

INVESTIGATION OF POLY AROMATIC HYDROCARBONS ADSORPTION USING CHITOSAN AND ITS SYNTHETIC DERIVATIVES

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ABSTRACT

Polyaromatic hydrocarbons such as pollutants that are present in water, these compounds are resulting from various human activities such as incomplete combustion or oil extraction and production and synthesise of chemical substances. These compounds enter to the water in diverse ways, it should be noted that these substances are harmful to human health and cause various disease. In this study, from chitosan that has been synthesized from shrimp shells and synthetic derivatives of chitosan, such as Nano chitosan and synthesized membranes with chitosan by glutaraldehyde and also synthesized Nano chitosan membrane with glutaraldehyde as absorbing PAHs from contaminated water has been used. and results by the device of uv-visible (ultraviolet spectroscopy) has been analyzed and results that have the best performance by two-absorbing Nano chitosan and Nano chitosan membrane was obtained that these results are in this way, the Nano chitosan could be absorb 100% percent and Nano chitosan membrane could be absorb 1.96% of PAHs present in the sample. By testing BET with two above absorbent to find reason of superiority of Nano chitosan than Nano chitosan membrane we conclude that Nano chitosan with specific absorbency level that is about three times of special absorption level of Nano chitosan membrane could be have more ability to absorb than Nano chitosan membrane.

KEYWORDS: chitosan, Nano chitosan, chitosan membrane, Nano chitosan membrane, poly-aromatic hydrocarbons, ultraviolet spectroscopy

INTRODUCTION

Water is a vital matter for the whole of nature and living, and has special ability in self-purification, in this way that settles the pollutants substances or these materials decompose into the water or somewhat lower concentration of these materials that are not harmful to the environment. Sources of water pollution are divided into 6 categories: 1. biodegradable pollutants that come from human and animal wastes. 2. Plantation pollutions, such as phosphates and nitrates. 3. Heat is one of the sources of water pollution because it reduces the amount of oxygen dissolved in water. 4. Sediments are polluted sources of water that can be having organic or inorganic sources. 5. Hazardous chemicals that mostly enter the water by human and industrial activities. 6. Radioactive pollutions (7), the oldest human efforts to water is related to 200 BC That by putting a piece of hot metal into the water and pure sands or passing water and clean or is coal. (2) But today, with various pollutants such as polyaromatic hydrocarbons to be infected.

Polyaromatic hydrocarbons, which are compounds in their structure at least two or more benzene rings, exist is called polyaromatic hydrocarbons. Chemical properties of polyaromatic hydrocarbons is in this way have low volatility and are sparingly soluble in water And the number of aromatic rings increase their solubility is less, well dissolved in organic solvents and are lipophilic, Polyaromatic hydrocarbons are all solid And in the case of absorption in soil surface create a link with some special materials. (3) These compounds with different ways enter the water that is in order: Significant amounts of PAHs, during oil extraction, and its transmission or in oil refining process enter the environment. Or at the time of extraction of coal mines amount of PAHs, in the form of dust, As well as when it be heated Coal in processing plant this material as gas or through industrial wastewater enter to the environment the coal processing plant, (4) the other entry of these compounds into the environment is by the incomplete combustion of fossil fuels and the other incomplete combustion of organic matter. Some of these materials through pesticides and plastic paint and insulation of the roof enter the environment. (5) Animal waste and disintegration of streets and compounds that are used for de-icing streets floor as well as urban construction is the release of this material. (6) Ability of these compounds to create acute disease is not yet fully recognized. But in contact with the pollutants that are combinations of PAHS in the workplace cause: Itching, nausea, diarrhoea, anxiety and restlessness. It is not clear which of PAHS cause these diseases. But a mixture of PAHS cause itching and skin inflammation in humans and animals. Anthracite and naphthalene and benzpyrene clearly cause skin rashes. While the anthracite and benzpyrene cause skin allergens. Long-term and chronic effects of these substances can cause, including cataracts and kidney and liver damage and jaundice. If the naphthalene breathe significantly or enter the digestive system cause the disability of red blood cells.

Workers who are exposed to these compounds, the risk of skin cancer and lung and bladder and stomach in these individuals is increased. PAHs are available in food sources such as meat and fried fish and in tea and coffee are vegetable oils and grain. Also conducted research in the Netherlands, 17 of these compounds in the food basket of 18-year-old man has been found that half of these compounds are carcinogenic. It should be noted that the concentration of these substances in urban and rural areas increase in the winter, due to the need for energy. concentrations of polyaromatic hydrocarbons in sextet water districts of Tehran is vary from 10 Nano grams per litter to 300 Nano grams per litter. In addition PAHs in the coastal waters of Bushehr Province oil extraction activities in the Persian Gulf are also identified and measured, That range of total concentration of combination of PAHs in Waters stations of under studied on the coast of Bushehr Province in July has been among 1.8 to 4.1 Nano grams per litter, as well as the concentrations of these compounds among 2.8 to 5.9 Nano grams per litter in February. That has been with two sources of oil and fuel, with the dominance oil compounds.

