

Determination of Adsorption Capacity of Novel Molecularly Imprinted Materials for Herbicides

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Abstract: In order to improve the traditional method of adsorbing water residues and improve the adsorption efficiency, we prepared molecularly imprinted polymer modified by eutectic solvent and established molecularly imprinted polymer adsorbent based on eutectic solvent. Based on the standard curve of atrazine, the adsorption capacity of the molecularly imprinted materials for atrazine was determined. It is beneficial for the preparation of molecularly imprinted materials based on eutectic solvent and the feasibility of their application in herbicide adsorption. Methods: using choline chloride and methacrylic acid to prepare low melting solvent, atrazine as template molecule, molecularly imprinted polymer was prepared. Using this kind of molecularly imprinted polymer as adsorbent, the following experiments were carried out: 1. The standard curve of atrazine was drawn by HPLC; 2. The adsorption capacity of the new molecularly imprinted polymer was tested; 3. The reusability of the adsorption material was verified. Results: through the static and dynamic adsorption capacity experiments, des-mip had the highest adsorption performance, and showed better absorption effect than MIP. In the reusability experiment, des-mip shows better recovery under the premise of introducing des. The intra day and inter day recoveries of des-mip were 74.9% - 78.8% and 83.8% - 86.8%, respectively. The intra day and inter day recoveries of aa-mip were 69.2% - 72.3% and 68.5% - 71.9%, respectively. The relative standard deviation of des-mip and aa-mip was less than 2%. The reusability of des-mip and aa-mip is verified. Conclusion: the molecular imprinted polymer with eutectic solvent has better herbicide removal ability than the other three materials.

Keywords: Eutectic solvent; Molecularly imprinted polymer; Atrazine; Environmental sewage.

1. Introduction

As the global population continues to grow, modern agriculture increasingly relies on synthetic chemical pesticides such as herbicides, insecticides, and fungicides. These chemicals play a significant role, contributing up to 30% to boosting crop yields. The cessation of chemical substances like pesticides would place millions worldwide at risk of starvation. However, due to the difficulty of degrading these agents and their strong water solubility, there have been increasing instances of pesticide residues found in food and drinking water in recent years. Some pesticides have been proven to cause cancer and disrupt the endocrine system in humans [2]. In China, the area of farmland pollution has reached 2.667 to 1010 hectares, with pesticide residues and excessive fertilization being major contributors, amounting to 1.010 to 10 hectares. This environmental cost of agricultural production is receiving growing attention from ecological and environmental scientists. Atrazine, a substance that can cause feminization in male frogs, is listed as an endocrine disruptor in the United States, the European Union, and Japan [1]. While atrazine can be removed from drinking water using charcoal filters, treating it in lakes and ponds is more challenging. In recent years, the residues of atrazine in food and drinking water have been confirmed to be carcinogenic to humans and affect fetal development. Therefore, researching the ecological and environmental safety of pesticides and other synthetic chemicals is imperative. Developing and improving the detection and separation methods of atrazine in the environment is of great significance.

The removal of herbicides like atrazine has always been a topic of interest. Traditional methods usually involve the use of activated carbon, and studies have also explored using thermally activated persulfate technology and photocatalytic

oxidation methods for atrazine removal. Numerous molecularly imprinted materials have been used for adsorption in both domestic and international research, such as the selective adsorption of diclofenac in water and the recognition and selective adsorption of bisphenol A by magnetic molecularly imprinted materials.

Molecularly imprinted polymers (MIPs) are prepolymers formed by the interaction of template molecules with functional monomers through covalent, non-covalent, or metal interactions. The functional monomers are polymerized under the action of a cross-linking agent, fixing the template molecules in the polymer and ultimately creating cavities that are complementary to the template molecules in size, shape, and functional group orientation. These cavities not only retain an orderly arrangement of functional groups that are chemically complementary to the template molecules but also maintain their entire spatial conformation. This enables the material to bind specifically to the template molecules when they encounter each other again [1].

Molecularly imprinted polymers are often used for the selective extraction or purification of target substances. This is due to their high molecular recognition capability, special selectivity, and broad range of pH tolerance. Because of their specificity and selectivity, MIPs are widely applied in the field of chromatographic analysis. In recent years, more and more studies have focused on their adsorption capabilities [2].

