

Preparation the Sensor of Imprinting Molecular Polymer Based on Polyaniline to Recognize Agricultural Toxin Chlorpyrifos and Diazinon

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Abstract: Polyaniline as an intelligent organic polymer has been noticed since many years ago. Recently there have been some efforts on its applications such as ion selective membranes, batteries, conducting dyes, chemical and gas sensors and etc. Using of conducting polymers as sensors has opened a new field in their applications and it is at the initial steps. On the other hand detection of organophosphorus compounds due to their wide applications in insecticides and pesticides, chemical warfare agents are great importance. Regarding this, in present research sensing behavior of molecular imprinting polymer powder base on polyaniline in compare with organophosphorus agronomy pesticides as like as a sample via measurements and FTIR conductance by using a four-point probe method. Among sensing properties studied in this work can mention to analyte concentration, temperature, polymer response time. Molecular imprinting polymer selectivity examined in compare with structure of molecules similar to analyte. In all of the cases conductivity of molecular imprinting polymer remarkable in comparing to molecular non-imprinting polymer because of analyte effect on polymer structure. Preparation process of molecular imprinting polymer and sensing properties did with this method for like compounds namely of diazinon, chlorpyrifos at the results show that molecular imprinted surface in combination with conductometric method is a useful approach for the sensing applications.

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1. Introduction

About 60 years past from the emergence of chemical sensors, devices which have different names but all are recognized by general name as "sensor" have been classified at different groups including physical and chemical sensors. After 60 years, chemical sensors enjoyed large development in human life, industry and modern technology as well [1].

The sensors based on electrical conductivity are considered as one of those sensors. Lack of selectivity is among deficiencies of these sensors. This feature has limited the application of these sensors in different industries [2]. The proposed method in this research work is to increase the selectivity of sensor based on the electrical conductivity by molecular molding in order to produce Polymer. In recent years, conductive polymers carried out applications in this field, and in this case, polyaniline has potential capabilities [3].

Those vapors and compounds which are able to oxidize and reduce conjugated chains of polyaniline should be naturally able to impact on electrical properties of polymer. Therefore, those compounds which are subject to a kind of electron deficiency and positive charge, both can impact on electrical and conductive properties of polyaniline by separating electron from full electron chains and producing positive charge centers in these chains and

compounds which are able to inject electron and producing negative charge centers on these chains [4]. With a closer look at the structure of organic phosphorous compounds and nature of bonds between P=O and/or P=S, it is noticeable that phosphorus atom in this bond has little positive charge due to bond between $d\pi-p\pi$ and $2p$ orbitals of oxygen's atom and/or sulfur and according to electronegativity of atoms participating in bond, and also little positive charge on the phosphorus atom in bond of P=O is more rather than P=S due to the higher electro negativity of oxygen's atom rather than sulfur. Consequently, it is expected that compounds with this bond, impact polyaniline through oxidation mechanism and/or p-doping [5]. According to little extent of positive charge of phosphorus atom it is expected that this impact to be higher for the organic phosphorous compounds with P=O bond rather than compounds with P=S. Also it is expected that by substituting group which are able to participate at π bond, this impact would be reduced and by substituting electron-killer groups, this impact would be increased [6]. At this part of research work, changes of polymer conductivity being exposed to agriculture toxins (pesticides), (in the role of sample) would be analyzed by electrical conductivity device with four-point method and results would be reported completely at conduct curves in terms of time, temperature and density.

It is notable that all used toxins were analyzed, in lower density level than human's toxic [7].

2. Experimentals

2.1. Instrumentals: Fourier Transform Infrared spectra (FT-IR) of the samples in KBr pellets were recorded on an (Perkin-Elmer) spectrometer. Scanning electron microscopy (SEM) was performed by a (Hitachi, S-4160) at an operating voltage of 10KV. Prior to scanning, the specimens were coated with a very thin layer of gold.

