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ORIGINAL RESEARCH PAPER

Selective removal of dicamba from aqueous samples using molecularly imprinted polymer nanospheres

Tooraj Beyki; Mohammad Javad Asadollahzadeh*

Department of chemical engineering, Shahrood Branch, Islamic Azad University, Shahrood, Iran

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Abstract

For the first time, uniform molecularly imprinted polymer (MIP) nanoparticles were prepared using dicamba as a template. The MIP nanoparticles were successfully synthesized by precipitation polymerization using methacrylic acid (MAA) as functional monomer, trimethylolpropane trimethacrylate (TRIM) as cross-linker and acetonitrile as porogen. The produced polymers were characterized by differential scanning calorimetry (DSC) and their morphology was precisely examined by scanning electron microscopy (SEM). The MIP nanospheres were obtained with the average diameter of 234 nm. Batch-wise guest binding experiments were carried out to determine the removal efficiency of the produced MIP nanoparticles towards the template molecule in aqueous solutions. The MIP showed outstanding affinity toward dicamba in aqueous solution with maximum removal efficiency of 87.5% at 300 $mg.L^{-1}$ of dicamba solution. The MIP exhibited higher adsorption efficiency compared with the corresponding non-imprinted polymer (NIP) as well as outstanding selectivity towards dicamba relative to the template analog in an aqueous solution. Moreover, effects of pH on removal efficiency and selectivity of MIP were evaluated in detail.

Keywords: *Dicamba; Molecularly imprinted polymer; Molecular recognition; Nanospheres; Precipitation polymerization; Water treatment*

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INTRODUCTION

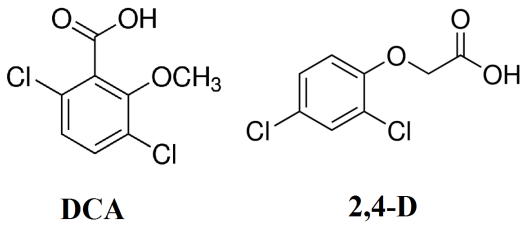
As evident, the effective control of a variety of diseases and pests, especially weeds, certainly leads to advantageous agricultural productions. Herbicides are the chemically compounds that are widely used in farms, gardens, parks and other agricultural lands to control the growth of weeds and herbs. Thus, the herbicides are the most plentiful pollutants found in the environment and in agricultural products. It is well established that the presence of herbicides in the aquatic environment are of great concern because of the potential impact on human health and the environment even at low concentration levels. Currently many herbicide compounds have been detected in sewage effluent, surface water, and groundwater.

A typical example is dicamba (DCA), 3,6-dichloro-2-methoxybenzoic acid, a common systemic auxin-type and low-cost herbicide and widely used for pre- and post-emergence control of annual and perennial broadleaf weeds (see Fig. 1). Its chemical structure and mode of action in plants is similar to that of the phenoxy herbicides, like 2,4-D (2,4-Dichlorophenoxyacetic acid), both act like natural plant hormones known as auxins. These hormones help to control plant growth. When plants are treated with DCA, they grow in

* Corresponding Author Email: *m.asadalahzadeh@iau-shahrood.ac.ir*

abnormal and uncontrollable ways, and often, the plants die. It is used for rye, asparagus, barley, corn, oats, soybeans, sugarcane and wheat farms. It is also applied on golf courses, residential lawns, and rights-of-way along utility lines, roadsides and railways [1-3]. Furthermore, DCA is very soluble in water, stable to chemical hydrolysis and highly mobile in soil [4]. Accordingly, DCA has been considered as one of the most frequently detected herbicide in water bodies thus far. DCA can inhibit some of the organisms important in soil nutrient cycling and thus impair soil fertility. In humans, exposure to DCA can cause genetic damage in blood cells, nervous system disorder and an increased frequency of cancer of the lymphatic system. It also may be associated with decreases in body weight, liver damage, fetal loss and irreversible eye damage sometimes. Furthermore, DCA is toxic to aquatic organisms [5-7]. Hence, the maximum contaminant level of DCA is set as 200 $mg.L^{-1}$ in drinking water by EPA of United States [8].

