Electronic supplementary materials

Fabrication of Co_3O_4 quantum dots incorporated poly acrylamide ethylene glycol dimethacrylate as a new fiber for solid phase microextraction and trace determination of organophosphorus pesticides in environmental water samples

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2.1. Reagent and materials

All reagents with analytical grade were purchased from Merck (Darmstadt, Germany, www.merck.de) and used without any subsequent purification. A stock solution (1000 mg L^{-1}) of OPPs (degrees of purity were > 98%) was prepared by dissolving an appropriate amount of OPPs. The applied standard solutions for extraction procedures were prepared daily via serial dilutions of the stock solution with deionized water. The river water was taken from Darakeh River, the wastewater was taken from Tehran City, the lake water was taken from Chitgar Lake, and the agricultural wastewater was taken from Shahriyar Gardens.

2.3. Calculation of preconcentration factor

The preconcentration factor (PF) of SPME procedure was calculated according to the following equation:

$PF = C_{a,final}/C_{s,\ initial}$

$C_{a,final}$ is the final concentration of analyte from SPME fiber that is obtained from peak area response of the analytes in the SPME fiber compared with direct calibration curve. $C_{s,initial}$ is the initial the analyte concentration in the sample solution.

3.2.3. The Effect of pH

The extraction of OPPs by Co_3O_4QDs-poly AM-EDGMA was carried out through the interaction of Sulfur and phosphorus groups of analytes with Co_3O_4QDs incorporated in Co_3O_4QDs-poly AM-EDGMA and hydrophobic adsorption. As a result, pH plays an important role in the extraction of target molecules by the proposed sample preparation method. The effect of pH on the OPPs extraction from water samples was studied in the range of 4.0 - 8.0 and the obtained data were summarized in Fig S.1. As can be seen in the log D scheme, the structure of fenitrothion, malathion and ethion are pH independent (http://www.chemicalize.org). By reducing the pH value of the solution, the extraction recovery of the diazinon also decreased, for in the low values of pH, diazinon is in its ionic form. Diazinon is in the molecule form at higher pH values and is in the ionic form at lower pHs [1]. Hence, according to the obtained data, and the stated explanations, the optimum pH selected for extraction of OPPs with the proposed sample preparation method was 7.0.