Deep Eutectic Solvents (DES) are low-melting mixtures composed of specific stoichiometric ratios of hydrogen bond acceptors and donors, exhibiting melting points significantly lower than the melting points of their individual pure components. The physicochemical properties of deep eutectic solvents are akin to those of ionic liquids. Additionally, DES are simpler to prepare, cost-effective, less toxic, and biodegradable compared to ionic liquids [3-4]. These

solvents have found widespread application in material preparation. Owing to the abundant hydrogen bonding system and appropriate viscosity of DES, solid particles exhibit excellent dispersion within these solvents, facilitating polymerization [5]. In recent years, DES has been utilized as an additive in the preparation of molecularly imprinted polymers (MIPs), significantly enhancing their affinity and selectivity. In 2016, DES was first employed as a functional monomer in MIP preparation [6–7]. The rich hydrogen bonding system and suitable viscosity of DES provide an optimal synthetic environment for polymerization reactions, thus promising broad application prospects in MIP preparation. The combination of deep eutectic solvents and molecular imprinting technology has led to the development of nanoscale MIPs. This innovation overcomes the traditional limitations of MIPs, offering improved selectivity, higher binding capacity, increased sensitivity, and faster binding kinetics. These advancements have been widely applied in proteins, blood, sensors, and other areas, heralding new developments in molecular imprinting technology [8].

In summary, this experiment introduces deep eutectic solvents into molecularly imprinted materials, attempting to utilize this type of MIP for atrazine adsorption. The study aims to validate the efficiency of these materials in adsorbing atrazine, providing substantial support for their feasibility in herbicide adsorption applications.

2. Experimental Materials

2.1. Reagents

Atrazine (97%) was provided by Beijing Solebao Technology Co., Ltd.; pure water (Watson's drinking water); pre-prepared molecularly imprinted materials; and methanol (>99.9%) were supplied by Concord Technology (Tianjin) Co., Ltd.

2.2. Instruments

Micropipettes (1-1000 μ l, Beijing Dalong), Agilent High-Performance Liquid Chromatograph (LC-1260 model), One ten-thousandth balance (BSA124S model) purchased from Sartorius, Germany, centrifuge (Anhui Jiawen Instrument Equipment Co., Ltd.), magnetic stirrer (IKA Laboratory Technology Co., Ltd.), electric thermostatic blast drying oven (DHG-9030A model) from Tianjin Xingke Science and Technology Co., Ltd., vortex oscillator IKA Laboratory Technology Co., Ltd., and Agilent High-Performance Liquid Chromatograph (LC-1260 model).

3. Experimental Methods

3.1. Drawing the Atrazine Standard Curve

Accurately weigh 0.01600g of atrazine on an analytical balance and make up to 100mL with pure water in a volumetric flask to prepare a 16 μ g \cdot mL⁻¹ stock solution. Use a micropipette to take the stock solution and prepare gradient dilutions to obtain atrazine standard solutions of 8, 6, 5, 4, 3, 2, 1, and 0.4 μ g \cdot mL⁻¹. Measure the absorbance peak area at 263nm using a high-performance liquid chromatograph, and draw the standard curve based on the concentration and peak area. (Figure 2)

Chromatographic conditions: chromatographic column (15mm \times 4.6mm, C18, 5 μ m); mobile phase: methanol: water (80:20 v/v); injection volume: 10 μ l; flow rate: 0.6mL/min; UV detector wavelength: 263nm; temperature: 35 $^{\circ}$ C.

3.2. Determination of Material Adsorption Capacity

The adsorption capacity of the material is represented by the adsorption amount q_e . Under certain pressure and temperature conditions, if m mg of the material adsorbs atrazine from the solution and the adsorbed solute is x μ g, then the adsorption capacity per unit weight of the material, q_e , is calculated as:

$$q_e = x/m = V(C_0 - C_e)/m$$

Where q_e : material adsorption amount, i.e., the weight of the substance adsorbed per unit weight of the material, μ g/g;

x : weight of the adsorbed substance, μ g;

m : amount of material added, mg;

V : volume of the water sample, mL;

C_0, C_e : concentrations of the substance in the water before and after adsorption, respectively, μ g/mL.

The adsorption capacities of the prepared DES-MIP, AA-MIP, DES-NIP, and AA-NIP were evaluated using both dynamic and static methods.

Static: 3 mg of each material was added to atrazine standard solutions with concentrations of 2, 4, 6, and 8 μ g \cdot mL⁻¹ (1.5 mL each). The mixtures were shaken at room temperature for 4 hours, followed by centrifugation (10000 rpm, 10 minutes). The supernatant was filtered and analyzed using a high-performance liquid chromatograph to calculate the adsorption capacity.