2. Materials and Methods

Chitosan produced from shrimp shells and determine the degree of deacetylation chitosan and the synthesis of 3-derived from chitosan, called Nano chitosan and Nano chitosan membrane and chitosan membrane. Then perform testing the absorption of anthracite by four absorbent solution and the results of analysis of tests.

2.1 production of chitosan from shrimp shells

In the first phase amount of 340 g skin dried shrimp were prepared for four hours in a soda solution of 5% by weight - volume put up meat and offal sticking to the skin of shrimp solved and dried, and milled to skin be ready for the second stage will be Then 1500 cc by 1 N soda solution was prepared and skin of shrimp for two hours at 85 ° C was placed in the solution, the protein in shrimp shell, dissolved solution Skin is removed and the remaining skin then filtered shrimp served and rinsed with distilled water until the pH is neutral. The remaining shrimp shells for an hour in the solution of hydrochloric acid were placed normal 0.25 to mineral is separated and was washed with distilled water until the pH is neutral. In the next stage of chitin obtained was washed with acetone to bleach until its color be white and transparent and the final stage of preparation of chitin chitosan, chitin obtained for this purpose for 5 hours in the solution of concentrated 50% interest in the man with agitation and was heated at 100 ° C, this stage is called deacetylation section. Obtained chitosan weight is 71 grams. From the chitosan obtained to ensure the formation of product and purity of that spectra of FT-IR, was taken and matched to the reference spectra.

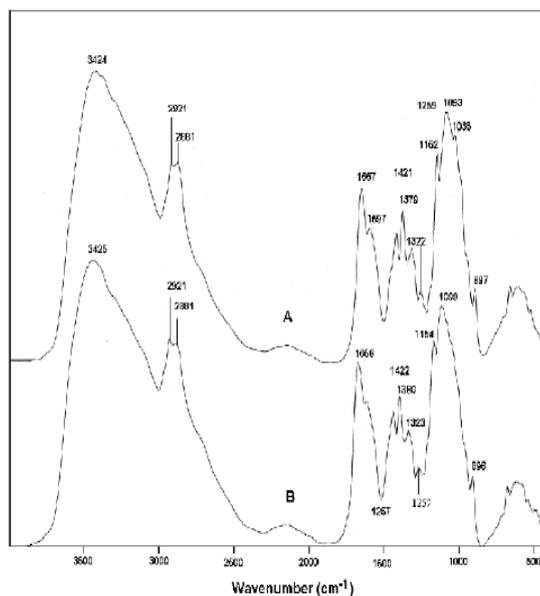


Figure 1 standard spectra of chitosan

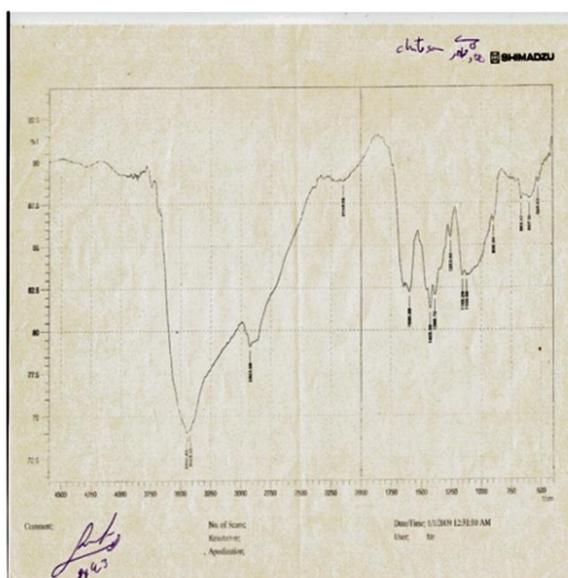


Figure 2 FTIR spectra taken from chitosan

2.2 Interpretation of spectra

By comparing the spectra of chitosan in the shape and chemical structure of this compound be confirmed the correctness of formation of the material provided by IR absorptions. Absorption at a wavelength of 3423 cm⁻¹ is related to first amine functional group. Absorption related to wavelength of cm⁻¹ 3444 belongs to the hydroxyl functional group. Absorption at a wavelength of 1425 cm⁻¹ is belongs to the functional group of CH₂OH. In addition FTIR spectra taken from chitosan synthesized that is the right shape correspond with the standard spectra, in the standard spectra, spectra of A chitosan obtained from shrimp skin.