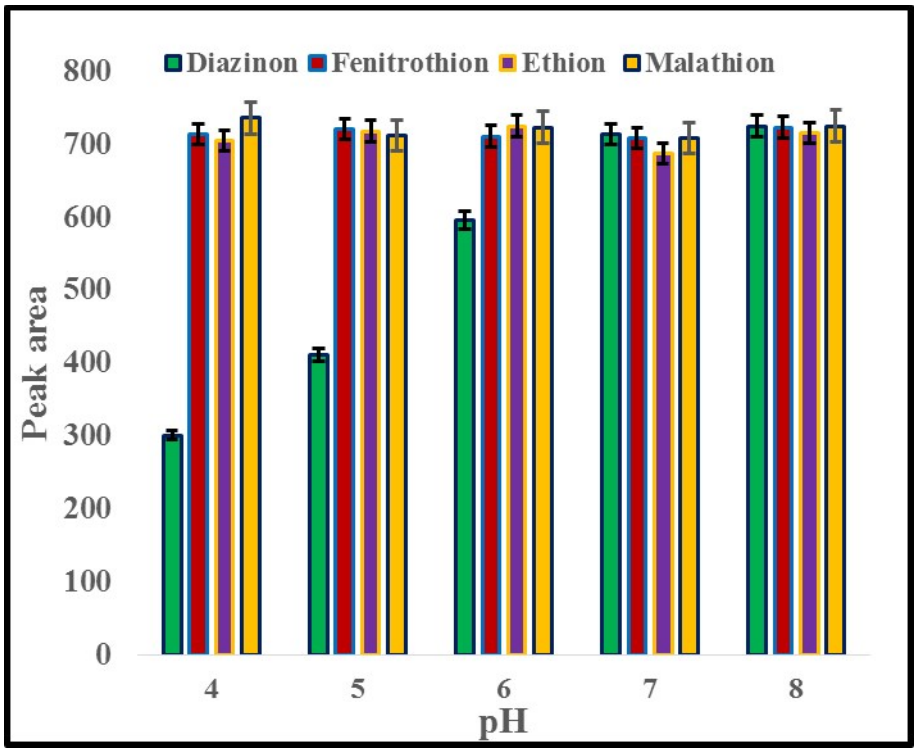

Fig. S.1. The effect of pH (extraction temperature: 70 °C, adsorption temperature: 260 °C, extraction time: 40 min, stirring speed: 750 rpm, and ionic strength: 10% w/w)

3.2.4. Extraction temperature

Extraction temperature is a rather important parameter in SPME procedure, for it can affect the volatile and adsorbed amount of analytes. Generally, an increase in the extraction temperature can accelerate the mass transfer of the analytes from aqueous sample to the SPME fiber [2]. The effect of extraction temperature of OPPs was studied from 30 to 70 °C (Fig. S.2). The extraction efficiency of almost all OPPs increased steadily as extraction temperature increased from 30 to 60 °C. Hence, 60 °C was chosen as the operating extraction temperature for subsequent experiments.

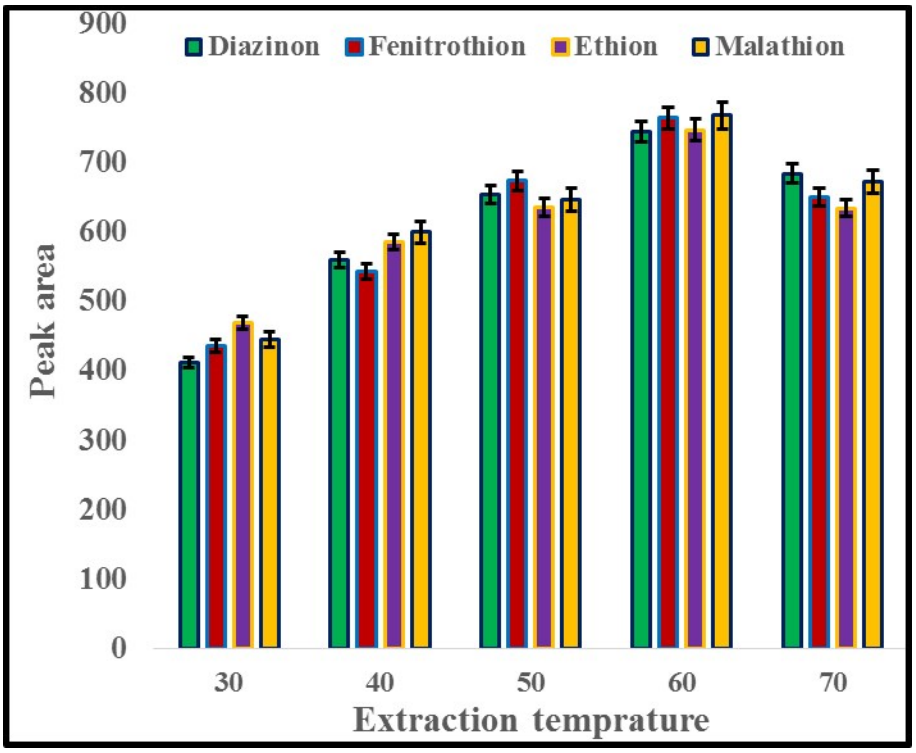

Fig. S.2. The effect of Extraction temperature (pH of Solution: 7.0, adsorption temperature: 260 ^{o}C, extraction time: 40 min, stirring speed: 750 rpm, and ionic strength: 10% w/w)

3.2.5. Extraction time

The mass transfer of analytes from the sample solution to the SPME fiber was a time-dependent equilibrium process, which meant that the maximum extraction amounts could be attained under equilibrium conditions[3]. The extraction time was investigated from 10 to 40 min. As shown in Fig. S.3, 30 min was chosen in further experiments.

