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RESEARCH PAPER

Synthesis of Carbon Quantum Dots from Olive Stones for Efficient Adsorption of Benzene from the Ambient Air

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ABSTRACT

In this research Carbon Quantum Dots (CQDs) made from the olive stones has been revised considering different parameters and factors including temperature, moisture, benzene concentration, the amount of adsorbent and contact time with three different methods and the amount of adsorption of three adsorbents to eliminate the benzene vapor from the ambient air. In the first adsorbent, the primary CQDs activated with nitric acid (CQDs-HNO_3), and in the second adsorbent activated with KOH (CQDs-KOH), and in the third one activated with Ionic liquid (CQDs-Ion) were all studied. A pilot was made for the tests which were all equipped with a measurement device of volatile organic compounds with a photoionization detector, and a sensor for indicating the moment concentration of benzene. The most percentage of elimination of benzene in 60 seconds with an adsorption amount of 20 mg/L was calculated. In this study, the most percentage of benzene elimination amounting 70% for CQDs -KOH and the least percentage of elimination for CQDs-HNO_3 was 51%. The coefficient correlation R^2 for CQDs-KOH adsorbent was 0.990 as the maximum amount. The research results showed that the activated adsorbents with ionized liquid with a specific area of 524 m^2/g at the temperature of 35 °C and the moisture of above 50% has more effective reaction compared to CQDs-KOH adsorbent with the specific adsorption area of 550 m^2/g. This result is due to the great amount of volume of porosity of the adsorbent CQDs-ion of 1.56 cm^3/g compared with the other adsorbents.

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INTRODUCTION

In recent years volatile organic compounds (VOCs) are referred to as one of the most poisonous pollutants in cities and industries which is a threat to the health of public (1, 2). Regarding the quality of the air in closed environments, many research has been done in recent years (3). The concentration of the pollutants in buildings, basements, underground garages, factories, tunnels and vehicles is reported more than the hygienic standards (4, 5). One of the closed environments which should be considered is the cabin of the vehicles. Research has shown that gasoline in many countries especially in the USA contains large amounts of harmful chemicals (5-7). These compounds are Benzene, Toluene, Ethylbenzene and Xylenes which can penetrate to the cabin of vehicles while refueling or leaking fuels into the car. Research has proved penetrating this steam into the vehicle cabin caused by fuel is obvious (8). Regarding this, benzene is one of the most important known volatile organic compounds (VOCs) and on the basis of the research done by International Agency for Research on Cancer benzene is a cancer-causing compound (9, 10). This compound is very poisonous and it has symptoms of leukemia, blood cancer and so on (11, 12). The standard of this compound is 3 µg/m^3 in developed countries like Japan; meanwhile the volume percentage of this compound inside the fuel is less than 1% by volume according to Japan which was decreased to less than 0.64% by volume in recent years (13-15). Unfortunately, the benzene concentration in consumed fuel in Iran is very high, 1 to 5% and more by volume. The fuel used in Iran has low quality and contains a high concentration of volatile organic compounds (especially benzene) and since 2005 Methyl tert-butyl ether (MTBE) has been replaced with tetraethyl lead to improve fuel octane (5).

Today, nanoparticles have many applications for the detection of pollutants and microscopic organisms(16-18). Different methods have been suggested to adsorb volatile organic compounds vapors. The most applicable is to use adsorption by an adsorbent. Some researchers use active carbons of charcoal (19, 20), wood, bamboo and other lignocellulose (21, 22). Active carbon is the most used due to much porosity, cheapness and the size of adsorbent pores capacity (23). Studies show that activated carbon is used to eliminate low concentrations of volatile organic compounds in the long period of usage (24). Also, different sorbents based on various techniques were used for removal of hazardous pollution such as benzene, toluene and VOCs form air or water matrices(25-28). The adsorption method can be used as an ideal and applicable one and in this way wide range of volatile organic compounds can be eliminated from the air by advanced adsorbents due to high volume pores (29, 30). Active carbon has the potential to convert and to absorb color, odors, taste and pollution in different industries (31). Some of research has been carried out on promoting cabin filter applicability and many pollutants like dioxide nitrogen and some volatile organic compounds have been decreased or eliminated by cabin filters smeary to adsorbent. Nowadays different sources are used to produce active carbon (32-34). The focus is the cheap material and powerful applicability to produce active carbon (35, 36). Commonly used materials include charcoal, bamboo, lignin wood and fruit stones and grains (23, 37). Many of the commercial active carbons have the adsorption areas of 500 up to 1500 m^2/g and maximum 3000m^2/g (38). Regarding the olive stone used to produce active carbon, very little study has been done. Olive is regarded as a side product in extracting oil in industry and the stone constitute the most volume of extract. Most of the olive oil producers are located in the Middle East and East Asia and totally they produce 98% global olive oil (39). About 100 thousand tons of Olive is produced and there are very few applications in Iran. The research shows that 10% of olive fruit in the Stone weigh 16-47 % and most of its part is carbon (40, 41). The amount of porosity and adjustable pores and adsorption capacity is of great importance. The Olive stone consists of lingo cellulose material. Nowadays olive, waste and stone draw the attention to produce active carbon and it can be used to control the pollution of the volatile organic compounds(31, 42, 43).

Limited research has been done on CQDs made from olive stone and very few scientific sources exist about this adsorbent and (41, 44, 45). Regarding the active carbon produced by the olive stone which can eliminate benzene has been carried out seldom and none of research focused on CQDs produced from the olive stone. This research was done for the first time with a specific pilot and it’s expected that the results can be used in vehicle cabin filter to eliminate volatile organic compounds especially benzene.

