Research Article

Investigation of the Polyaniline Nanoparticles as the Substrate of Molecular Imprinted Polymer

Mina Mobram

Department of chemistry, college of science, Saveh Branch,
Islamic Azad University, Saveh, Iran
*Corresponding author: Email: minamobram@yahoo.com
Tel: +989351206077

ABSTRACT:

The current research work deals with investigation of the polyaniline nanoparticles as the substrate of the molecular imprinted polymer. Molecular imprinting is an interesting way to emulate the natural molecular identification that will be realized by preparing artificial identification sites with preset election for different target analyses. In this method, the target analyte acts as a template and will be connected to functional monomers through covalent or non-covalent bonding during the process of polymerization. Among all the conducting polymers, polyaniline is known for its unique electrical conductivity which can be controlled by the degree of oxidation of the main chain and protonation. Also, it shows different color changes with respect to the degree of oxidation and the surrounding ph. The results and investigations conducted in this study suggest that molecular imprinted polymers can be successfully developed by using aniline as monomer and preparation of linear polymer, and by using method of conductometry, the presence or absence of imprinted substances can be observed in the polymer according to the changes in conductivity caused by these phenomena.

Keywords: Polyaniline, nanoparticles , Molecular Imprinting Polymer (MIP), Conductive polymers.

[I] INTRODUCTION

Conductive polymers are a class of electronic materials that have been used extensively due to having a combination of electrical and optical properties of metals or semiconductors and mechanical properties of polymers. So that with studying, understanding and applying their chemical and dynamical properties, a connection line will be obtained into the molecular and bio-molecular world which will be a basis for the development of dependent intelligent systems through the development of communication within the system. Products made of polymers are conductive and show high resistance to the flow of electric current. The fusion of polymer with electric conductive materials is among the methods of building conductive polymers. If an electron be removed (oxidation) or be added to a polymer chain with π links, which the valence layers of its molecules is completed, in that case, the electrical conductivity properties can be created by making suitable arrangement, similar to the metals.

In the late 1970s, a new class of polymers were discovered that were able to conduct electricity [1]. The conductivity is due to the structural form of the polymer that allows electrons to be transferred along the polymer chain, in case of being in the specific oxidation state. These polymers can be stimulated by electrons and they can take on many different forms by applying a little energy [2]. Polyaniline is known from nearly a hundred years ago. But for the first time,

MacDiarmid et al. in 1985 discovered that polyaniline has the electrical conductivity property. In addition to the electrical conductivity properties, polyaniline shows a good stability against environmental factors such as oxygen and water. Also, Polyaniline has a thermal stability, so that polyaniline is stable up to 420 ° C in the base form [3].This polymer is a special conductive polymer in comparison with other polymers such as polypyrrole and poly-thiophene, because the electron capture mode can be controlled under acid/base reactions. This characteristic of Polyaniline, along with reversible oxidation-reduction reactions, simple and cheap synthesis methods, conductivity, the resistance and stability in the environment in recent decades has led to allocate further investigations and to be used in various fields. The connection of Polyaniline as a polymer substrate to the target molecule as the analytic and also, the extraction of analytic from the molecular imprinted polymer is a method that can be directly used in the preparation of gas sensors and solutions. Electrically conductive polymers are known as very suitable candidates for MIP systems. A combination will be achieved from creating a composite which includes molecular imprinted polymers and conductive polymers; this combination should also have molecular selectivity properties and conductivity with high sensitivity. These kinds of materials have a special attraction in the field of sensor technology [4].

Molecular imprinted polymers are synthetic polymers with certain surface cavities made by the template molecules. Molecular imprinting is a very suitable technique for preparing polymeric materials with recognition sites which has a high affinity for the target molecule due to the shape and arrangement of functional groups. This technique is a modern technique in which the created cavities and positions during polymerization, in the later stage, can act as receptors similar to antibodies against specific chemical species. Molecular imprinted polymers are called antibody mimic, because of the

similarity in the performance of antibodies and molecular imprinted polymers. These kinds of compounds contain extraordinary chemical and mechanical resistance, because of the nature of these cross-linking bonds in these types of polymers, so that, they can be used in dangerous chemical environments, such as acidic and alkaline environment or in the presence of organic solvents. There is an obvious capability that molecular imprinted polymer can be synthesized for different chemical and biological species with different structures of metal captions to very complex compounds such as proteins and Bio-organisms. These polymers are available in various metal forms of polymer thin films to particles with Nano scale dimension.