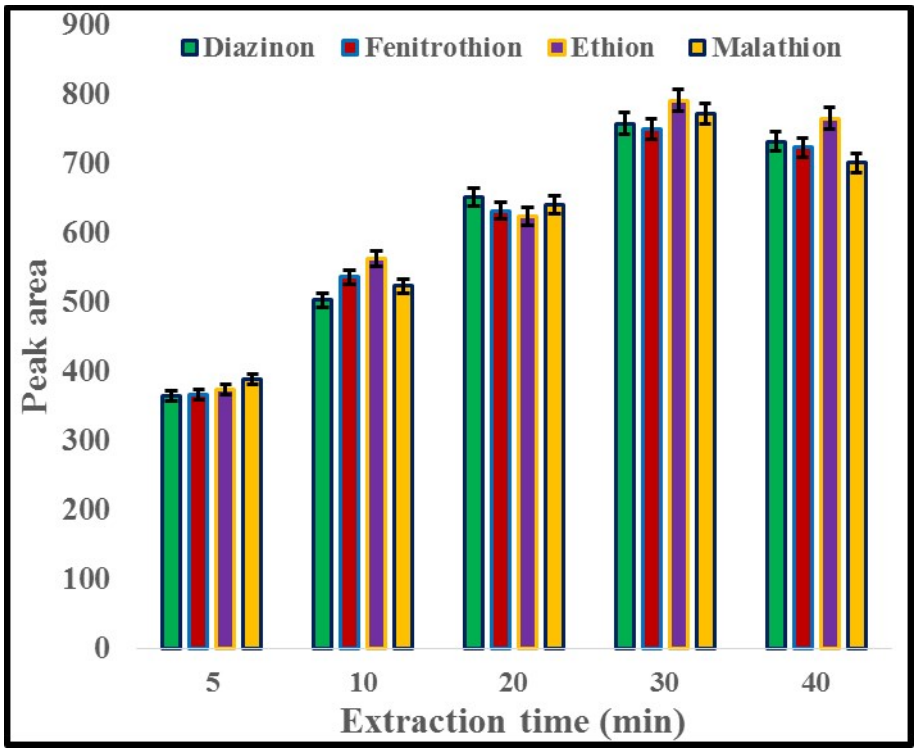

Fig. S.3. The effect of Extraction time (pH of Solution: 7.0, adsorption temperature: 260 °C, extraction temperature: 60 °C, stirring speed: 750 rpm, and ionic strength: 10% w/w)

3.2.6. Desorption temperature

Desorption temperature was carried out by inserting the fiber into a hot IMS injector for analysis. Considering the lifetime of the fiber and the existence of crossover contamination in subsequent experiments [4], desorption temperature was optimized. As shown in Fig. S.4, the desorption temperature was studied in the range of 150 to 260 °C. The peak areas of the OPPs increased as the desorption temperature increased from 150 to 260 °C.