Dynamic: 3 mg of each material was added to an 8 μ g \cdot mL⁻¹, 1.5 mL atrazine standard solution and agitated using a vortex oscillator at room temperature for varying durations of 0.5, 1, 2, 3, and 4 hours. Following centrifugation (10000 rpm, 10 minutes), the supernatant was filtered and analyzed using a high-performance liquid chromatograph to determine the adsorption capacity.

3.3. Reusability Test of the Materials

Six rapid and simple adsorption devices were prepared (Figure 1). Filter paper was cut into circular shapes to prepare 6 units of 2.5 mL syringes, each lined with four layers of filter paper, followed by the addition of 50 mg of material, and finally, another four layers of filter paper. Two types of materials, both with and without DES templates, were allocated into three syringes each and labeled with concentrations of 1, 4, and 8 μ g/mL. A 1 mL standard solution was introduced into each adsorption device, followed by elution with 1.5 mL of methanol. The eluate was filtered and collected in vials for analysis using high-performance liquid chromatography, with a constant volume (1.5 mL) of eluate collected. This process was repeated three times on the same day ($n = 3$) using the same adsorbents. The same steps were performed the following day to verify the day-to-day recovery rate. The recovery rates and RSD values for both types of materials were calculated.



Figure 1. Rapid and Simple Adsorption Device

4. Experimental Results

4.1. Atrazine Standard Curve

The absorbance peak area at 263nm was measured using

high-performance liquid chromatography. A standard curve was plotted, correlating concentration with the absorbance peak area. (Figure 2)

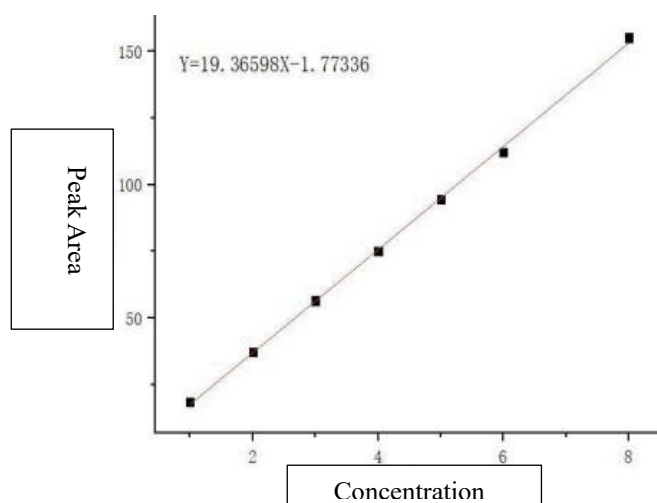


Figure 2. Atrazine Standard Curve

4.2. Static Adsorption

The materials were shaken with atrazine solutions of

varying concentrations, as shown in Figure 3.

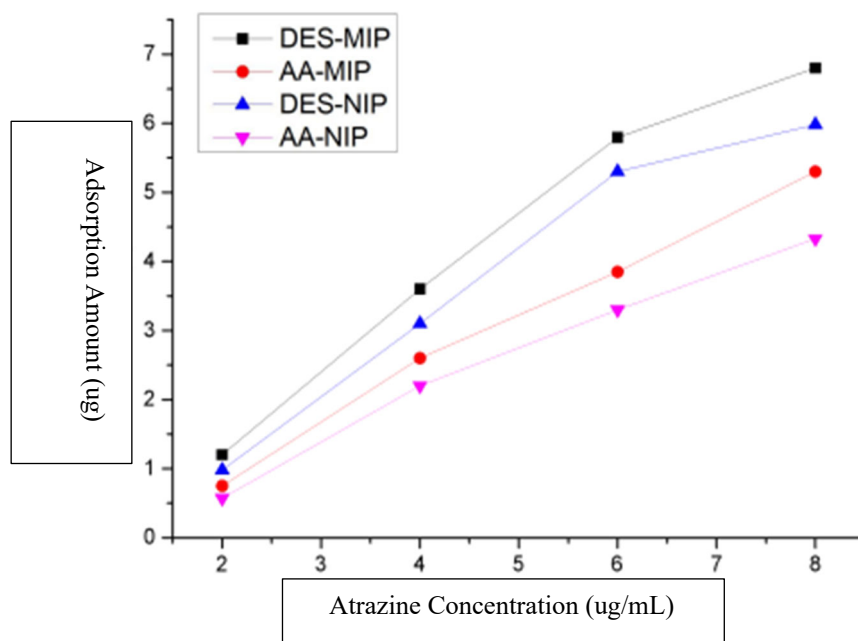


Figure 3. Static Adsorption Capacity

4.3. Dynamic Adsorption

The materials were agitated with an 8 $\mu\text{g/mL}$ atrazine solution, as depicted in Figure 4.