2.2. Preparation of polyaniline

In order to produce polyaniline chemically, protonic acid solution is used. Therefore, solutions (300 ml distilled aniline and Pro-sulfate Ammonium -APS- are prepared with the same molar ratios in 1 molar acid hydrochloric) in two separate containers. Then the temperature should be decreased to -5 to -10 C by putting in container which contains ice and sodium chloride, and then while monomer container is in mixing, Ammonium persulfate should be added to 1 molar acid hydrochloric. After few moments, polymerization would be started and temperature of container would be increased to some extent. Gradually, the transparent monomer solution will be darkened that would indicate the formation of polyaniline. Solution would be stirred strongly for an hour at 5 C and four hours at room temperature. Molecular mass at lower temperature would be increased and consequently, conductivity of polyaniline would be increased. After that, contents which contain green sediment of polyaniline would be smoothed by Buchner funnel. The sediment would be washed by distilled water to the point that it would be colorless under filter with methanol. Soluble part in methanol which contains oligomers of polyaniline would be separated from polymer due to washing with methanol. The sediment would be washed again with distilled water in order to remove the remained methanol in polymer (solution under filter is green at this level). In the next step, polymer would be dried at 50-60 C.

2.3. Supplying the molecular form of polymers

Providing the molecular form of polymers based on polyanilinesensitive to diazinon.

In order to make polyanilinesensitive to diazinon, it is necessary to do polymerization of polyaniline in the presence of diazinon toxin and/or being immersed in desired PANi Toxin. Given the fact that there is possibility of toxin degradation in acidic solution, as a result, the second method should be used.

In order to prepare molecular form of polymer which is sensitive to diazinon, at first, 0.5g PANi in alkaline solution of ammonia 25% should be stirred for 24 hours and then it will be smooth and completely dry. Afterwards, doped polymer is solved in 25 ml N-methyl pyrrolidone (NMP) and 2g diazinon would be added to it.

After that, when it was stirred for 8 hours, accordingly the uniform film would be prepared gradually by gradual temperature.

That film would be dried on the desiccator under vacuum condition for 24 hours. The resulting polymer powder can be prepared as primary powder then it can be dried to be prepared for rest of the work.

2.4. Supplying the molecular form of polymer based on polyanilinesensitive to chlorpyrifos

In order to prepare polyaniline which is sensitive to chlorpyrifos, it is necessary to do polymerization in the presence of chlorpyrifos toxin and/or being immersed in desired PANi Toxin. Given that there is possibility of toxin degradation in acidic solution, therefore the second method should be used. Then the doped polymer should be solved in 25 ml N-methyl pyrrolidone (NMP) and 2g chlorpyrifos would be added to it. After being stirred for 8 hours, as a result the uniform film would be prepared gradually by gradual temperature. That film would be dried on the desiccators under vacuum condition for 24 hours. The resulting polymer powder can be prepared as primary powder then it can be dried to be prepared for rest of the work.

2.5. Extracting Diazinon from Molded Polymer

In order to merge sensing operation one should be able to separate sample (toxin) from the created hole in polymer. Chloroform solvent was used in this case. Thus the prepared molecular form of polymer was grinded in porcelain mortar after being completely dried. Comminuted polymers were washed with chloroform solvent for 5 minutes. Then they were smoothed and dried. When the polymer was dried, its conductivity was increased due to the exit of samples which have been absorbed.

2.6. Extracting Chlorpyrifos from Molded Polymer

In order to merge sensing operation one should be able to separate sample (toxin) from the created hole in polymer. Chloroform solvent was used in this case. Thus the prepared molecular form of polymer was grinded in porcelain mortar after being completely dried. Comminuted polymers were washed with chloroform solvent for 5 minutes. Then they were smoothed and dried. When the polymer was dried, its conductivity was increased due to the exit of samples which have been absorbed.

3. Results and Discussion

Assessing the sensing properties of molecular form of polymer based on polyaniline for diazinon. Affective parameters on conductivity degree and sensing principles were assessed with the order of time of reaction, density, temperature, 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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3.1. Assessing the time of reaction in sensor

One standard solution of diazinon and acetone (50 ppm) was prepared to assess the reaction time of this sensor. 0.05g polymer powder was washed with chloroform in 2.5ml from 50ppm and the density of diazinon was estimated at different times (15, 30, 45, 60, 75 min) and after being dried completely, its conductivity was measured by four point device.