According to the statements mentioned above, the necessity for developing a selective, simple, reliable and adapted wastewater treatment process is of great concern. Current research indicates that selective uptake using molecularly imprinted polymers is a promising approach for the removal of trace pollutants in water. Molecularly imprinted polymers (MIPs) are special tailor-made synthetic polymers with specific selective molecular recognition abilities. MIPs are manufactured by copolymerization of functional and crosslinking monomers around a target molecule called template. Then, removal of the template forms specific binding sites that are complementary to the template in shape, size and chemical functionality. Now, these polymers have the capability to rebind selectively to the template from other compounds. Compared with other natural competitors, MIPs have intrinsic advantages, including easy and inexpensive preparation, robustness, and high chemical and thermal stability in harsh conditions [9,10]. MIPs can be used in many different fundamental fields, such as sensors and biosensors [11,12], catalysts and mimic antibodies [13,14], pharmaceutical applications [15,16], the stationary phase in HPLC [17,18], solid phase extraction [19,20], membrane separation [21,22] and enantioseparation [23,24]. They have great ability for separation of a target pollutant in a complex sample in which compounds have similar properties. Therefore, it makes MIPs



DCA **2,4-D**

Fig. 1. Chemical structure of dicamba and 2,4-D

attractive as a considerable adsorbent for removal and enrichment of pesticides, herbicides, heavy metals and other pollutants from waste and drinking water [25-28]. For example, MIPs have been effectually used for the selective removal of 2,4-D herbicide from water [29,30].

The traditional method for preparation of MIPs is bulk polymerization in which crushing, grinding, and sieving of the monolith are necessary. This process is easy to operate, but time-consuming, labor intensive and wasteful procedure since only less than 50% of the ground polymers are recovered as useable material [31]. The recognition rebinding cavities could be destroyed during the crushing and grinding procedures. As a result, the particles have heterogeneous binding sites distribution with poor site accessibility and low mass transfer kinetic properties for the target molecule. Thus, the irregular particles generally give low separation yield [32]. Compared with bulk polymerization, precipitation polymerization is a more economical and labor-saving method often used for preparing MIPs with uniform shape in good yield. The obtained particles are spherical shape, sub-micron scale and monodispersed. The method is based on the precipitation of the polymeric chains out of the solvent in the form of particles as they grow more and more insoluble in an organic continuous medium [33]. The obtained particles can be used directly without the grinding and crushing procedures. In addition, use of any stabilizers and surfactants are not necessary. Thus, we preferred to prepare MIP directly in the form of spherical particles by precipitation polymerization.

In the present investigation, we prepared a molecularly imprinted polymer for the first time exclusively using DCA as the template by precipitation polymerization. The objective of this study is to prepare and characterize DCA imprinted polymer that can be used effectively for adsorption of DCA from aqueous samples. The

characteristics of the MIP, including adsorption properties, molecular recognition selectivity, and the effects of pH were investigated in detail.

EXPERIMENTAL

Materials

Dicamba (DCA), Trimethylolpropane trimethacrylate (TRIM) and Azobisisobutyronitrile (AIBN) were obtained from Sigma Aldrich (Steinheim, Germany). AIBN was re-crystallized from methanol before use. In order to remove the polymerization inhibitor, Methacrylic acid (MAA, Darmstadt, Germany) was distilled in vacuum prior to use. Acetonitrile, methanol and all the other solvents were HPLC grade and purchased from Merck and were used without further purification.

Synthesis of polymer nanoparticles

Molecularly imprinted nanoparticles were synthesized using precipitation polymerization under the conditions described in Table 1. First, the template molecule, DCA, was dissolved in a mixture of acetonitrile (ACN) in a thick-wall glass tube equipped with a screw cap and then the functional monomers (MAA) were added. The mixture was homogenously dispersed by sonication in an ultrasonic bath (VGT-1730, QTD, Korea) for 5 min. After that, the mixture was mixed gently for 15 min to create hydrogen interaction between MAA and DCA. Thereafter, the crosslinker (TRIM) and initiator (AIBN) were added and the solution was dispersed by sonication for 5 min. The solution was then purged with N_2 gas for 15 minutes to get rid of oxygen in the solution, which would have retarded the synthesis process due to the annihilation of free radicals produced from the decomposition of the initiator. Subsequently, the reaction vessel was sealed under N_2 atmosphere to prevent air from entering it. Finally, polymerization was carried out by inserting the reaction vessel in a water bath (WB14, Memmert, Germany). In addition, for polymerization to take place, temperature was increased from 25°C to 60°C within 1 h and thereafter kept for 23 h. After polymerization, polymer particles were collected by centrifugation (Hermle, Z36HK, Germany) at 21,000 rpm for 15 min. To remove template from the polymer matrix, unleached imprinted polymer was washed by a mixture of methanol/acetic acid (9:1, v/v) five times for 1 h, until no template was detected in the washing solvent by spectrometric measurement (at 280 nm) (model 6305; Jenway, England). The template extraction of the polymer created the cavities, leading to the specific sorption of the template. In addition, the removal of other materials from the polymer took place (e.g. residual monomers or oligomers and initiator fragments). Residual acetic acid was removed with methanol. Also, the polymer particles were rinsed in the same volume of distilled water and acetone, and finally the resulting leached imprinted polymer was dried in oven at 50°C for 24 h.

