

Improving the Efficiency of Imprinting in Poly(HEMA) for Polyaromatic Hydrocarbon Using Silver Ions

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ABSTRACT: Molecularly imprinted polymer for a typical polyaromatic hydrocarbon, naphthalene, was synthesized. Silver ions are incorporated during the synthesis and the equilibrium uptake of the template molecule (naphthalene) by the imprinted polymer was found to be many folds higher than the uptake of the molecule by the imprinted polymer prepared in the absence of the metal ions. The enhanced adsorption was attributed due to the improved interaction between the template mole-

cules and the monomers which is reasoned to be induced by the silver ions. It appears that the adsorption capacity of molecules without having any functional groups could be increased by the methodology reported here. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3275–3278, 2008

Key words: molecular imprinting; silver ions; naphthalene; poly(hydroxyl ethyl methacrylate)

INTRODUCTION

Molecular imprinting is an elegant and simple approach to create antibody-like affinity sites in highly crosslinked synthetic polymers.^{1–3} This methodology has been used extensively to create highly selective matrices for solid phase extraction, as stationary phases particularly for the separation of chiral molecules, as sensing elements in the design of biosensors, etc.^{1–10}

Molecularly imprinted polymers (MIPs) are widely synthesized using covalent and noncovalent approaches. Considering the fact that noncovalent interactions are prevalent in the biological domain, noncovalent approach has proven to be most widely preferred method for generating affinity sites in polymeric matrices. In this approach, the monomers and template molecules are mixed together in a suitable medium and polymerized. High degree of crosslinking is mandatory to preserve the shape and size of the cavity of the template molecules. After the polymerization process, the template is removed by extensive extraction. Prior to polymerization, the template molecules interact with the monomers through H-bonding, electrostatic, or hydrophobic interactions. Functional groups present in the template and monomer engages in such interactions.

Many polyaromatic hydrocarbons are ubiquitous and many of them are toxic.^{11,12} Extensive efforts have been directed to detect and quantify such chemicals in air, water, soils, etc.^{11–13} Often sample enrichment is needed prior to analysis of these components. Solid phase extraction is the widely preferred method for sample enrichment. Considering the potential advantage of MIPs, usage of such matrices for the isolation appears to be interesting. Because polyaromatic components does not have functional groups (e.g., —OH, —COOH, —NH₂, etc), it is a challenge to create adequate and efficient affinity sites in the MIPs for such molecules. Dickeret et al. have reported polyurethane based MIP for polyaromatic components.¹⁴ Krisch et al. prepared MIP for 1-hydroxyl pyrene using divinyl benzene and styrene.¹⁵ It is assumed that affinity sites are created through the hydrophobic interaction between the aromatic moieties present in the template and aromatic isocyanate used as monomer.

Vinyl monomers are widely used for the preparation of MIPs considering this fact, polymers based on such monomers are easy to prepare and are known to provide efficient imprinting. Recently, Lai et al. have synthesized and evaluated MIPs for PAHs using varied vinyl monomers.¹⁶ The extent of uptake was, however, less presumably due to the lack of sufficient affinity sites in the polymers.

Because of the absence of additional groups in the PAHs, efficient imprinting could not be expected in MIPs based on vinyl monomers. Inducing electrostatic interactions between the monomers and PAHs prior to polymerization could be an interesting

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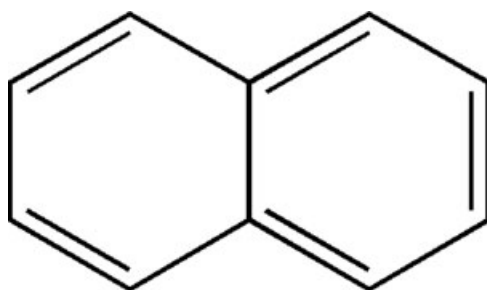


Figure 1 Structure of naphthalene.

approach in the synthesis of MIPs for PAHs using vinyl monomers.