3.2. Assessing the effect of temperature

0.05g polymer from polymeric powder was put in 2.5ml of 50ppm standard solution for an hour with different temperatures in order to assess the effects of temperature on penetration rate of sample to holes and create doping in polymer. After being dried, the conductivity was measured.

3.3. Assessing the extent of sensor selectivity

In order to assess the extent of selectivity of this sensor, 0.05g of polymeric powder in 2.5ml of one standard solution from the same molecule with chlorpyrifos molecule was assessed for an hour, and then the conductivity was measured after being dried.

3.4. Assessing the durability time of conduction

In order to assess the durability time of conduction, conduction of molecular form of polymer and conduction of observant polymer were measured after one week, one month and three months respectively and compared with each other.

3.5. Assessing the molecular form of polymer: 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 monomer 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 massification of poly aniline.

In assessing the role of temperature also, it has proven that polymer viscosity would be increased by decreasing the temperature to -5°C.

Used starter in this work is ammonium persulfate and is in rate of mole to mole with monomer. Starters such as $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{Cr}_2\text{O}_7$ in aniline polymerization, would cause high polymerization efficiency, conductivity and viscosity but by using FeCl_3 and KIO_3 resulting polymers would have high efficiency and in contrast have very low viscosity. Polymerization in the presence of KClO_3 and KBrO_3 leads to polymers with low efficiency and viscosity.

3.6. Extracting the analyte sample from the molecular form of polymer

One of main steps in molecular form of polymers is the step of extracting sample from molded polymer, thus it is necessary to break non-covalent bonds between doping factor and polymer, and then doping factor should be removed from the current holes in polymer. Also, the used solvent in this step should not damage the form of polymer and/or cause it to be solved; therefore the chloroform solvent was proper.

Results proved that the best time for extracting the sample is 5 minutes because more time leads to damaging the whole structure of polymer.

3.7. Molecular form of polymer sensitive to diazinon based on poly aniline

The extents of conductivity of polymer before and after extracting the analyte sample are as following:

Conductivity before extraction = 0.36 mS/cm

Conductivity after extraction = 0.08 mS/cm

The conductivity before washing with chloroform is more than after washing for the reason which was described before.

3.8. Molecular form of polymer sensitive to chlorpyrifos based on poly aniline

The extents of conductivity of polymer before and after extracting the analyte sample are as following:

Conductivity before extraction = 0.78 mS/cm

Conductivity after extraction = 0.096 mS/cm

As it is noticeable, the conductivity before washing is much more and the reason is that some chlorpyrifos molecules exited from the surface of polymer due to absorbed molecules which have been washed.

3.9. Assessing the sensing properties of diazinon molecular form of polymer

The Sensing properties of polymer would be assessed after extracting the analyte sample when it was exposed to sample again.

3.10. Reaction time of sensor

Figure 1 has reported the conductivity changes against the reaction time of sensor for the density of diazinon 50ppm in ambient temperature. It can be observed that as time increased, penetration rate of sample has been increased within the empty hollows of polymer. The most increase would reach at the time of 60 minutes. After that time, it has been decreased due to the filling active sites of polymer. Increasing conductivity and long reaction time would prove the presence of hollowness in polymer.

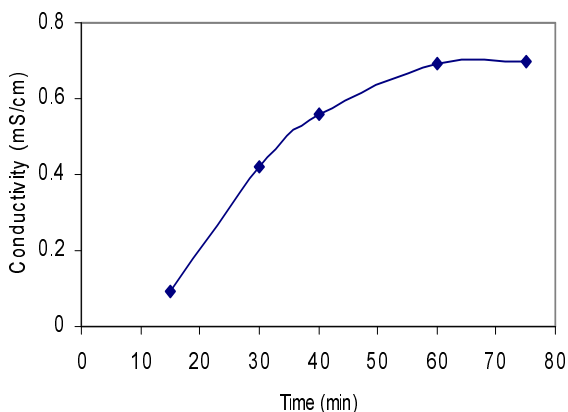


Figure 1 : Conductivity changes based on time increasing for diazinon toxin

3.11. Effect of sample density

The Relation between sample density and conductivity change in MIP of diazinon has been reported in figure 2. In this step, different densities of sample reacted with polymer for an hour at ambient temperature. It has been observed that the sample density has positive relation with conductivity which means that by increasing the density, conductivity will be increased too, where sample absorption has been stopped and polymer conductivity remains fixed due to satiating of active sites in polymer.