2-3 calculate the degree of produced acetylation chitosan

The first method is based on the base line (a) according to the following equation: 1)

$$DD=100-[(A_{1655}/A_{3450})\times 100/1.33]$$

That in this formula absorption in the first wavelength means 1655 wave number / cm is calculated as follows: 2)

$$\text{Log}(DF_1/DE)=(A_{1655})_{\text{amide}}$$

DF1 and DE is absolute height of measured of the infrared spectrum from synthesized chitosan. And also: 3)

$$\text{Log}(AC/AB)=(A_{3450})_{\text{hydroxyl}}$$

In this formula absorption at a wavelength of 3450 Wave number / cm is based on the absolute height of AC and AB. According to calculations by the first method is DD = 87.83%.

The second method according to the base line (b) as follows: 4)

$$DD=100-[(A_{1655}/A_{3450})\times 115]$$

In this method absorption at a wavelength of 1655 Wave number / cm is calculated as follows: 5)

$$\text{Log}(DF_2/DE) = (A_{1655})_{\text{amide}}$$

That DF2 and DE absolute height is of measured of the infrared spectrum obtained from chitosan. To calculate absorption at the wavelength of 3450 Wave number / cm is as follows: 6)

$$\text{Log}(AC/AB) = (A_{3450})_{\text{hydroxyl}}$$

In this formula absorption at the wavelength of 3450 Wave number / cm is based on the absolute height are AC and AB. The result from the second method: is DD = 91.9%.

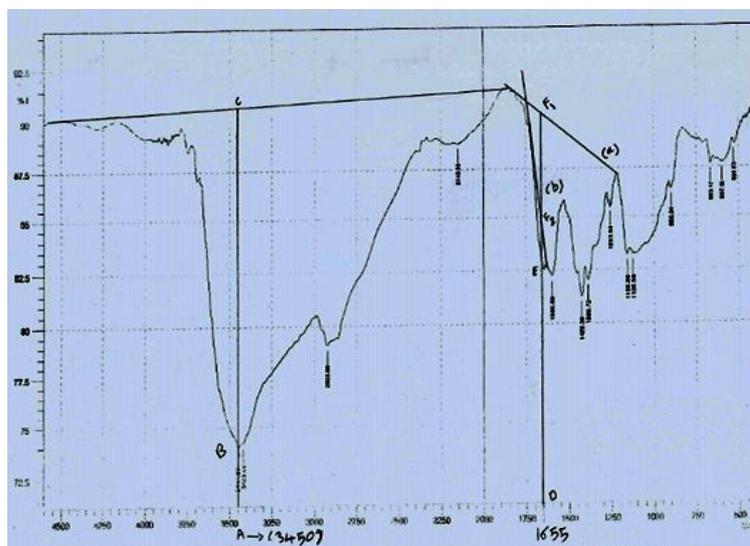


Figure 3 related to calculate the degree of deacetylation chitosan

2.4 Preparation method of Nano chitosan

15 grams of chitosan in the acetic acid solution (2% weight - weight) was poured into the beaker, and the heater stirrer at a temperature of 50 ° C with the magnetic stirrer was mixed for half an hour until completely be solved. Then chitosan solution is poured into a spray device and with the pressure created by compressed air spray device was created on a molar soda solution was sprayed.

As a result, the nanoparticles were deposited. Solution by using Whatman filter paper to reaching neutral pH (7) was washed with distilled water. Neutral solution containing the nanoparticles into the Buchner funnel (on the Orlon), which filter paper was placed in the funnel floor was poured and to the solution was given 24 hours long lasting until the water soluble to be separated from the solution as much as possible.



Picture No. 4 ESEM taken from Nano chitosan

As can be seen in the picture the average size of the particles is in the nanometre.

2.5 Manufacturing membrane

In this study, two types of membranes have been synthesized. The first case chitosan membrane and second case membrane has been Nano chitosan. Production method of both membranes is the same, as follows:

The first membrane: 5 g chitosan (wetted distilled) water was poured into the beaker, Then 50 ml of glutaraldehyde was added to the beaker and without stirred at room temperature for two hours, the chitosan was placed into glutaraldehyde, until reaction is carried out, after the reaction of membrane was washed with distilled water Until remove the unreacted glutaraldehyde the membrane produced were stored in distilled water.