Metal ions can complex with many organic compounds so that various types of association products are formed. Complexes are formed by the weak charge transfer interactions. The compounds act as electron donors and metal ions act as the electron acceptors. The use of charge transfer complexes of metal ions and their utility in chromatographic separation of organic species are widely known.¹⁷ The use of Ag (I), particularly because of its ability to form complexes with a wide class of compound, has been studied more extensively than that of other metal ions.¹⁸ The specific use of Ag (I) has been termed as "argentation chromatography" and it is a widely used separation technique. It can be reasoned that prior to polymerization, addition of metal ions such as silver, could impart enhanced interaction between the monomers and PAHs. This communication use this approach to synthesis MIPs based on 2-hydroxyl ethyl methacrylate for a model PAH, naphthalene (Fig. 1).

MATERIALS AND METHODS

2-Hydroxy ethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA) were obtained from Sigma-Aldrich, Bangalore, India. Other analytical grade reagents were from E.Merck, Mumbai, India.

Cary model 100 Bio UV-visible spectrophotometer is used for the quantitative estimation. Calibration plots were prepared between the concentration of standard solution of naphthalene in acetonitrile and absorption at 254 nm. This plot was used for determining the amount of naphthalene adsorbed by the polymers. Energy dispersive X-ray analysis was carried out using EDS model 6051 SP (Oxford instruments, London, UK) attached to a Hitachi model S-2400 Scanning Electron Microscope.

Preparation of the Polymers

Different polymeric formulations were prepared as follows. HEMA (2 g), 4 g EGDMA, and 100 mg

naphthalene were dissolved in 10 mL each of acetonitrile. To each of these solutions, 50, 100, 150, and 200 mg silver nitrate were added and stirred to dissolve. The solutions were bubbled with nitrogen, sealed and subjected to gamma irradiation at a rate of 0.3 Mrad/h to initiate polymerization.¹⁹ After 5 h, the polymers were isolated, powdered, and extracted with acetonitrile to remove the template. The amount of ingredients other than silver nitrate is kept constant to know the influence of the effect concentration of silver ions on the imprinting efficiency. The complete removal of the template was ensured by measuring the absorption of the extract at 254 nm. Polymer without the addition of template was also prepared to serve as control. In this formulation, exactly same quantity of silver nitrate was added before polymerization to know whether silver ions have any influence on the adsorption by nonimprinted polymer. The polymers then washed with deionized water to remove any adsorbed silver ions and dried at 50°C. MIP was also prepared for naphthalene without adding silver ions to know the influence of silver ions on the imprinting. The MIPs prepared in the presence of silver ions are designated as MIP-silver.

Interaction of the Polymers with the Template

Fifty milligram polymer was placed in an acetonitrile solution containing 0.5 mg/mL of naphthalene under mild stirring at room temperature (25°C). After 12 h, the absorption of the solution at 254 nm was measured. From the difference in absorption of the solutions before and after placing the polymers, the quantity adsorbed by the polymer was estimated.

RESULTS AND DISCUSSION

Energy dispersive X-ray analyses of the polymers have shown that the polymers do not contain any silver ions. The extent of water uptake of both nonimprinted and imprinted polymers was also nearly identical (2.87 for MIP and 2.72 for nonimprinted polymer) reflecting that the porosity is identical.

It is assumed that 12 h is sufficient to attain the equilibrium adsorption. The equilibrium adsorption of naphthalene by the imprinted and nonimprinted polymers is shown in Table I. It is interesting to see that MIP-silver adsorbed substantially high quantity of naphthalene comparing to nonimprinted or imprinted polymer prepared in the absence of silver ions.

The ratio between the equilibrium adsorption by the MIPs and nonimprinted polymer could be considered as a measure of the imprinted efficiency. Table I apparently suggests that creation of affinity sites is remarkably high in the MIP-Silver.