In order to verify that the rebinding of the template was due to molecular recognition and not due to a non-specific binding, a control non-imprinted polymer (NIP) was prepared according to the same procedure, but excluding the target molecule, DCA.

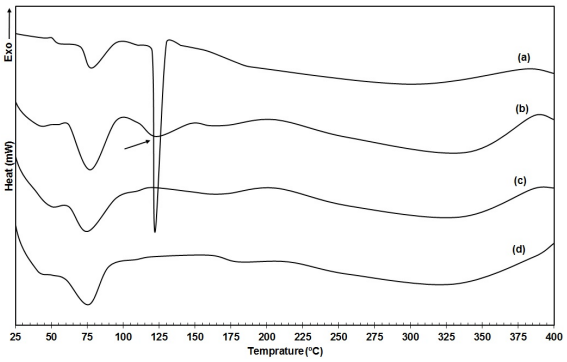


Fig. 2. DSC thermograms of a) dicamba, b) unleached MIP, c) leached MIP and d) NIP

Table 1. Preparation of dicamba imprinted polymers

Template	Functional monomer	Crosslinker	Initiator	Porogen
DCA	MAA	TRIM	AIBN	ACN
0.1 mmol	0.12 mmol	0.12 mmol	0.0974 mmol	50 mL

Characterization of polymer nanoparticles

Thermal properties of polymer particles were investigated by a Mettler DSC 823 (Mettler Toledo, GmbH, Switzerland) equipped with a Julabo Thermocryostate Model FT100Y (Julabo Labortechnik GmbH, Germany) under N_2 atmosphere. A Mettler Star software system (version 9.x) was used for the data acquisition. Indium was used to calibrate the instrument. The samples were scanned at a heating rate of 20 °C.min^{-1} in 25–400 °C temperature range.

The shape and the surface morphology of the polymers were estimated by SEM (TESCAN,

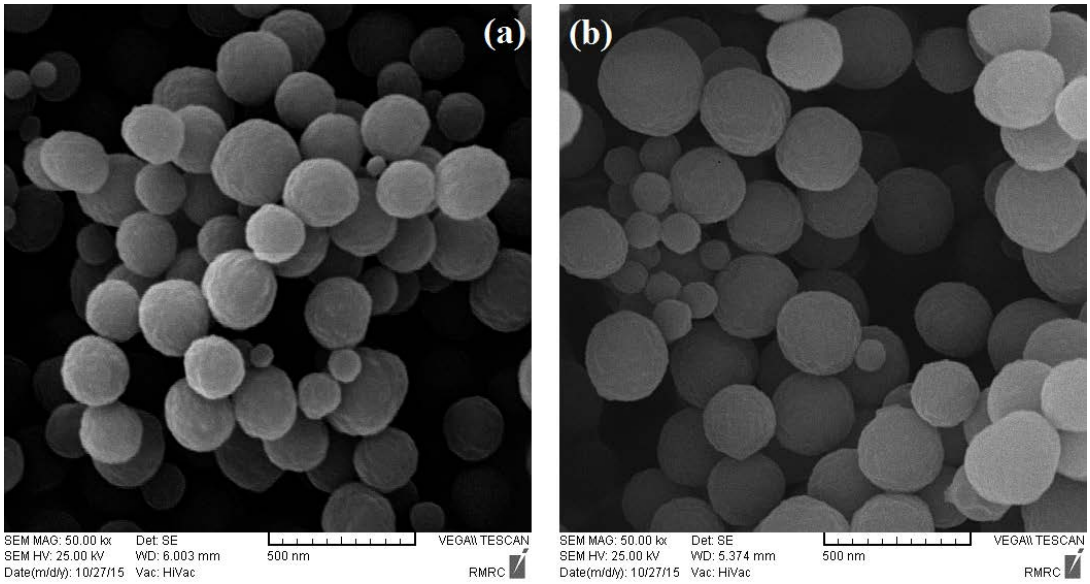


Fig. 3. Scanning electron micrographs of a) MIP and b) NIP

VEGAII, Czech). Polymeric particles were sputter coated with gold before the SEM measurement.