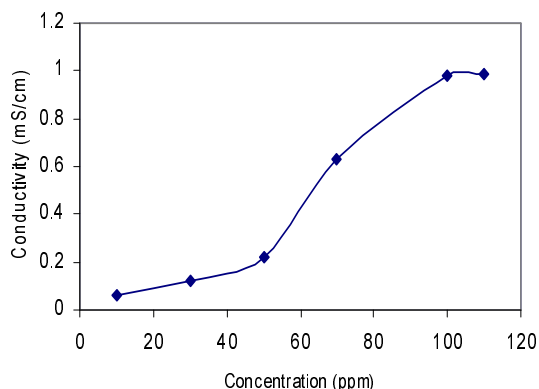


Figure 2 : Conductivity changes based on the density increase in diazinon

3.12. Effects of doping temperature

Figure 3 shows the curve of temperature changes of diazinon molecule penetration than 50ppm density for an hour against conductivity .

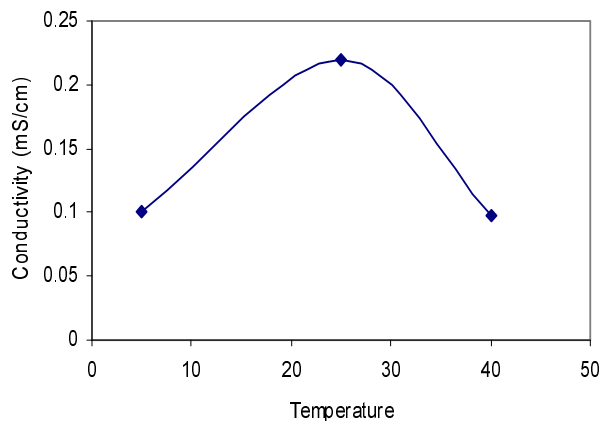


Figure 3: Conductivity changes based on temperature increasing for diazinon toxin

3.13. Assessing the selectivity of diazinon sensor

The ability of polymer to distinguish between sample and nuisance species which have the same structure with sample enjoys lots of importance for sensing applications. Extent of conductivity of diazinon polymer against the same molecule with diazinon equals to 0.055mS/cm. This result shows the sensitivity and selectivity of diazinon MIP .

3.14. Assessing durability time of conduction

Figure 4 shows the conductive durability of MIP after washing with chloroform and being exposed to 50 ppm diazinon density at weeks 1, 2, 3 , 4 and 5 . First, it has been observed that conductivity is fixed and then decreased finally being fixed again. This little decrease shows the destruction of those samples which have been absorbed, and fixed conductivity represents the consistency in MIP method and conductivity consistency .

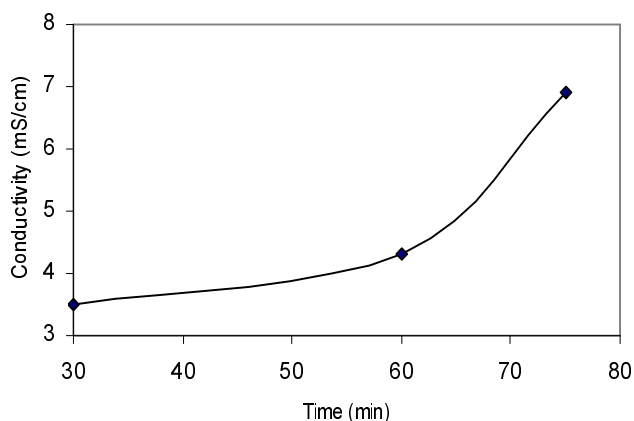


Figure 4: Conductivity changes of MIP after exposed to 50 ppm diazinon

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

After several years, many studies have been done on the factorial groups of phosphate esters, amidthioates phosphor, amidates phosphor, amidthioates and relative compounds, then the absorbing frequencies ranges of factorial groups such as (P=O), (P=S), (P-N-C), (P-X) have been represented. Starting point of these studies has been on the phosphoric toxins by IR spectroscopy in 1950's. In the following section, some of absorbing frequencies of factorial groups would be described in the phosphoric compounds.

