*Journal of Health and safety at Work 2021; 11(1): 11-14*

**ORIGINAL RESEARCH PAPER**

# Development of A Sample Preparation Method for evaluating Trace Residue of Bentazon Pesticide in Biological Matrices Using Dispersive Solid Phase Extraction (SPE) Method Based on Molecular Imprinted Polymer (MIP)

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Received: 2018-10-05 Accepted: 2019-10-12

## ABSTRACT

**Introduction:** Pesticides are among the broadest chemical compounds used in the world and are also considered as the most dangerous compounds for living organisms. Although pesticides have significant impact on improving agricultural and food products, the processes of their production, formulation, storage, transportation, and marketing as well as the extensive use of these materials lead to occupational exposure, environmental pollution, and the presence of their residues in foodstuffs. Bentazon as a herbicide is considered as one of the most common pesticides used in agriculture and horticulture. Its effects on human health are widespread and of concern. Occupational and environmental exposure assessment of this compound is, therefore, considered necessary by conducting accurate and valid methods. The purpose of the present study was to synthesize a molecular imprinted polymer (MIP) as a specific adsorbent in the preparation process of bentazon for its selective analysis in biological matrices.

**Material and Methods:** For synthesis, a precipitation polymerization method was used. This method has been used to prepare particle size distribution and shape appropriately. By applying the aforementioned method, nano particle size is obtained within the sub-micron and nano range. So, crushing and sieving of the sorbent is not necessary. The MIP was synthesized with 1: 4: 30 ratio of template molecule (bentazone): functional monomer (methacrylic acid): cross-linking monomer (ethylene glycol di methacrylate), respectively. Due to particle size and high porosity, the sorption and recovery of template compound was performed faster and with higher efficiency. Some variables affecting the efficiency of MIP for sorption and desorption of analyte were investigated and optimized. They included pH of solution, MIP amount (mg), and sonication time (min) in the sorption step and volume of eluent (ml), sonication time (s), and acid percentage in the desorption step.

**Results:** The optimum levels of factors for the proposed method were pH of solution: 2، sonication time for sorption 7.3 min, polymer amount of 30.814 mg, acid percentage 1.1, and sonication time for desorption 165 s. According to the obtained results, the interfering factors in the matrix have no significant effect on the determination of analyte. The limit of detection (LOD) and relative standard deviation (RSD) of the optimized method were 0.79.ppb and 2.8931 %, respectively.

**Conclusion:** The results of this study indicated that the proposed method can be used to extract the bentazon herbicide from complex matrices such as urine samples with high efficiency and selectivity.

**Keywords:** *Molecular imprinted polymer, Bentazon herbicide, Dispersive solid phase extraction*

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## 1. INTRODUCTION

Pesticides are among the broadest chemical compounds used in the world and are also considered as the most dangerous compounds for living organisms. Although pesticides have significant impact on improving agricultural and food products, the processes of production, formulation, storage, transportation, and marketing of them in addition to their extensive use lead to occupational exposure, environmental pollution, and the presence of their residues in foodstuffs. Bentazon herbicide is one of the most common pesticides used in agriculture and horticulture (1). Various concentrations of Bentazon are used by farmers, depending on the types of plants and weeds, but the approximate Bentazon concentration in aqueous solution is reported 0.0025-0.0065 (٪ v / v). It is a selective herbicide for control of broad leaf weeds and sedges in beans, rice, corn, peanuts and mint (2). It has been found that Bentazon is one of the most important contaminants in terms of frequency of detection and maximum concentration in groundwater in 15 European countries (3). Its effects on human health are also widespread and of concern. Occupational and environmental exposure assessment of this compound is, therefore, considered to be necessary by applying accurate and valid methods. Matrix solid-phase dispersion (MSPD) is one of these effective methods. This methodology combines the aspects of several analytical techniques in which extraction and clean-up are performed at the same time. MSPD has achieved extensive applications (4,5). The C18 is used as a common sorbent in MSPD. Attapulgite clay (ATP) has also been studied for its sorbent properties and has been used for one application (6-8). The commonly dispersants in MSPD (C18, C8, silica, florisil, etc.) do not have high efficiency in extracting complex matrices and structural analogs. Therefore, MIPs (9) with high molecular detection, high stability, and low cost were suggested (10-13). In this study, the MIPs were synthesized and characterized as a novel and specific sorbent in the process of sample preparation. In this regard, the ultrasonic assisted-dispersive solid phase extraction procedure based on the MIPs was proposed for the selective extraction of Bentazone from urine samples. Ultrasound as a robust technique was applied to facilitate the extraction of the target analyte in the sorption and desorption steps to yield a much higher efficiency.