TABLE I
Equilibrium Adsorption of Print Molecule by the Polymers

Polymer	Quantity adsorbed ($\mu\text{g}/100\text{ mg}$)	Ratio (MIP/Nonimprinted)
MIP-silver	66.0 ± 2	27.50
MIP	3.3 ± 0.4	1.38
Nonimprinted	2.4 ± 0.2	1.0

The amount adsorbed by MIP-silver shown here is by the formulation prepared by adding 100 mg silver nitrate.

The adsorption of MIP is comparable to the value of nonimprinted polymer reflecting that it is nonspecific adsorption rather than due to the creation affinity sites by imprinting. These parameters again reflect that some sorts of interaction are very much needed for the creation of affinity sites. The lack of functional groups in the template molecule could be the reason for the inefficiency of the MIP. On the other hand, MIP-silver adsorb the template molecule considerably indicating that affinity sites are indeed created by the imprinting which could be traced to the enhanced interaction between the template and monomers presumably due to formation of charged species between the template molecule and silver ions.

The affinity of the imprinted polymer toward the template molecules was assessed by comparing its uptake of anthracene. The results summarized in Table II apparently suggest that sites created in the MIP are specific to naphthalene.

The adsorption capacity of the MIPs prepared using varied amount of silver nitrate is shown in Figure 2.

It can be seen that there is a nominal increase in the adsorption in MIP prepared by incorporating 100 mg silver nitrate. The adsorption of the template by other formulations remain the same indicating that maximum efficiency is attained in formulation prepared by adding 100 mg silver nitrate.

The MIP is extracted with chloroform after attaining the equilibrium adsorption to remove the template. Subsequently the matrix is again treated with solution containing naphthalene. The MIP-silver adsorbed $60\ \mu\text{g}$ of the template which is comparable to its uptake when it is treated with the template so-

TABLE II
Equilibrium Uptake of Anthracene by the Imprinted and Nonimprinted Polymers

Polymer	Quantity adsorbed ($\mu\text{g}/100\text{ mg}$)
MIP-silver	6 ± 1.5
MIP	2.8 ± 0.7
Nonimprinted	2.2 ± 0.4

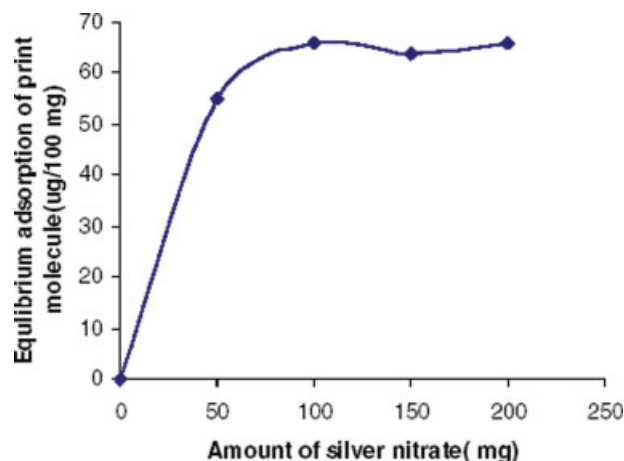


Figure 2 Equilibrium uptake of print molecule by MIPs prepared using varied amount of silver nitrate.

lution for the first time (see Table I) reflecting that the affinity sites are intact after the extraction. This data further reflect that the reusability of the MIP.

Naphthalene is a polycyclic aromatic hydrocarbon and widely used as an intermediate in chemical and plastics industry. It is used in the manufacture of insecticides and fungicides. Occupational exposure to naphthalene is reported in the case of processing or handling of coal tar and mineral oil base products.^{20,21} Moreover, naphthalene is the most abundant compound in creosote vapor 4, being the 10–16% (w/w) of creosote oil (used as wood preservative). Because household mothballs contain naphthalene, suspected cases of poisoning of infants have been reported.²² High levels of naphthalene metabolites were found in the urine of psoriatic patients treated with coal tar pitch.²³ Because of its high volatility, naphthalene uptake occurs mostly via inhalation; the skin is another important route of uptake.

The study apparently indicates that affinity sites for templates such as the one used in this communication can effectively be created by simple approaches like the one reported here.

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