Rebinding experiments

To evaluate the binding affinity of the imprinted polymer, in static adsorption experiment, 100 mg of MIP particles were mixed with 30 mL of DCA in water solutions in different concentrations (100–1,000 mg.L^{-1}, pH=7) and shaken at 150 rpm for 3 h (Stuart, S1500, UK) to measure the removal efficiency of the polymers. The polymer particles were separated centrifugally at 21,000 rpm for 30 min then the supernatant was filtered via an ultrafiltration membrane. The unbound DCA in the supernatant was measured by UV-visible spectrophotometer at 280 nm. The removal efficiency was calculated by subtracting the equilibrium concentrations from the initial concentrations according to the following equation:

$$\text{Removal Efficiency } (\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of DCA (mg·L^{-1}). The initial pH values of 300 mg.L^{-1} of DCA in water solutions were adjusted from 2 to 11 using HCl and NaOH. Then 100 mg of the polymer particles were dispersed in 30 mL of each pH solution. The mixtures were shaken in 150 rpm for 3 h. The polymer particles were centrifuged at 21,000 rpm for 30 min and then the supernatant was passed through an ultrafiltration membrane and free concentration of DCA after the adsorption was determined by UV-visible spectrophotometer at 280 nm. In order to compare specific and non-specific interactions with DCA, a control procedure was performed using NIP particles. To validate the selectivity of MIP, 2,4-Dichlorophenoxyacetic acid (2,4-D) was chosen as the competitor of DCA in competitive recognition studies (see Fig. 1). The imprinted polymer (100 mg) was added to two flasks containing 30 mL of 2,4-D and DCA–water mixed solution, each with concentration of 300 mg.L^{-1} (at pH=7), respectively, shaken at room temperature for 3 h and separated centrifugally. After filtration of the supernatant via an ultrafiltration membrane, the unbound DCA and 2,4-D in the supernatant were measured by UV-visible spectrophotometer at 280 nm and 284 nm, respectively. Also, all the experiments were performed in triplicate.

RESULTS AND DISCUSSION

Characterization of polymer nanoparticles

DSC analysis was performed to investigate the thermal characteristics of polymeric particles. Fig. 2 describes DSC plots of DCA, unleached and leached MIP and NIP. DSC thermograms of MIPs and NIP show that the decomposition process started approximately at 275 °C. All polymers had similar thermal characteristics, but an endothermic transition was observed at about

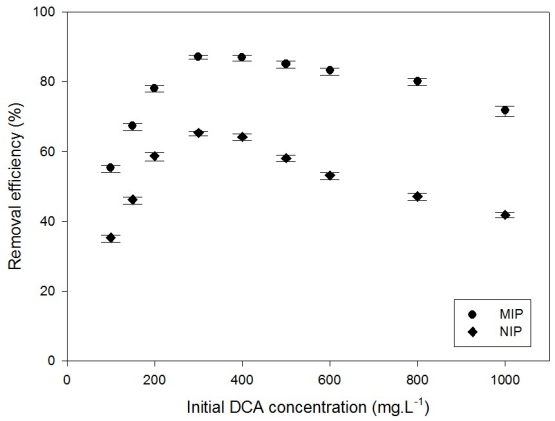


Fig. 4. Removal efficiency of MIP and NIP towards dicamba (100 mg of polymer, pH=7)

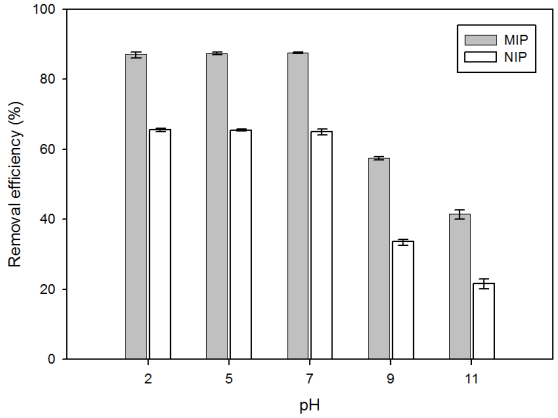


Fig. 5. Effect of pH on the removal efficiency of dicamba by MIP and NIP in water solution (100 mg of polymer, 300 mg.L^{-1} of DCA water solution)

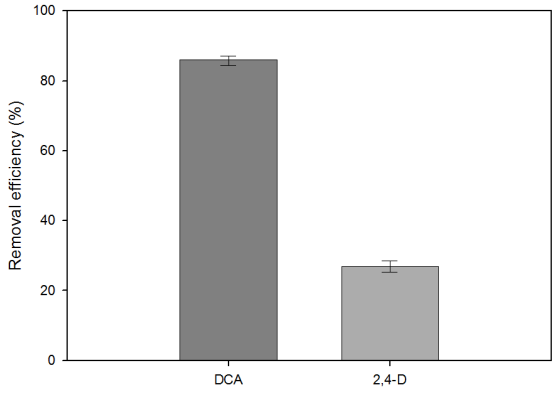


Fig. 6. Competitive adsorption of MIP for template and template analog (100 mg of polymer, 300 mg.L^{-1} of DCA/2,4-D water solution, pH=7)

122 °C for unleached MIP (shown with arrow). This transition is related to the melting process of the loaded DCA in unleached MIP.