The second membrane: 5 grams of chitosan Nano (to case of gel are available: Means with water available at solution has the gel case) was poured within beaker. Then 50 cc glutaraldehyde added to the beaker. This solution without stirring and left at room temperature for two hours to Nano chitosan and glutaraldehyde within beaker, to make reactions with each other. After the reaction of membrane was washed with distilled water until produce unreacted glutaraldehyde, the membrane Nano products were stored in distilled water. Then reaction was performed to verify the infrared spectrum (FT-IR) was taken from produced membrane. That is Figure 5.

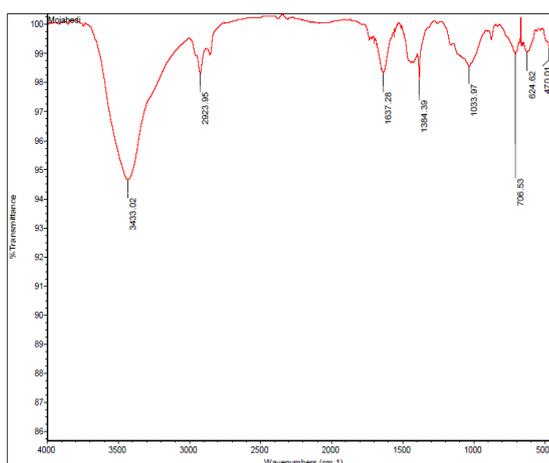


Figure No .5 infrared spectra taken from chitosan membrane

Absorption that imine functional group in the infrared spectrum provides, Frequency in wavelength of 1640 cm⁻¹ up to 1690 cm⁻¹ With the intensities ranging from strong up to weak. By examining taken spectra, it was observed that the average frequency at the wavelength of 1637.28 cm⁻¹ exist that indicates the imine functional group in the membrane, and indicates the presence and forming side links of chitosan and glutaraldehyde.

2.6 Calculation of dry matter of membranes and Nano chitosan

Because chitosan is dry and in the adsorption process is used as dry but its Nano and two membrane are made of moisture absorbed and are kept as wet , so should the amount of dry material, calculated and in proportion to the dry chitosan be used in the process of absorption.

Dry matter two membrane and of Nano chitosan after drying in an oven at a temperature of 50 ° C was calculated result is as follows. Dry matter percentage of Nano chitosan, 3.2% of the gel constitutes. Dry matter percentage of Nano membrane, 6.2% of the gel (membrane) constitutes. Percentage Chitosan membrane, 20% of Chitosan membrane moist, constitutes. Based on this information it was decided to absorption tests adsorbent dosage is as follows. Chitosan 1/0 g, Chitosan membrane, 5.0 g Nano membrane 1 g, Nano 1g

2.7 way of testing absorption by four types of absorbent

Anthracyte solution must first be prepared, for this solution in the absorption tests used, in order was done: 1 g of anthracite, in the solution of 100 ml acetone and 900 cc water was solved and within round-bottom flask gated was kept up do not evaporate its acetone and the solution remains unchanged. Tests conducted at different pH were done and also different temperatures to achieve optimal absorption.

2.8 testing absorption

It should be noted that the initial pH of the solution prepared by anthracite is equal to 5. In this experiment, four beaker of 250cc by 50cc anthracite solution, made in the stage was filled and in the jar test device for mixing and homogenization of the environment was placed then each of the four human values, respectively, 1.0 grams of chitosan, 5.0 grams of chitosan membrane, 1 g of Nano chitosan and 1 gram of Nano chitosan membrane synthesized were added in the previous steps and in the a temperature of 15 ° C and pH = 5 by impeller speed of 40 cycles per minute were stirred. Then at 30, 60 and 90 minutes from the solution were sampled. Samples prepared by the smooth Buchner filtration and were analyzed by the device of uv-vis, of course, at the wavelength of maximum anthracite solution prepared in the previous steps. The results obtained from the analysis of anthracite solution to obtain the maximum wavelength in the fourth chapter have been given.

2.9 tests conducted in the pH = 7

In this experiment, four beaker of 250cc by 50cc anthracite solution, made in the stage was filled and in the jar test device for mixing and homogenization of the environment was placed then each of the four human values, respectively, 1.0 grams of chitosan, 5.0 grams of chitosan membrane, 1 g of Nano chitosan and 1 gram of Nano chitosan membrane synthesized were added in the previous steps and in the a temperature of 15 ° C and pH = 7 by impeller speed of 40 cycles per minute were stirred. Then at 90 minutes from the solution were sampled. Samples prepared by the smooth Buchner filtration and were analyzed by the device of uv-vis, of course, at the wavelength of maximum anthracite solution prepared in the previous steps. It should be noted that to achieve pH = 7 to each of the four beaker anthracite solution containing 20 drops of baking soda (sodium bicarbonate acetate) was added. And the accuracy of the desired pH was measured by pH paper that was equal to 7.

