



Polyaniline nanoparticles for the selective recognition of aldrin: Synthesis, characterization, and adsorption properties



M.O. Munyati^{a,*}, A. Mbozi^a, M.N. Siamwiza^a, M.M. Diale^b

^a Department of Chemistry, School of Natural Sciences, University of Zambia, P.O. Box 32379, Lusaka, 10101, Zambia

^b Department of Physics, Faculty of Natural & Agricultural Sciences, University of Pretoria, Private Bag X20, Hatfield, 0028, South Africa

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ABSTRACT

We report the preparation, characterization, and property evaluation of molecularly imprinted polyaniline nanoparticles that can be used for the selective recognition of aldrin. The molecularly imprinted polyaniline nanoparticles were prepared by inverted emulsion polymerization using aldrin as a template and aniline as a functional monomer. The prepared nanoparticles were characterized using UV–vis spectroscopy, Fourier transform infrared spectroscopy, and nuclear magnetic resonance spectroscopy. The spectral data confirmed that aldrin was successfully incorporated into the polymer matrix. Atomic force microscopy and scanning electron microscopy analyses revealed that the prepared nanoparticles were spherical in nature with sizes ranging from 60 to 100 nm for nonimprinted particles and from 500 to 1500 nm for imprinted particles. The surface morphology changed from smooth to rough upon the incorporation of aldrin molecules. The electrical properties were evaluated using a four-point probe coupled to a source meter. The nonimprinted nanoparticles showed an electrical conductivity of 4.149 S/cm, which was reduced to 0.546 S/cm in molecularly imprinted polyaniline. The equilibrium dissociation constant and free equilibrium concentration were found to be 0.6 and 0.799 ng/ μ L, respectively. The adsorption characteristics of aldrin and dichlorodiphenyltrichloroethane (DDT) were investigated to determine the selectivity of the imprinted nanoparticles. The distribution coefficients for DDT and aldrin were 0.76 ng/ng and 1.31 μ L/ng, respectively, indicating that the imprinted nanoparticles had a stronger affinity for aldrin than for DDT.

1. Introduction

The accumulation of persistent organic pollutants [1], particularly organochlorine pesticides, in the environment resulting from their use in the agriculture and public health sectors is a continued source of concern. This concern has driven the development of low-cost, easy-to-use sensing devices that make use of smart materials with high specificity, selectivity, and sensitivity for analytes. Currently, there is a need for new synthetic methods for advanced, tailor-made functional materials with specific recognition capacity and long-term stability. Molecularly imprinted polymers represent one of the most promising classes of new and highly selective functional materials [2–6]. Their combination of selective recognition and chemical strength makes them a leading candidate material for chemical sensors.

Conducting polymers are an important class of materials because of their potential applications in various electronic devices such as

chemical sensors, electrochromic displays, and light-emitting diodes [7]. Among the various conducting polymers, polyaniline is one of the most promising because of its facile synthesis, low cost, exceptional environmental stability, relatively high conductivity, and unique redox behavior. Therefore, polyaniline is used in a variety of applications such as antistatic materials, anticorrosion coatings, batteries and energy storage, organic light-emitting diodes, and chemical sensors. Although the use of conducting polymers as transducers in chemical sensors has been described in the literature, the reported sensing devices are limited by their lack of selectivity toward the target analytes. Molecular imprinting techniques allow conducting polymers to be chemically functionalized with highly specific recognition sites within the polymer matrix, resulting in enhanced selectivity [2–4]. The integration of molecularly imprinted conducting polymers as sensitive layers in chemical sensors provides a viable route toward devices for the selective and sensitive detection of environmental pollutants.

Abbreviations: AFM, atomic force microscopy; FTIR, fourier transform infrared; HCl, hydrochloric acid; UV–Vis, ultraviolet–visible; H-NMR, proton-nuclear magnetic resonance; KBr, potassium bromide; S/cm, siemens per centimeter; SEM, scanning electron microscopy; K_D , equilibrium dissociation constant; C, free equilibrium concentration; B_{max} , apparent maximum binding capacity

* Corresponding author.

E-mail address: omunyati@unza.zm (M.O. Munyati).

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Molecularly imprinted polymers are commonly synthesized by the bulk polymerization of monomers in the presence of templates followed by crushing or grinding, sieving, and sedimentation of the obtained polymer. However, this process is tedious and time-consuming, and the resulting particles have random shapes and sizes, thus limiting their applicability. Furthermore, the interaction sites in the molecularly imprinted polymers are destroyed during grinding, thereby reducing the loading and recognition capacity. Polymerization strategies such as emulsion and precipitation polymerization are well suited for preparing particles with specific shapes and desirable characteristics [8–10]. In particular, emulsion polymerization has attracted considerable attention because it provides good control over particle size and morphology. Molecularly imprinted polymer particles with controlled sizes and functionality can be easily obtained using emulsion polymerization. Nanosized molecularly imprinted polymers offer better properties than larger particles because of their large surface areas, which result in increased sensitivity.