3.15. FT-IR spectrum investigation

The band relates to stretching vibrations of P=O group is strong and appears on 1150-1400 cm^{-1} region. This band sometimes might appear as twin band which this issue is related to rotational isomers. Electronegative groups compete with oxygen atom for absorbing electron from phosphor atom and cause that absorbing frequencies to move to higher regions by structuring p^+-o^- and creating the stronger bond. Assymmetric Stretching vibrations of P-O-C in aliphatic compounds cause very strong wide bands that have been appeared at 950-1070 cm^{-1} scope. P-N-C group gives one intermediate to strong band in 930-1110 cm^{-1} region that it might be due to the asymmetric stretch of P-N-C group. This group also shows one intermediate to strong band in 680-750 cm^{-1} region that is due to the symmetric stretch.

Peak of stretching vibrations of P=S bond places at 655-865 cm^{-1} region that is intermediate peak with high intensity. With this condition, the relative peak to factorial group of P-S in places at region would be around 550-730 cm^{-1} . P-Cl bond, gives one intermediate to strong band at 435-610 cm^{-1} region and its location depends on the connected atoms to phosphor. Absorbing band which appeared at

1675 cm^{-1} region relates to the stretching the frequency of C=O group. It should be noted that C=O bands appear on amidate esters at 1690 cm^{-1} but in synthetic compounds, resonance between free electron pair on the nitrogen and its connected carbonyl group would cause reduction in stretching the frequency.

Figure 5 shows FT-IR spectrum of polyaniline and its significant peaks are: 3420 cm^{-1} (stretching vibration of Amine NH), 1400 cm^{-1} (vibration of CH₂ group), 1227 cm^{-1} (stretching vibration of CN), 3000 cm^{-1} (stretching vibration of aromatic C-H), 1596 and 1492 cm^{-1} (aromatic ring).

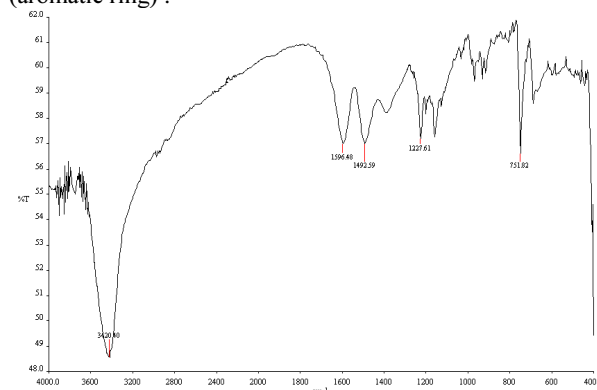


Figure 5: FT-IR spectrum related to polyaniline

Figure 6 shows FT-IR spectrum of observant polymer that its significant peaks are: 3400 cm^{-1} (stretching the vibration of amine NH and stretching vibration of OH that overlapped), 1590 cm^{-1} (scissor-like vibration of NH group), 1450 cm^{-1} (stretching vibration of C=C), 3100 cm^{-1} (stretching vibration of aromatic C-H), 2950 cm^{-1} (stretching vibration of aliphatic C-H).

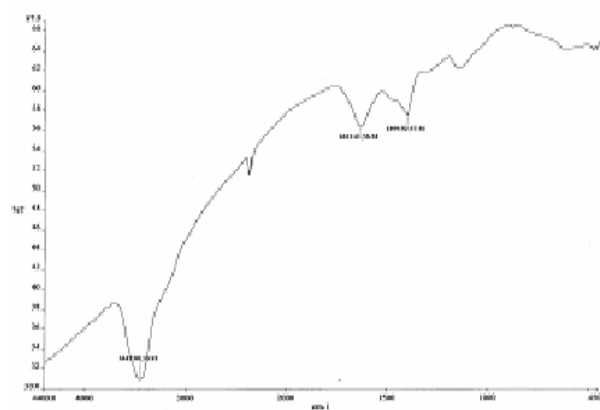


Figure 6: FT-IR spectrum related to control polymer
Infrared spectrum of molecular form of polymer (MIP) is shown before and after the exiting diazinon molecule by washing with chloroform solvent and after reconnecting (50ppm density) in Figure 7. In addition to significant groups in NIP, groups related to sample consist of: 1300