4.4. Verification of Material Reusability

Recovery rates of DES-MIP for various concentrations of atrazine during the day and night are shown in Table 1.

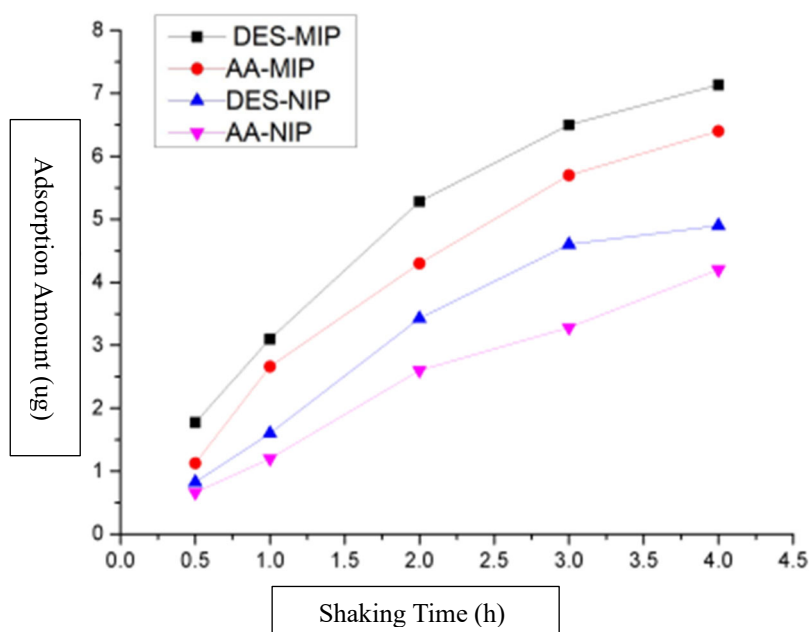
Table 1. Recovery Rates of DES-MIP After Adsorbing Atrazine

Concentration ($\mu\text{g/mL}$)	Daytime		Nighttime	
	Recovery Rate (%)	RSD (%)	Recovery Rate (%)	RSD (%)
1	74.9	1.3	85.5	1.8
4	77.6	1.6	83.8	1.5
8	78.8	1.4	86.8	1.7

Recovery rates of AA-MIP for various concentrations of atrazine during the day and night are shown in Table 2.

Table 2. Recovery Rates of AA-MIP After Adsorbing Atrazine

Concentration ($\mu\text{g/mL}$)	Daytime		Nighttime	
	Recovery Rate (%)	RSD (%)	Recovery Rate (%)	RSD (%)
1	69.2	1.9	68.5	1.5
4	70.9	1.8	71.2	0.7
8	72.3	1.4	71.9	1.0

**Figure 4.** Dynamic Adsorption Capacity

5. Conclusion

The atrazine materials selected for this experiment were of good quality, and the solutions prepared were accurate. The standard curve conformed to a linear relationship, making this atrazine suitable as a representative herbicide for further experiments.

Through both dynamic and static adsorption capacity tests, DES-MIP demonstrated the highest adsorption performance, exhibiting better absorption effectiveness than MIP.

In the reusability experiments, under the introduction of DES, DES-MIP showed better recovery rates compared to AA-MIP.

6. Discussion

6.1. Discussion of Experimental Results

Atrazine, a synthetically produced herbicide, was developed by the Geigy Chemical Company in 1952, patented in Switzerland in 1958, and commercially produced in 1959 [3]. Also known as simazine, its chemical name is 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine, a triazine herbicide. As shown in Figure 1, the atrazine standard curve conforms to a linear relationship with a correlation coefficient of 99.9%, and the standard curve equation is $Y = 19.36598X - 1.77336$.