The main approach to prepare molecular imprinted polymer is the use of a primary array which includes the template molecule complex and polymerizable monomers. Then the target molecule will come out from the polymer cavities through various methods. As the target molecule comes out, what remains is a set of cavities the size of the target molecule and with the arrangement of functional groups in a particular condition in the space. The arrangement of functional groups is in such a way that allows the target molecule to enter the cavity for the second time and interact with the functional groups. This property creates a specific mode that actually the target molecule can be identified by the internal cavity of the polymer, not only via the size but also through the type of the functional groups on the target molecule and their arrangement in the space. Up to now, three types of molecular imprinting has been reported which include covalent, non-covalent and hybrid or semi-covalent approach. In the covalent approach, a single molecule covalently connects to the molecule with polymerization abilities. Bond of this type of polymer, based on covalent bonds, is reversible. After copolymerization behavior of the bonding agent, the template molecule, chemically, detaches from the cross linked polymer [5]. Non-covalent technique is much more common than

covalent techniques, because of its simple production, template's fast reconnection and more diversity in monomers with polymerization ability [6]. The template molecule interacts with a polymer through non-covalent interactions such as ionic, hydrophobic (water- repellent) and hydrogen bonding during both phases of imprinting and reconnection [7]. The best way is to combine these two methods.

[II] MATERIALS AND METHODS
2.1. Instrumentals
Fourier Transform Infrared spectra (FT-IR) of the samples in KBr pellets were recorded on an (Perklin-Elmer RX1) spectrometer. Scanning electron microscopy (SEM) was performed by a (Hitachi, S-4610) at an operating voltage of 10KV. Prior to scanning, the specimens were coated with a very thin layer of gold. To measure the conductivity a four-point conductivity meter by (WTW, Inolab Cond 7110) was used.

2.2. The preparation of linear polyaniline polymer with Iprodion + Carbendazim
In a beaker, 1 gram Iprodion+Carbendazim was dissolved in 20 ml of distilled water and then, 5.0 ml aniline was added to it and placed in an ice-water bath and then it was placed on the magnetic heater. A primer solution containing 1.19 gram of dissolved ammonium per sulfate in 10 ml of distilled water was prepared in a beaker and was added drop by drop to the contents of the first beaker within 10 minutes. Polymerization was continued for 2 hours. Then, the solution became smooth by using a Buchner funnel and was dried in an oven at 70 °C and then, their conductivity was measured.

2.3. The preparation of non- imprinted polymer (NIP) for Iprodion+Carbendazim
Some of the linear polymer from previous step was poured in a beaker and 5 ml of chloroform was added to it.
The beaker was covered with a Para-film and was remained in that condition for 2 hours in order to form template on the polymers. Then, the solution became smooth with a Buchner funnel. At first, it was washed with a small amount of chloroform and then with distilled water and was dried in an oven at 70 °C and then, the conductivity was measured.

2.4. The preparation of molecular imprinted polymer (MIP) based on Polyaniline for Iprodion+Carbendazim
Firstly, eight standard solutions of 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07 and 0.08 mol/l were made from the poison of Iprodion+Carbendazim, in 25 ml of chloroform solvent. Then, 0.1 gram was added to each separated solution of non-imprinted polymer of Iprodion+Carbendazim. Dishes were covered by Para-film and were placed in a fixed location for a period of 4 hours. After this term, solutions became smooth with Buchner funnel and dried in an oven at 70 °C and their conductivity was measured.