cm^{-1} (stretching vibration of P=O), 830 cm^{-1} (flexural vibration of P-O-C), 500 cm^{-1} (flexural vibration of P=S), 2931 cm^{-1} (stretching vibration of aliphatic C-H), 3290 cm^{-1} (stretching vibration of N-H), 1600 cm^{-1} (stretching vibration of C=O) have been observed which show the presence of sample in polymer. Now in reference to figure B, (MIP after washing) these groups have been observed milder which shows lower sample due to the surface washing. Also in Figure C, after reconnecting, the expected significant groups have been observed.

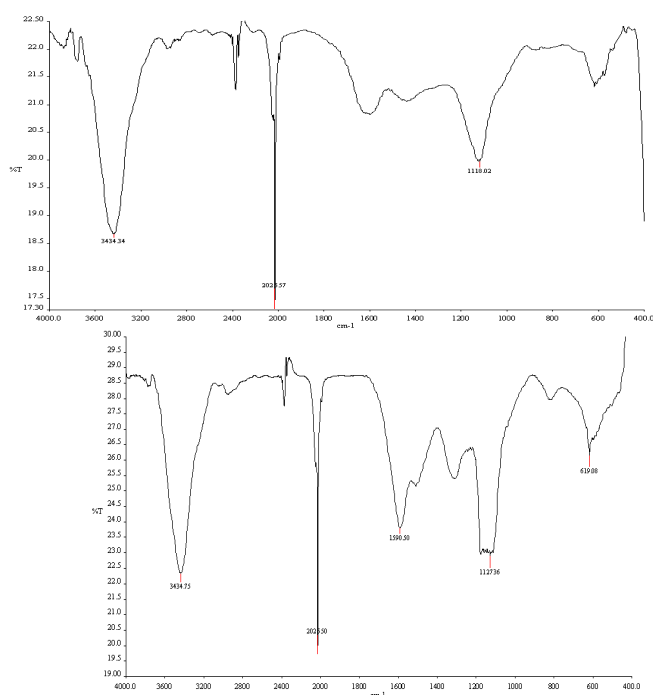


Figure 7 : FT-IR spectrums related to polymers of diazinon toxins

3.16. Studying scanning electron microscopic

Here there is scanning electron microscopic image for the observant polymer in Figure 8. The image shows the smooth surface without pores compared with MIP which is due to lack of sample in polymer.

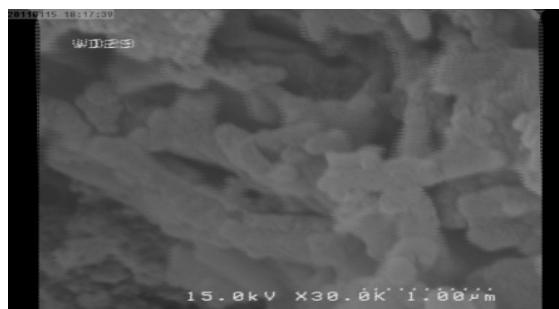


Figure 8: Scanning electron microscopic image for observant polymer

4. Conclusion

We have synthesis polyaniline as molecular imprinting polymer for sensing organophosphorus agronomy pesticides. This polymer is good candidate to sensor material for toxic agents. The sensing behavior of molecular imprinting polymer was measured for molecular imprinting polymer (MIP) and non-imprinting polymer (NIP) by FTIR and using a four-point probe method. Among sensing properties studied in this work can mention to analyte concentration, temperature, polymer response time. Sensing results for diazinon and chlorpyrifos showed that molecular imprinted surface in combination with conductometric method and IR are a useful approach for the sensing applications.

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