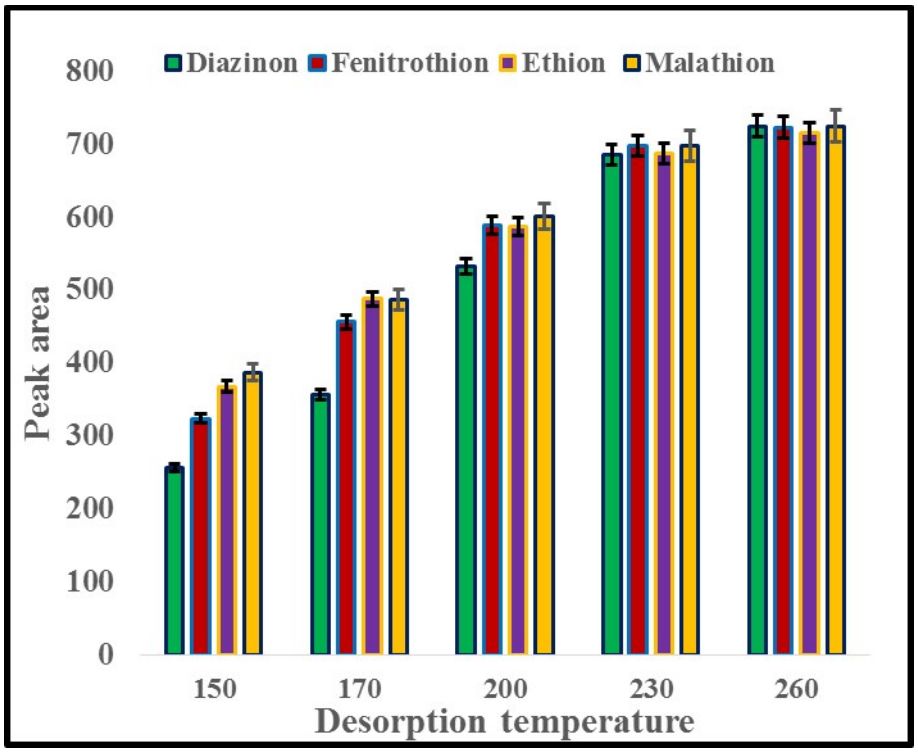

Fig. S.4. The effect of desorption temperature (pH of Solution: 7.0, extraction time: 30 min, extraction temperature: 60 °C, stirring speed: 750 rpm, and ionic strength: 10% w/w)

3.2.7. Stirring speed

Stirring enhances mass transfer and reduces the time required to reach thermodynamic equilibrium [5]. In this experiment, the stirring rate was investigated within the range of 250 and 1000 rpm. When the stirring speed increased from 0 to 750 rpm, the extraction efficiency increased because of the convection effects, while extraction efficiency decreased at higher rates (Fig.S.5). Therefore, 750 rpm was selected as the optimal stirring speed for subsequent experiments.