2.5. Checking the sensor's response time
At first, from the poison of Iprodion+Carbendazim, a 0.01 mol/l standard solution was prepared in 25 ml of chloroform solvent. Then 5 beakers were taken and each of them was filled with 0.1 gram of non-imprinted polymer of Iprodion+Carbendazim. 3 ml of the prepared standard solution was added to each beaker. Beakers became smooth with a Buchner funnel after 15, 30, 45, 60 and 75 minutes respectively. Then all of the polymers were dried in an oven at 70°C and their conductivity was measured.

2.6. Evaluation of the selectivity of the sensor
First of all, a 0.01 mol/l in 25 ml of chloroform solvent was prepared from three poisons of the Benzimidazole family that includes Thiophanate-methyl, Carbendazim and Iprodion+Carbendazim in order to evaluate the selectivity of the sensor. Then, 0.1 gram non-imprinted polymer of Iprodion+Carbendazim was poured in a beaker and 3 ml of the mixture of three poisons was added to it and placed in a fixed position for 1 hour at room temperature. Then, the solution became smooth with Buchner funnel and was dried in an oven at 70 °C and its conductivity was measured.

[III] RESULTS

3.1. Conditions of polymerization in providing the molecular form of polymer

4 hours was considered in order to integrate the process of polymerization for preparing molecular form of polymer. Since the used polymer in this work is aniline which changes into polyaniline during the reaction, therefore the long polymerization time for synthesis is not proper. Reaction efficiency from 1 to 24 hours is the same. However, the reduced viscosity will be appeared after 4 hours. Thus, the polymerization would be completed after 4 hours and long time leads to the slow basification of polyaniline. In assessing the role of temperature also, it has proven that polymer viscosity would be increased by decreasing the temperature to -5C. Used starter in this work is ammonium per sulfate and is in rate of mole to mole with monomer.

3.2. Molecular imprinted polymer sensitive to Iprodion+Carbendazim based on polyaniline

The amount of polymer's conductivity before and after extraction of analytic is as follows:

Polymer conductivity before extraction = 8.6×10^{-3} ms/cm

Polymer conductivity after extraction = 2.4×10^{-5} ms/cm

It can be seen that the conductivity, before being washed with chloroform, is much more than the amount of conductivity after the washing process and this is due to the removal of some Iprodion+Carbendazim molecules from the surface of the polymer, in other words, the leaching of molecules that have been absorbed is the reason of this increase.

3.3. The sensor's response time

The amounts of conductivity and their changes have been reported in diagram 1 against the sensor's response time for the concentration 0.01 mol/l of Iprodion+Carbendazim at room temperature. It is seen that with the increase in time, the penetration rate of analytic into the polymer cavity will increase. The maximum amount of conductivity is in 75 minutes. Increasing the polymer conductivity and its long response time proves the existence of cavities in the polymer.
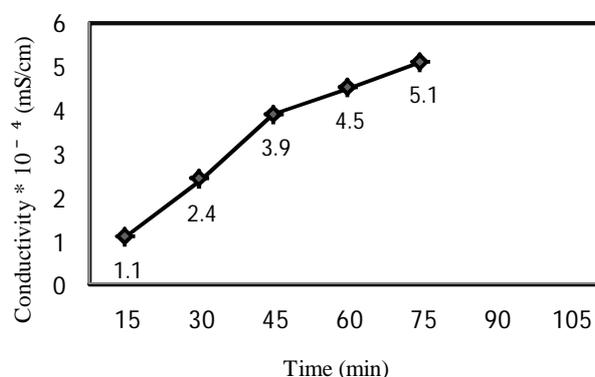

Diagram 1: Conductivity changes based on time increasing for Iprodion+Carbendazim toxin