2.9 tests conducted in the pH = 10

In this experiment, four beaker of 250cc by 50cc anthracite solution, made in the stage was filled and in the jar test device for mixing and homogenization of the environment was placed then each of the four human values, respectively, 1.0 grams of chitosan, 5.0 grams of chitosan membrane, 1 g of Nano chitosan and 1 gram of Nano chitosan membrane synthesized were added in the previous steps and in the a temperature of 15 ° C and pH = 9 by impeller speed of 40 cycles per minute were stirred. Then at 90 minutes from the solution were sampled. Samples prepared by the smooth Buchner filtration and were analyzed by the device of uv-vis, of course, at the wavelength of maximum anthracite solution prepared in the previous steps. It should be noted that to achieve pH = 9 to each of the four beaker anthracite solution containing 50 drops of baking soda (sodium bicarbonate acetate) was added. And the accuracy of the desired pH was measured by pH paper that was equal to 9

2.11 tests conducted on Nano Chitosan in the pH = 5 and at 30 and 50 ° C

In this experiment, four beaker of 250cc by 50cc anthracite solution, made in the last stage was filled and on the heater stirrer for mixing and homogenization of the two different temperatures was placed. However, rotation of 200 cycles per minute and the values of 1 g Nano Chitosan added to each of the beakers at 90 minutes from the solution were sampled. Samples prepared by the smooth Buchner filtration and were analyzed by the device of uv-vis.

2.12 testing on three adsorbents of chitosan and chitosan membrane and Nano chitosan membrane in the pH = 5 and temperature of 30 ° C

In this experiment, four beaker of 250cc by 50cc anthracite solution, made in the last stage was filled and on the heater stirrer for mixing and homogenization up to desired temperature was placed. However, by rotation of 200 cycles per minute, and the values of 1 g Nano chitosan membrane and 1.0 grams of chitosan and 5.0 grams of chitosan membrane added to each of the beakers and after the elapse of 90 minutes from the solution was sampled. Samples prepared by the smooth Buchner filtration and were analyzed by the device of uv-vis.

2.13 testing the BET on two absorbent Nano chitosan and Nano chitosan membrane

To examine the differences in the performance of these two absorbent were taken BET test of them that its results has been given in the results and discussion.

3. RESULTS AND DISCUSSION

3.1 uv-visible test results on anthracite solution prepared in order to obtain maximum absorption

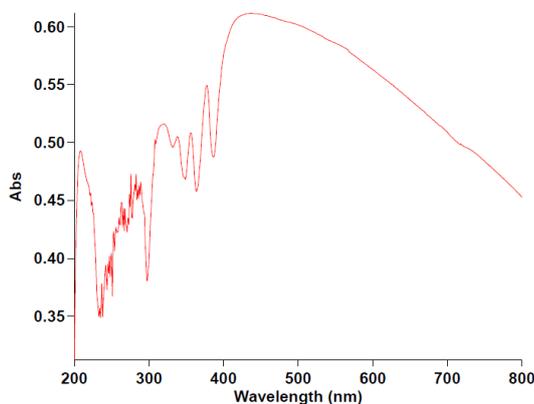


Figure No .6 ultraviolet spectra taken from the anthracite solution before adding absorbents

As can be seen the maximum wavelength is 437 nanometre.

3.2 The results of the analysis of uv-visible in the pH = 5 and at three time 30, 60 and 90 minutes at 15 ° C

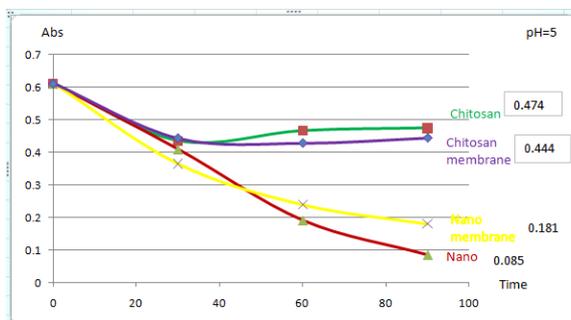


Figure 1 compares the different absorptions in the pH = 5 for each of the four absorbent in the temperature of 15 ° C

As the above diagram is shown for two absorbent chitosan membrane chitosan in the pH = 5 and temperature of 15 ° C, after 30 minutes, increasing absorptions, exist but in continue in the times 60 and 90 minutes the amount of anthracite absorbed almost unchanged remains. But about two absorbent of Nano chitosan and Nano chitosan membrane in order to increase the time from the 30 to 60 and 90 minutes the amount of absorption also increases. That the best absorptions Nano chitosan obtained in these conditions that is equal to 0.085.