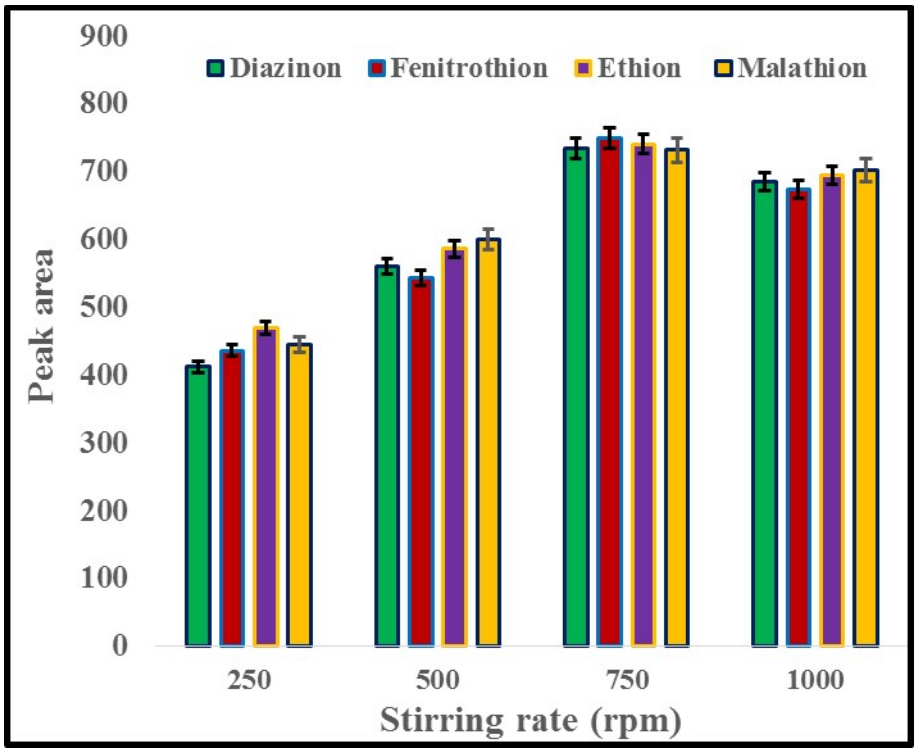

Fig. S.5. The effect of stirring rate (pH of Solution: 7.0, extraction time: 30 min, desorption temperature: 260 °C, extraction temperature: 60 °C, and ionic strength: 10% w/w)

3.2.8. Salt addition

The influence of ionic strength on the extraction efficiency was investigated by dissolving different concentrations of NaCl (0-20%, w/v %) in the solution. As seen from Fig. S.6, the extraction efficiency occurred to ascendant tendency with an increase in the amount of NaCl. This phenomenon can be explained by the "salting out" effect [6], by which the addition of salt concentration decreases the solubility of the analytes in the aqueous phase and avails sorption of the analytes to the fiber coating. Finally, 10% was chosen for the optimum concentration of salt in subsequent analyses.

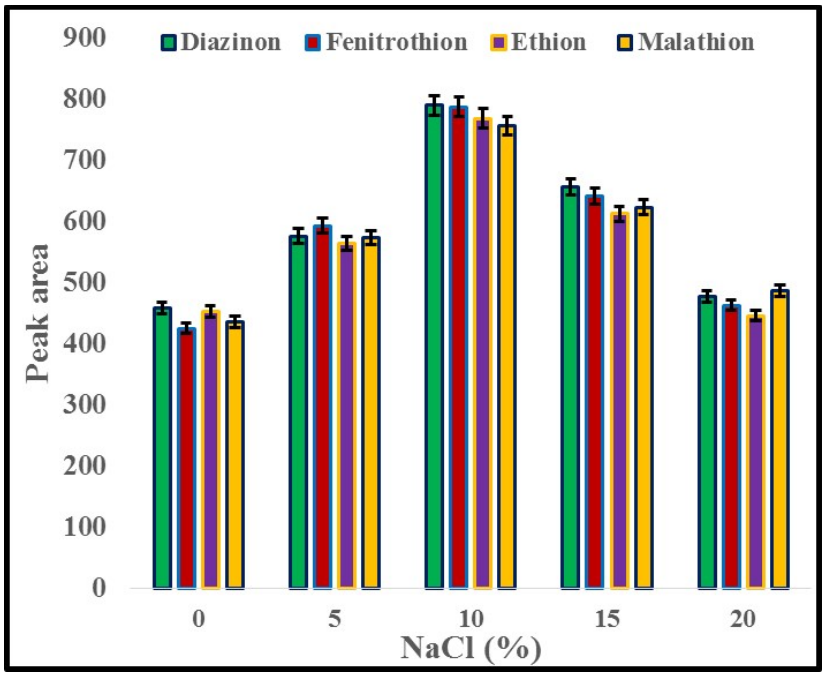

Fig. S.6. The effect of salt addition (pH of Solution: 7.0, extraction time: 30 min, desorption temperature: 260 °C, extraction temperature: 60 °C, and stirring speed: 750 rpm,)