3.4. The impact of analyte concentration

The obtained conductivity values in investigating the impact of analytic concentration and their relationship related to molecular imprinted polymer of Iprodion+Carbendazim has been reported in diagram 2. At this point, varying concentrations of analyte reacted with the polymer at room temperature for 4 hours. It can be seen that analytic concentration is directly related to the conductivity, this means that with increasing concentration, conductivity will also increase.
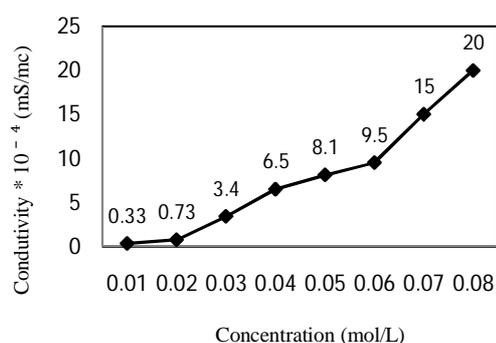

Diagram 2: Conductivity changes based on density increase in Iprodion+Carbendazim

[IV] DISCUSSION

4.1. Investigating the selectivity of the sensor Iprodion+Carbendazim

The polymer's ability in detecting analyses from invasive species, which are structurally similar to

analytic (selectivity), is very important for sensor applications. The conductivity of the molecular imprinted polymer of Iprodion+Carbendazim against Carbendazim and Thiophanate-methyl, which is structurally similar to Iprodion+Carbendazim molecule, was 2.3×10^{-5} mS/cm. This conductivity is close to the conductivity of the obtained molecular imprinted polymer after the extraction of analytic, and this result shows the sensitivity and selectivity of the MIP Iprodion+Carbendazim towards this poison.

4.2. The study and comparison of the microscopic properties of molecular imprinted polymers

The image of scanning electron microscope (SEM) for the non-imprinted polymer (NIP) related to the Iprodion+Carbendazim is illustrated in figure 1. The image shows a porous surface which is due to the absence of analytic in the polymer. The diameter of emerged cavities is about 200 nm.
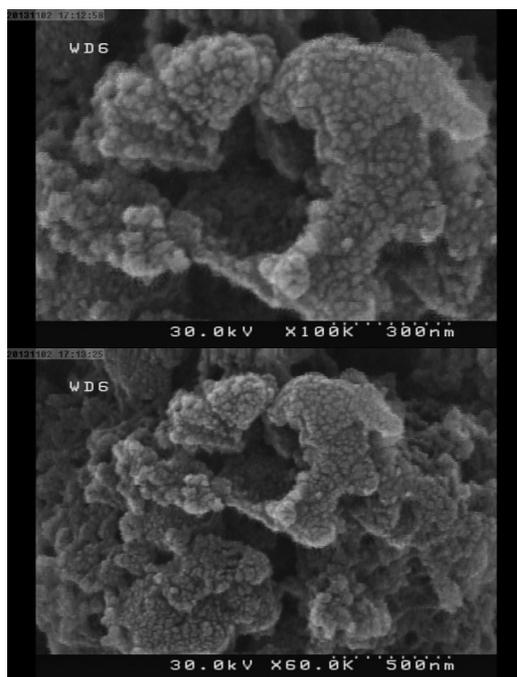

Figure 1: Scanning electron microscopic (SEM) image for non-imprinted polymer (NIP) of Iprodion +Carbendazim toxin

Figure 2 shows the images of scanning electron microscope (SEM) for the molecular imprinted polymer related to Iprodion+Carbendazim after reconnecting analytic in 0.02 mol/l concentrations. The surface of polymer with almost no pores, in comparing with non- imprinted polymer, shows the presence of analytic. The number of pores is less than NIP, which is due to the presence of molecules that are trapped in the inner cavities.
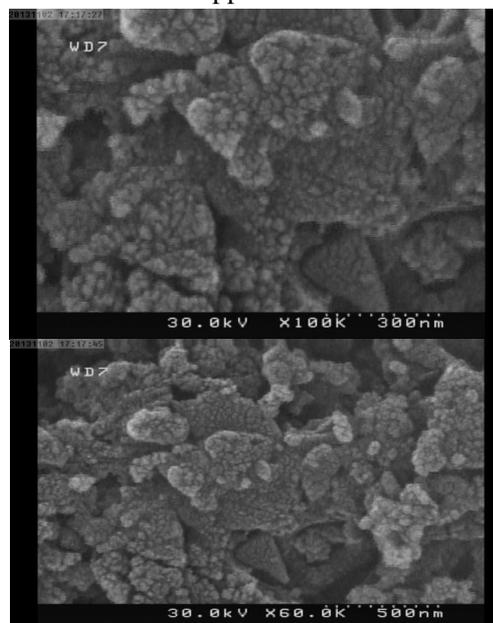