The morphological structures of the MIP and NIP were detected by SEM. As can be seen in Fig. 3, spherical and nanometer particles were obtained by precipitation polymerization. The average particle diameters of the MIP and the NIP nanospheres are 234 nm (Fig. 3a) and 320 nm (Fig. 3b), respectively. The significant difference in size of imprinted and non-imprinted polymer is due to the influence of template compound on the particle growth during the precipitation polymerization. In the absence of DCA, functional monomer can form hydrogen-bonded dimers in the non-imprinting system and the pre-polymerization solution contains both functional monomer dimers and free functional monomer. In the imprinting system, there are additional molecular interactions between functional monomer and DCA, which might somehow affect the growth of the cross-linked polymer nuclei [34,35].

Rebinding experiments

To investigate the affinity of DCA-imprinted polymer and non-imprinted polymer, batch-wise guest binding experiments were carried out. The removal efficiency of DCA by MIP at each initial concentration, ranging from 100 to 1,000 mg.L^{-1} was compared with NIP (Fig. 4) that demonstrates the adsorption process efficiency. Maximum removal for MIP and NIP was 87.5% and 65.8% respectively. The results from rebinding experiments showed that imprinted polymer had more removal efficiency than non-imprinted polymer, indicating that there were specific binding sites for DCA. The template binding by the non-imprinted polymer can be explained with the presence of non-specific binding due to physical adsorption and to random interactions of the template molecules with functional groups in the polymer matrix.

The effect of pH is a significant factor in the imprinted and non-imprinted polymers adsorption process because it influences not only the properties of the MIP surface but also the specification of the target compound [36]. Hence, several batch experiments were performed by equilibrating 100 mg of the polymer nanoparticles with 30 mL of solutions containing 300 mg.L^{-1} of DCA under the desired range of pH. Fig. 5 shows the effect of pH on the removal efficiency of DCA by MIP

and NIP in water medium. The removal efficiency of DCA by MIP and NIP remained approximately unchanged as the pH value of the solution varied from 2 to 7, whereas the removal efficiency of DCA by MIP and NIP was close to the maximum value in this pH range. This adsorption suggests that the hydrophobic interaction and hydrogen bonding between DCA and the selective binding sites were the main driving forces for adsorption. However, the removal efficiency of DCA by MIP and NIP decreased significantly in the pH range of 9-11. At this pH range, the electrostatic repulsive interactions between DCA and MIP overcome the binding affinity and hydrophobic interactions and play an increased role in adsorption [37,38]. It was also found that the MIP had higher sorption efficiency than the NIP over the entire pH-range investigated, showing a good imprinting effect and adsorption performance.

In order to evaluate the selectivity of the synthesized MIP, 2,4-D was selected as potential interferes, as template analog, because of the similarity of their chemical structures to DCA. DCA frequently is used along with 2,4-D. 2,4-D is one of the most widely used herbicides in the world and a common systemic herbicide used in the control of broadleaf weeds [39]. The results of the adsorption experiments are shown in Fig. 6. According to the adsorption experiments, the removal efficiency of MIP to DCA was approximately 3.2-fold that of 2,4-D. MIP can recognize its template molecules due to the existence of memory cavities with fixed size, shape, binding sites and specific binding interactions between the target molecule and the sites. 2,4-D cannot bind as strongly as DCA because its size cannot match the cavities or its functional group position does not correspond to the functional groups in cavities and thus cannot bring about specific binding in the same way as DCA. 2,4-D binding to DCA imprinted polymer is as a result of the non-selective and nonspecific binding.

CONCLUSION

This study significantly demonstrated for the first time the potential of DCA-MIP synthesized by precipitation polymerization for the recognition and selective removal of DCA from aqueous samples. The results of rebinding experiments indicated that the prepared MIP exhibited outstanding adsorption ability and selectivity for DCA, proving the specificity of the synthesized MIPs towards the template molecule. Moreover, the prepared MIP showed attractive characteristics, including significant thermal stability, nano-spherical morphology, high removal efficiency and outstanding selectivity. The results illustrated in this study could be remarkable for future research toward development of new separations and devices such as diagnostic sensors and MISPE that are useful in closely related fields.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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