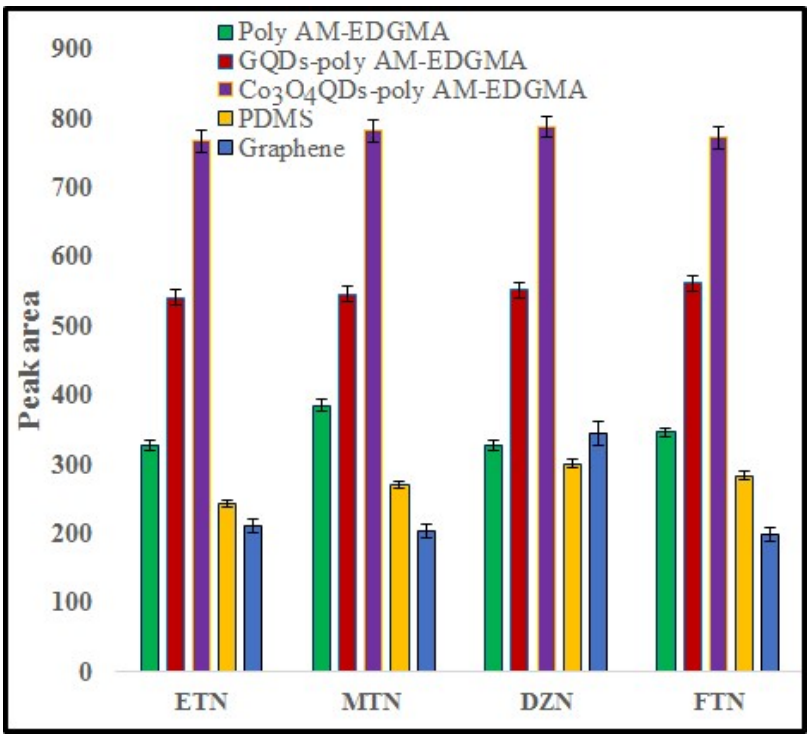

Fig. S.7. Comparison of extraction performance of OPPs with poly AM-EDGMA, GQDs-poly AM-EDGMA, and Co_3O_4QDs-poly AM-EDGMA fibers.

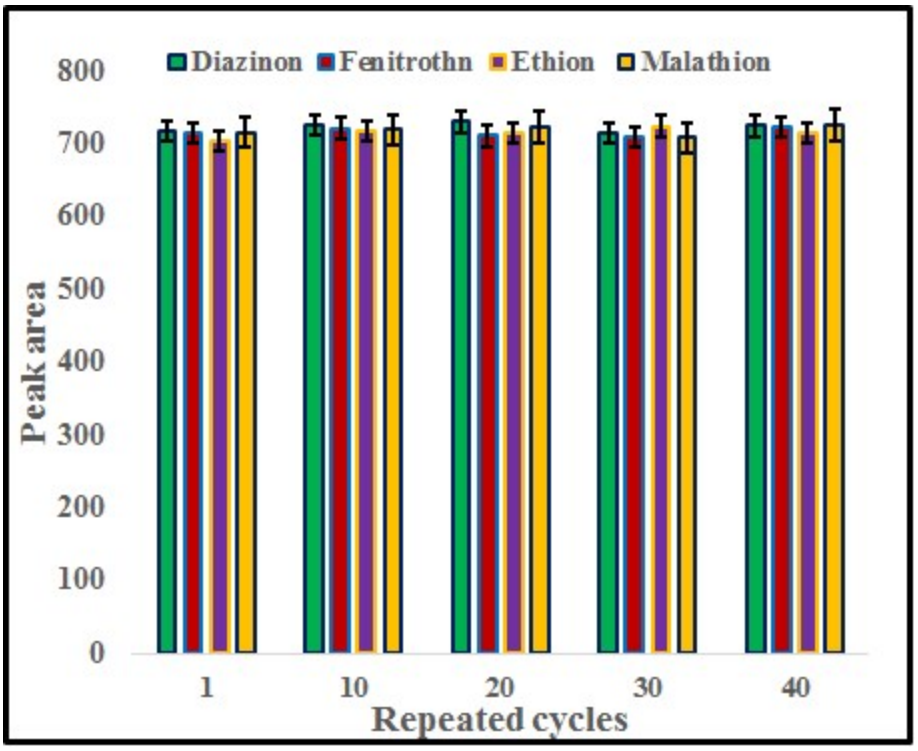

Fig. S.8. Stability of the Co_3O_4QDs-poly AM-EDGMA fiber for considered OPPs with the concentration of 50 ng mL^{-1} under optimum conditions.

References:

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