3.3 results obtained from the analysis by the device of uv-visible in pH = 7 for 90 minutes

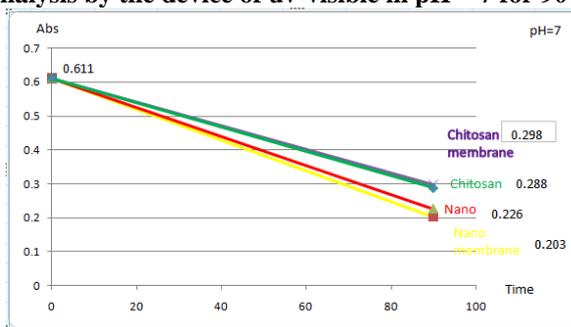


Figure 2 different absorptions in the pH = 7

According to the diagram the above it is concluded that all four absorbent in the pH = 7 after 90 minutes the amount of absorption rising from anthracite about chitosan and chitosan membrane the amount of absorption after 90 minutes is equal, But about the Nano chitosan and Nano chitosan membrane, Nano chitosan absorption is equal to 0.266 and Nano chitosan membrane absorption is equal to 0.203. That the best efficiency in this situation is Nano chitosan membrane.

3.4 Results obtained from the analysis by the device of uv-visible at pH = 9 for 90 minutes

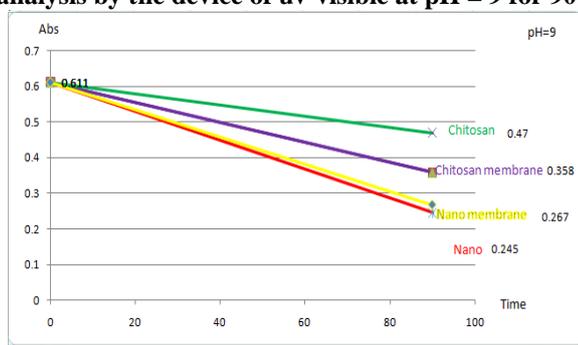


Figure 3 shows different absorptions at pH = 9

According to the above diagram to reach the conclusion that each of the four absorbent after 90 minutes at pH = 9 upward trend from the absorption of anthracite the absorption by chitosan the lowest amount, and absorption by the chitosan membrane is more than absorption by chitosan, but absorption by the two case of Nano chitosan and Nano chitosan membrane, is equal roughly, That in this terms of the two absorbents Nano chitosan and Nano chitosan membrane have the highest absorption amount.

And by comparing the diagrams of 4.2 and 4.3 and 4.4 to reach the general conclusion that the greatest amount of absorption at pH = 5 and 90 minutes, and related to two absorbents: Nano chitosan and Nano chitosan membrane and respectively is equal to 0.085 and 0.181. As a result should be expressed that pH = 5 compared to pH = 7 and pH = 9 has better efficiency.

3.5 The results of the analysis of uv-visible Nano chitosan in the two temperature of 50 and 30 ° C and pH = 5

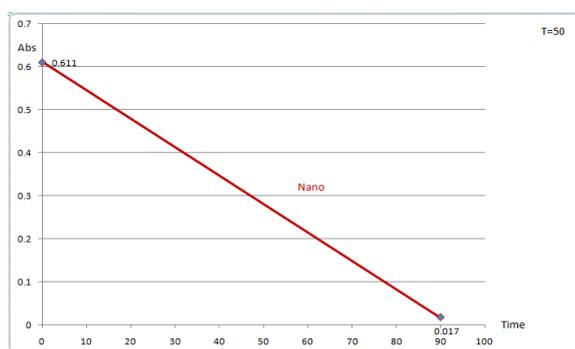


Diagram 4 related to absorption of anthracite by Nano chitosan at 50 ° C and pH = 5

By examining the diagram above it is concluded that the Nano chitosan at pH = 5 and at 50 ° C for absorption is equal to 0.017 after 90 minutes has reached show that anthracite absorption has been done a huge amount and the remaining amount is 2.7% of the initial solution.