The typical preparation of molecularly imprinted polymers via emulsion polymerization involves a nonconductive matrix. Thus, the resulting molecularly imprinted polymers are not ideal for use as transducers. The use of conducting polymers such as polyaniline provides an opportunity to develop molecularly imprinted polymers with specific recognition behavior along with the ability to function as a transducer. Most molecularly imprinted polymer systems require the addition of a crosslinker to maintain particle integrity (i.e., to stabilize the imprinted binding sites and facilitate mechanical strength). The inclusion of nonconductive crosslinking molecules in a conducting polymer matrix is detrimental to the intrinsic electrical properties of the material. In the case of polyaniline, its polymerization under certain conditions leads to a crosslinked and rigid three-dimensional structure that ensures particle integrity. Polyaniline nanoparticles with defined shapes and sizes can be prepared by emulsion polymerization [11–13]. When carried out in the presence of a template, polyaniline can be polymerized into nanosized molecularly imprinted polymers via a scalable process without grinding.

This paper describes a novel approach for the preparation of molecularly imprinted polyaniline nanoparticles using an inverted emulsion technique with aldrin as the template molecule to be imprinted. The imprinted nanoparticles were evaluated for their optical, electrical, and morphological characteristics. The capacity of the molecularly imprinted polyaniline nanoparticles to adsorb aldrin was evaluated based on their adsorption properties using the Langmuir model and Scatchard analysis. The ability of molecularly imprinted polyaniline to selectively recognize aldrin was evaluated by comparing the adsorption characteristics of aldrin and dichlorodiphenyltrichloroethane (DDT).

2. Experimental

2.1. Reagents and chemicals

Aniline, aldrin, sodium lauryl sulfate, benzoyl peroxide, hydrochloric acid, acetone, ethanol, and chloroform were all purchased from Sigma-Aldrich. All chemicals and solvents were used as received except for aniline, which was double-distilled before use. DDT was obtained from the University of Pretoria. Milli-Q doubly distilled ultrapure water was used in all experiments.

2.2. Instrumentation

Fourier transform infrared (FTIR) spectra were recorded using KBr pellets on a PerkinElmer Spectrum RXI FTIR spectrometer. Pellet samples were formed by mixing the sample with predried KBr in a 1:5 ratio. The sample was scanned over the range of 400–4000 cm^{-1} . ^1H nuclear magnetic resonance (NMR) spectroscopy was performed using a Bruker Avance 400 MHz spectrometer. Samples were analyzed in liquid form using deuterated chloroform as the solvent. Atomic force microscopy

(AFM) experiments were performed using a Bruker Dimension Icon atomic force microscope in ScanAsyst mode using polyaniline thin films. Scanning electron microscopy (SEM) images were recorded with a Zeiss Ultra Plus scanning electron microscope. Conductivity measurements were performed using a four-point probe coupled to a source meter. Aldrin and DDT in solutions were quantitatively analyzed by gas chromatography-time of flight mass spectrometry (GC-TOFMS).

2.3. Preparation of molecularly imprinted polyaniline

2.3.1. Polymer synthesis

Polyaniline nanoparticles were prepared by inverted emulsion polymerization. To prepare imprinted polyaniline nanoparticles, 1.44 g of sodium lauryl sulfate in 50 mL of water (0.1 M) was added to 60 mL of 0.2 M benzoyl peroxide in chloroform under constant stirring at room temperature, producing a milky white emulsion. A mixture of 1 g (10.84 mmol) of aniline monomer and 8 mg (0.0219 mmol) of aldrin template in chloroform was sonicated for 10 min to dissolve all materials and then slowly added to the milky emulsion and stirred for 30 min. Subsequently, 90 mL of dopant (1.5 M HCl) was added dropwise over a period of 30 min. During the course of reaction, the colorless emulsion turned green. The reaction proceeded for 24 h under stirring. The organic phase was separated and repeatedly washed with deionized water to remove all surfactants. The viscous organic solution was then treated with excess acetone to break the emulsion and precipitate the imprinted polyaniline nanoparticles. The precipitate was filtered and washed with acetone to remove any unreacted aniline. The obtained dark-green powder was dried under vacuum at room temperature.

Soxhlet extraction was used to extract the aldrin from the polyaniline nanoparticles. The imprinted polymer was repeatedly treated with dichloromethane to remove the aldrin molecules. The extraction was allowed to proceed for 8 h, at which point the aldrin was washed off the polymer. Nonimprinted reference nanoparticles were synthesized under identical conditions without the aldrin template. The general scheme for the preparation of the molecularly imprinted polyaniline nanoparticles is shown in Fig. 1.

2.3.2. Preparation of thin films

The prepared molecularly imprinted polyaniline nanoparticles were deposited on glass substrates. Before deposition, the glass substrates were washed with acetone, methanol, and distilled water and then dried in an oven at 60 °C. Polyaniline deposition was conducted by dip-coating as follows. A precleaned glass substrate was dipped for 5 min into a dispersion of molecularly imprinted polyaniline or nonimprinted polyaniline nanoparticles in chloroform. The slide was then withdrawn from the solution slowly so that the fluid had time to flow back down into the vessel. The glass substrate was then allowed to rest horizontally for 10 min until the solvent evaporated, leaving behind a thin film.

2.3.3. Rebinding experiments

The binding capacity of the nanoparticles was determined by adding 40 mg of molecularly imprinted polyaniline to five test tubes containing 1 mL of aldrin at concentrations ranging from 1 to 5 ng/ μL in hexane at room temperature for 20 h with shaking. The molecularly imprinted polyaniline particles were then allowed to settle for 30 min. The concentration of free aldrin in the solution was assayed by GC-TOFMS. The amount of analyte bound to molecularly imprinted polyaniline was calculated by subtracting the amount of free analyte from the initial concentration. The selectivity of the nanoparticles was investigated by comparing the adsorptions of aldrin and DDT on molecularly imprinted polyaniline.

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