Figure 2: Scanning electron microscopic (SEM) image for imprinted polymer (MIP) of Iprodion+Carbendazim toxin

4.3. Spectroscopy

Spectroscopy has many applications in determining the purity and also assessing the structural features and identifying quantification and qualification of compounds.

Strong stretching absorptions of C=O and C-O are two manifest characteristics in the spectrum of an ester which appear in ranges of 1 and 2, respectively. Usually, C-O stretching, adjacent to the ester carbonyl group, is one of the strongest and most broad bonds in the spectrum. The emergence of a C=C bond, adjacent to the carbonyl group, resulted in the decentralization of π electrons in the bonds of C=O and C=C. This effect increases the simple character of the C = O bond and will decrease its Constant force; as a result, the carbonyl absorption frequency will be reduced. Stretching absorptions of C = C bond will emerge in aromatic rings in pairs (at 3 and 4). The tensile C─N bond in amines will appear at

district 5. The tensile N─H bond in secondary aromatic amines has a strong band in the region 6, and its flexural absorption at the secondary amine, will absorb near region 7.

4.4. Study the FT-IR spectrum of Iprodion+Carbendazim

Figures 3 and 4 show spectrums of the molecular imprinted polymer related to Iprodion+Carbendazim, which the peaks of its index include: 127 cm^{-1} (stretching vibration of amine C-N) , 1788 cm^{-1} (C=O bond), 3180 cm^{-1} (C-H bond), 3210 cm^{-1} (flexural bond of N-H) , 1620 and 1478 cm^{-1} (aromatic C=C) , 667 cm^{-1} (stretching vibration of C-Cl).
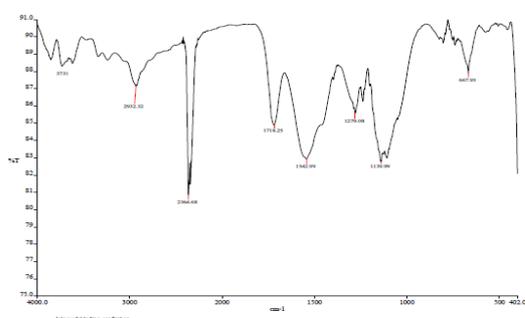

Figure 3: FT-IR spectrum related to the linear polyaniline polymer with Iprodion+Carbendazim
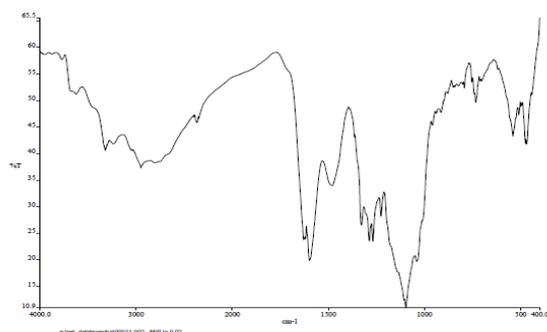

Figure 4: FT-IR spectrum related to MIP polymer of Iprodion+Carbendazim

[V] CONCLUSION

The results and conducted surveys suggest that molecular imprinted polymer (MIP) can be prepared successfully by the use of Aniline nanoparticles as monomer and preparation of linear polymer, and the presence or absence of imprinted materials in polymer can be observed by using conduct metric method, according to the changes caused by these phenomena. Affective parameters on conductivity degree and sensing principles were assessed with the order of time of reaction, density and selectivity of sensor, in order to evaluate the sensing properties of molecular form polymers and compare it with the observant polymers.

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