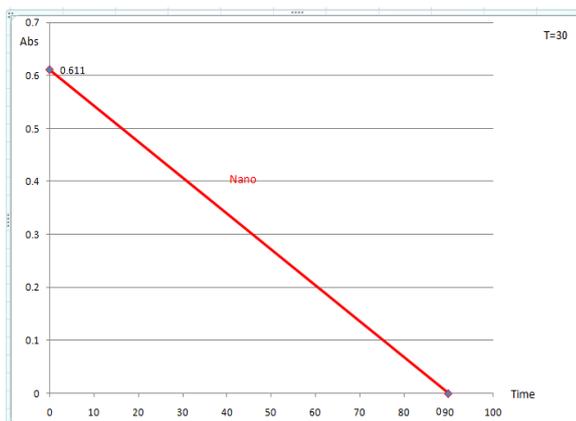


Diagram 5 on the absorption of anthracite by Nano chitosan at 30 ° C and pH = 5

In this diagram, also anthracite absorption at pH = 5 and 30 ° C after spending 90 minutes to complete, was conducted. Means amount of anthracite remaining after the absorption is zero, which represents the best performance.

3.6 results obtained from uv-visible analysis at 30 ° C and pH = 5 for three adsorbents of chitosan and chitosan membranes and Nano chitosan membrane.

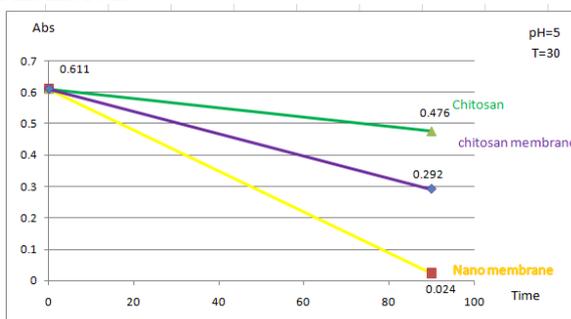


Diagram 6 indicates absorption of anthracite by 3 adsorbent of chitosan and chitosan membranes and Nano chitosan membrane is at 30 ° C and pH = 5

According to the diagram above are the following results: All three adsorbents at pH = 5 and a temperature of 30 ° C. After 90 minutes, absorb a greater amount of anthracite and have been increasing their absorption process. That the Nano chitosan membrane has the highest amount of absorption that the absorption of it, is 0.024 which shows after the process of absorption amount of 3.9% anthracite has been remained in solution.

3.7 final conclusion of all adsorbents at different pH and temperatures and times of all tests performed

After reviewing all the diagrams shows that the most complete absorption is related to Nano chitosan at 30° C and pH =5 and 90 minutes, that completely absorb anthracite and anthracite remaining in the solution is zero. In the next stage the Nano chitosan membrane have the best performance among the absorbers, at the same conditions Means 30° C and pH =5 and 90 minutes.

Anthracite amount remaining in solution after absorbing is 3.9 percent. To investigate the difference between performances of the two test adsorbent of BET was taken from the two adsorbent of. In the testing BET, the specific absorption square meters per gram scale and nanometre-scale pore diameter is obtained that to justify the difference of the two adsorbent of Nano chitosan and Nano chitosan membranes are useful.

3.8 BET test result from Nano chitosan and Nano chitosan membrane

BET testing results show that the average pore diameter in the Nano chitosan is equal to 2.337 and an average pore diameter In the Nano membrane is equal to 2.397 nm that not have significantly different from each other.

But given the level of specific absorption in the Nano chitosan is equal to $300.713 \text{ m}^2\text{g}^{-1}$ and compare it with special absorbing surface of Nano chitosan membrane, which is equal to $102.279 \text{ m}^2\text{g}^{-1}$ reach the conclusion that: Specific Absorption surface of Nano chitosan is 2.94 times (approximately 3-fold) more than the specific absorption Nano membrane, which it is absorbent of the difference In the anthracite absorption power between the two adsorbents.

So after finish all the tests we reach to this final result that Nano chitosan best absorbent when $\text{pH} = 5$ and a temperature is 30 degrees Celsius. According to the following reasons:

1. Having the highest levels of specific absorption, is equal to: $300.713 \text{ m}^2\text{g}^{-1}$
2. in $\text{pH} = 5$, that amine functional groups of RNH_2 , In the molecular structure chitosan is converted to RNH_3^+ with a positive charge that these changes will increase polarization and absorption of anthracite.
3. At 30°C ambient temperature is approaching and with spending a small amount of energy to be achieved to this temperature.