## 2. MATERIAL AND METHODS

For synthesis, a precipitation polymerization method was used. This method has been used to prepare particle size distribution and shape appropriately. By applying the aforementioned method, nano particle size is obtained within the sub-micron and nano range. So, crushing and sieving of the sorbent is not necessary. The MIP was synthesized with 1: 4: 30 ratio of template molecule (Bentazone): functional monomer (methacrylic acid): cross-linking monomer (ethylene glycol di methacrylate), respectively. Due to the particle size and high porosity, the sorption and recovery of template compound was performed faster and with higher efficiency. Briefly, the mixtures of 1mmol Bentazone, 0.34mmol MAA, 5.66ml EGDMA, and 100ml AIBN was dissolved in 120mL porogenic solvent (acetonitril). The solution was then sonicated for 10min and purged with nitrogen gas for 15min before being sealed under nitrogen protection. Polymerization was performed under 65◦C in oil bath for 18h. In order to remove the template molecule from the polymer structure, an elution was performed using a methanol-acetic acid mixture at a ratio of 80: 20 by ultrasonic in 12 steps of 20 min. A non-imprinted blank polymer (NIP, in the absence of template) was prepared and treated in an identical manner.

Some variables affecting the efficiency of molecular imprinted polymers for sorption and desorption of analyte were investigated and optimized. They included pH of solution, MIP amount (mg), and sonication time (min) in the sorption step and volume of eluent (ml), sonication time (s), and acid percentage in the desorption step.

## 3. RESULTS AND DISCUSSION

Optimization of variables using Box–Behnken design (BBD) revealed that the best optimal values for pH: 2.95, amount polymer: 30.814 mg and for ultrasound sorption time is 7.361 min.

The interactions between pH, MIP value, and constant ultrasound sorption time of 7.361 min with the rate of sorption of Bentazone polymer are shown in Figure 1. The horizontal axis of the diagram shows the amount of polymer. As it approaches the 30 mg range and pH in the vertical axis approaches 2, the rate of sorption of Bentazone polymer increases. By elevating pH value, the extraction of target molecules was decreased. The effective extraction of target molecules was carried out in the lower pH. The observation can

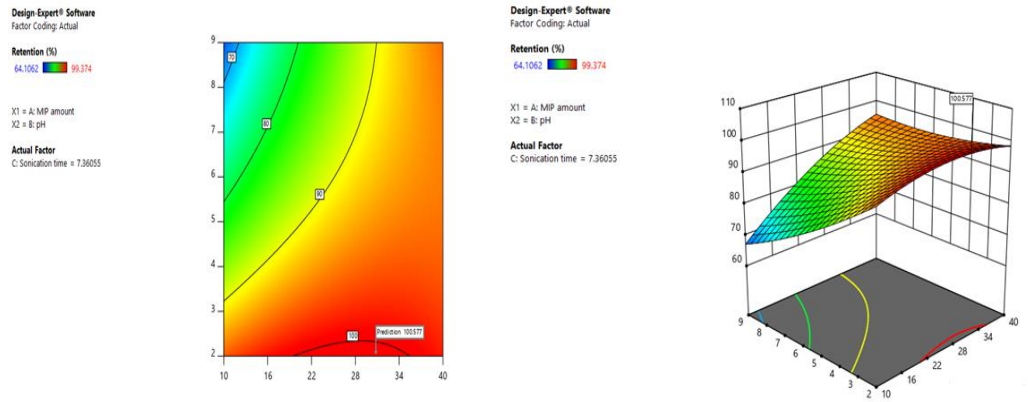


Fig. 1. Interaction of pH, amount polymer, constant ultrasound sorption time of 7.361 min with bentazone polymer sorption

