632 cm-1 describing that multiple surface OH groups are exist in the prepared sorbent due to SiO2 coating. In the FT-IR spectrum of N-Octadecyltriethoxysilane functionalized magnetic nanoparticles, there was two obvious peaks at 2858 and 2920 cm-1. The mentioned peaks are related to C-H stretching vibration of C-18 groups in the N-Octadecyltriethoxysilane functionalized magnetic nanoparticles.

* 1. *Optimization of the extraction process*

BBD was utilized for examination and optimization of three effective variables including sample's pH, 1-Octanol volume (organic extraction solvent) and magnetic based sorbent amount on the extraction of atrazine by the proposed hybrid extraction method. Because the number of the main parameters on the extraction of the studied target molecule using the proposed sample preparation method was minimum, BBD approach was used without screening step. Rotatable or “nearly" rotatable is a substitute option to fit quadratic models requiring 3 level for each variable. The Box-Behnken design is an independent quadratic design which does not comprise an embedded factorial or fractional factorial design. It should be noted that, one variable at a time was applied for selecting of factors range levels and the selected ranges are shown in Table 1S (ESM). BBD is suitable to find quadratic response surface. The presented model for BBD is as follow:



Where, *Y* is the response parameter (area), *bo* is an intercept, *bi*, *bii* and *bij* are constant regression coefficients of the model, and *Xi*, *Xj* ( i = 1,3; j = 1,3 and i≠j ) present the coded level of an independent parameter. The quantity of runs (*N*) to perform the study was *N*=2*k* (*k*−1) + *C*0, where *k* is the number of variables and *C*0 is the center point numbers. In the present work, *k* and *Co* were fixed at 3 and 3, respectively, which indicated that 15 tests need to be conducted. The acquired data expressed an accurate fitting with the second order polynomial equations. Obtained R-square (98.6%) and adjusted R-square (96.2%) was suitable. The given findings explain that theoretical and experimental data have an appropriate fitting.

**Table 1S.** Variables and their related levels used for Box-Behnken design (BBD).

|  |  |  |  |
| --- | --- | --- | --- |
| Variable | key |  | Level |
| Lower | Central | Upper |
| pH | A | 2.0 | 5.5 | 9.0 |
| 1-Octanol volume (microliter) | B | 5.0 | 22.5 | 40.0 |
| Magnetic sorbent amount (mg) | C | 5.0 | 15.0 | 25.0 |