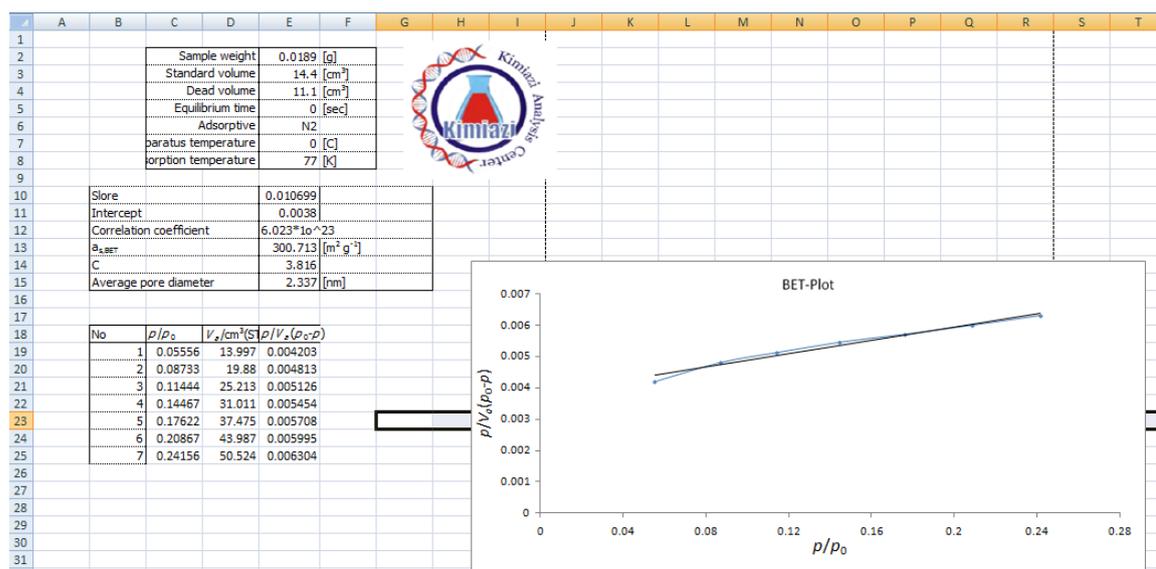


Figure 7. BET testing taken from Nano chitosan

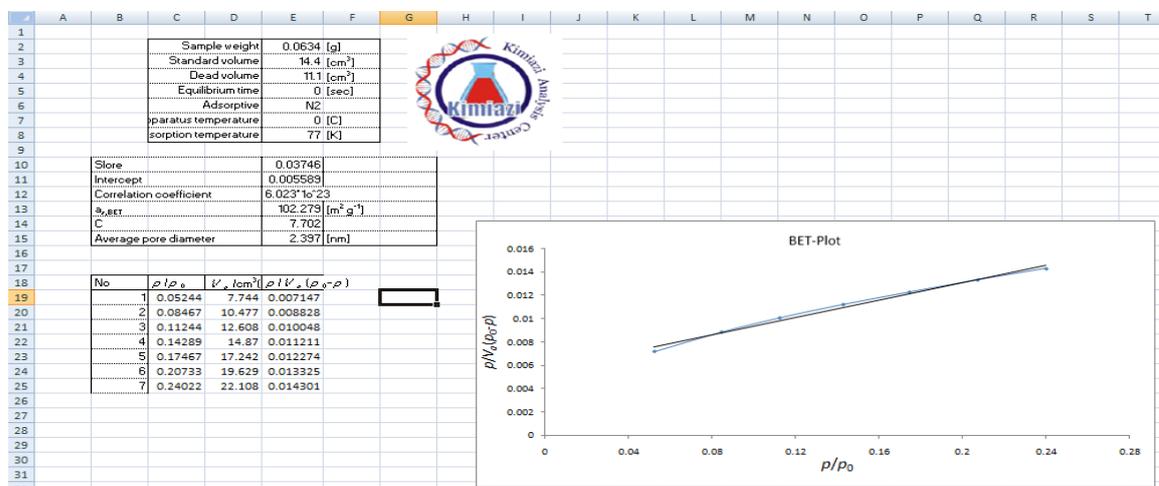


Figure 8. BET testing taken from Nano chitosan membrane

4. CONCLUSIONS

Chitosan as a biodegradable biopolymer that is also if converted into chitosan Nano can be used as efficient adsorbents for absorption of anthracite, water is used. 1. Testing absorption by the two adsorbents Nano chitosan and Nano chitosan membrane on other form compounds Aromatics such as naphthalene and phenanthrene done because these two adsorbents in the adsorption process have achieved the best results. 2. The tests will also be performed at pH acidic. 3. Nano chitosan membranes synthesized and other PAHs absorption test conducted on these synthetic membranes.

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