Adsorption Capacity Analysis: Based on Figure 3, the adsorption quantity of all nanoparticles increases rapidly up to a concentration of $6 \mu\text{g/mL}$. A further increase in concentration leads to a slower adsorption rate at $8 \mu\text{g/mL}$, although saturation is not reached due to the limited range of measured concentrations. It is observed that DES-MIP has the

highest adsorption performance and shows better absorption than MIP. As the adsorption time increases, both MIP and DES-MIP demonstrate an increase in adsorption capacity, with DES-MIP exhibiting a faster increase compared to MIP. According to Figure 4, the adsorption quantity of all materials increases with time, and DES-MIP shows the highest and fastest adsorption capacity among them. These performance changes are likely due to the introduction of DES monomers.

The reusability experiments indicate that DES-MIP demonstrates better recovery rates with the introduction of DES. The overall recovery rates did not reach 90%, possibly due to the limited precision of the rapid and simple adsorption device and suboptimal activation. As shown in Table 1, the daytime and nighttime recovery rates for DES-MIP are 74.9%–78.8% and 83.8%–86.8%, respectively. As indicated in Table 2, the daytime and nighttime recovery rates for AA-MIP are 69.2%–72.3% and 68.5%–71.9%, respectively. Moreover, the relative standard deviation (RSD) values for both DES-MIP and AA-MIP are less than 2%, affirming their reusability.

6.2. Material Preparation

Since the introduction of deep eutectic solvents (DES) by Abbott Laboratories in 2003, the past few decades have seen significant development in this field [9–10]. As a novel eco-friendly solvent, DES shares similarities with ionic liquids in terms of low melting point, high electrical conductivity, low vapor pressure, and good solubility. Additionally, DES surpasses ionic liquids in biodegradability, low toxicity, cost-effectiveness, and customizability, making it an excellent alternative to ionic liquids [11–13]. DES is formed by intermolecular hydrogen bonding between hydrogen bond

acceptors (HBA) and hydrogen bond donors (HBD) [14–17]. It has extensive applications in separation science, material synthesis, electrochemistry, and catalysis, holding great potential in the field of material science [18–21]. With its high viscosity and abundant hydrogen bonding, DES is suitable for material synthesis. The DES monomer, often used as a novel eco-functional monomer in the preparation of molecularly imprinted materials, is chosen for its high viscosity, hydrophilicity, and rich hydrogen bond system [22]. An attempt was made to prepare DES using choline chloride and acrylic acid, which forms stable hydrogen bonds (evidenced by high transparency and low viscosity) and is utilized as a functional monomer for MIP preparation.

DES, as a common functional monomer, and AA, as a control group, were used in this study.

6.3. Theoretical Methods

This experiment utilized quantitative analysis techniques and established control groups. High-Performance Liquid Chromatography (HPLC) was employed to measure the peak areas of atrazine at different concentrations. This facilitated the construction of an atrazine standard curve and the derivation of a linear equation. The adsorption capacities of materials were tested using dynamic and static methods. In the dynamic method, concentration was controlled by mixing materials with an 8 µg/mL atrazine solution and agitating. In the static method, time was controlled by agitating materials with atrazine solutions of 2, 4, 6, and 8 µg/mL concentrations. The resulting peak areas were substituted into the standard curve equation to determine the supernatant concentration, thus calculating the adsorption amount. This adsorption amount reflects the material's efficacy in removing atrazine. The reusability of the materials was evaluated based on recovery rates. Higher recovery rates indicate better reusability, and the relative standard deviation (RSD) was calculated to ensure the data's significance.

6.4. Summary and Outlook

The aim of this experiment was to determine the pollutant removal efficiency of molecularly imprinted materials introduced with Deep Eutectic Solvents (DES). In dynamic and static adsorption experiments, the time and concentration ranges were insufficient to achieve saturation adsorption, thus limiting a deeper analysis of adsorption efficacy. Potential operational errors in the fabrication and use of the rapid and simple adsorption device might have contributed to suboptimal recovery rates. However, the results indicate that molecularly imprinted polymers incorporating DES demonstrate enhanced removal capabilities for herbicides in water and improved reusability, serving as a reference for herbicide removal in wastewater treatment. DES is a novel and environmentally friendly solvent, offering advantages over traditional solvents (like ionic liquids and water) such as simplicity of synthesis, cost-effectiveness, and customizability. Research on enhancing the adsorption effects of molecularly imprinted polymers by incorporating DES is still in its infancy. Further exploration and refinement are needed to improve its removal efficiency.

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