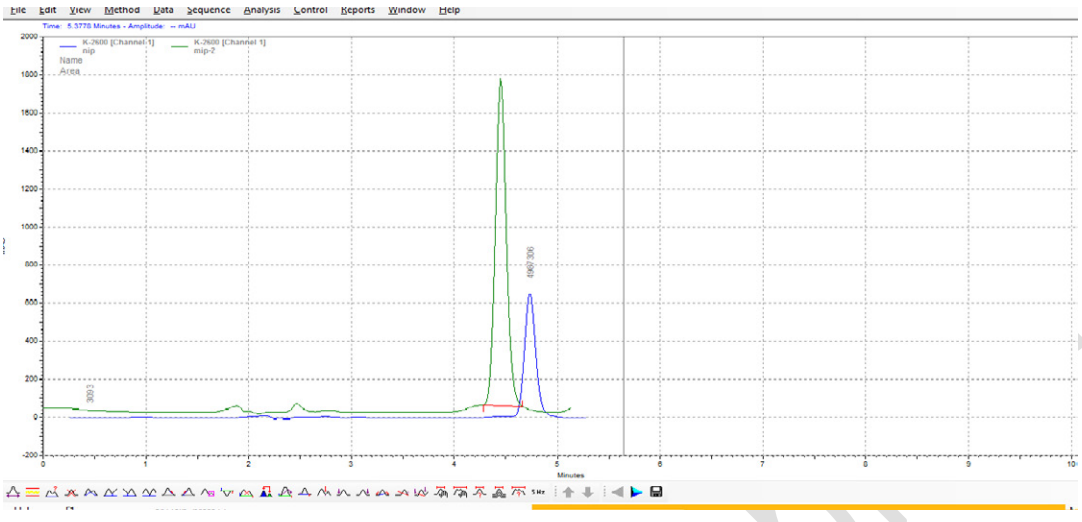


Fig. 2. Extraction chromatogram of MIP compared to NIP

Table 1. Comparison of Bentazone Recovery Rate by Molecular imprinted polymer and Non-Molecular imprinted Polymer

| Sorbent | Recovery (%) |
|---|---|
| (MIP) | **100.5172** |
| (NIP) | **22.06966** |

be attributed to the fact that at lower pHs, the target toxin is molecular, thus, the desired hydrogen bond is formed between the target molecule and the functional monomer. According to the above-mentioned interpretation and obtained data from BBD, pH 2.095 was used for the next experiments. Results for the selectivity of MIP were shown in Figure 2 and Table 1.

The efficiency of Bentazon bound to the MIP was higher than that of NIP. It indicated that the MIP provided high selectivity for Bentazon. The high selectivity is mainly due to the molecular size recognition of MIP to template molecule, the hydrogen bonding interactions between the carboxylic group in the MIP, and hydroxyl and carbonyl groups in Bentazon at identical positions.

## 4. CONCLUSIONS

This work proposed a novel MIP-MSPD method using MIP as selective MSPD sorbent to selectively extract and determine the bentzone pesticide. The new MIP was applied as a specific sorbent to improve the selectivity. The

MIP-MSPD method provides some advantages including higher selectivity, lower cost, easier preparation, and higher extraction efficiency compared to the traditional methods. The current method can potentially applied to determine the bentazone pesticide in real samples with no special sample pretreatment steps. In addition, the Box–Behnken design (BBD) provided the estimation of any interaction between the factors and obtaining more satisfactory results compared to the one-at a-time approach.

## 5. ACKNOWLEDGMENT

The study was founded by Tehran University of Medical Sciences (TUMS).

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