MATERIALS AND METHODS

Reagents and Materials

All chemicals were purchased from Merck, Fluka, and Sigma Aldrich companies, Germany. The milligram of liquid benzene (mg) was prepared (0.1-5 mg) and injected to the chamber which was supported by pure air. Benzene solution (99.7%) was purchased from Fluka and ten solutions of benzene as standard calibration were prepared before injected to the chamber. The validation of benzene concentration was checked in output of the chamber and GSB. The other chemicals such as HNO_3, HCl, acetone, methanol and ethanol with high purity (99%) and GC grade were purchased from Merck (Germany). The novel sorbent of CQDs-TSIL was synthesized by RIPI Nano laboratory. The CQDs (≈50 nm), with 80% purity was synthesized. The characterizations of CQDs-TSIL were achieved by different spectra.

The designing the pilot

In this research Phocheck Ex5000 and gas chromatography based on air /gas loop injection with flame ionization detector was used for benzene analysis in air (Agilent GC, 7890A, GC-FID, Netherland). This device is portable and it has a gas meter for detecting photoionization which is very sensitive. It has the capability of recognizing and measuring volatile organic compounds (VOCs) from the amount of 1 ppb up to 10000 ppm. Measuring the benzene concentration, Phocheck unit is used which is equipped with Krypton lamp 10.6 eV. This device can measure VOCs in the environment with low error and it is quick response. The speed of the flow rate is 220 ml/min and has an Erlenmeyer 100 ml used to store the benzene vapor. To measure the benzene concentration in fuel first 5 cc Euro 4 gasoline was poured in the Erlenmeyer and concentration of benzene determined in the outlet of Erlenmeyer by gas chromatography(GC) before flow to pilot, while the temperature and moisture sensor are active, all pilot valves will be closed, it takes 30 seconds to produce balance in the environment and the Phochek unit is still in a circle and opening of valve number 2 (valves number one closed). The primary concentration will be read after 10 seconds (Fig .1). It is necessary to mention that filter holder number B which has non-adsorbent filter (blank filter role) only for considering speed, pressure loss and the amount of benzene adsorption by blank filters in the circle. Firstly, the different concentration for benzene generated in various times, 2 s, 5s, 10s, 20s and 30s for calibration procedures. The results showed that the benzene concentration was obtained 1.28 mg L^{-1} (ppm) and 1.34 mg L^{-1} (ppm) in valve 2 by Phochek and GC-FID, respectively (n=5, RSD less than 5%). All other conditions of filter holders and filter (b) are the same as the filter holder (a). After reading the prime benzene concentration, the valve number 2 gets closed. The smeary filter with the revised quantum dot (CQDs, three different kinds) is placed in the filter holder. The valve No. 1 is open after 10 seconds and the amount of benzene was achieved 58 ppb, 64.7 ppb by GC-FID, respectively while valve number 2 is closed and attention should be paid to one-way valves near Phochek units which prevent return of VOCs and changing the position for valves No. 2 and 1, the pollutants will lead to measurement units. The

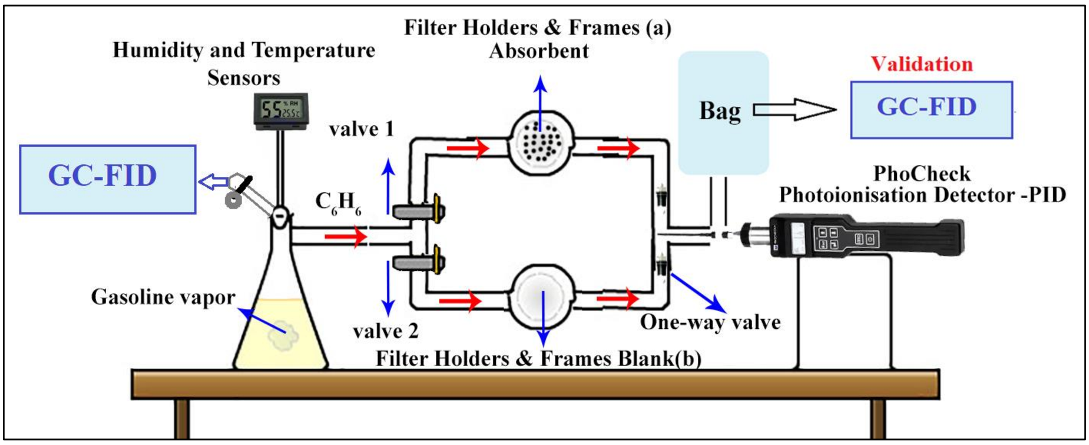


Fig. 1. Schematic of the experimental setup for benzene gas adsorption by Adsorbent

duration for changing valve is less than 1 minute. Based on results, the recovery of benzene removal with adsorbent is more than 95% which was validated by GC-FID. Temperature and moisture affecting the concentration of pollutants are measured. Necessary to mention the increased temperature provided by warm water and moisture are provided by injecting water drops in Erlenmeyer and controlled by a sensor in upper part of Erlenmeyer. At the end of each step, the prime concentration of VOCs and concentration after adsorption considering testing conditions for all three carbons quantum dots adsorbent was read. To increase the precision of the test, it was repeated three times and the average is reported. Also, TGS 2180 (China) as H_2O vapor detector (humidity) and Dräger (Pac 3500, Germany) as O_2 gas detectors were used for determining water vapor and oxygen gas in output of Erlenmeyer.

Preparation of powder from olive stones

All the stones are ground by Balmil machine

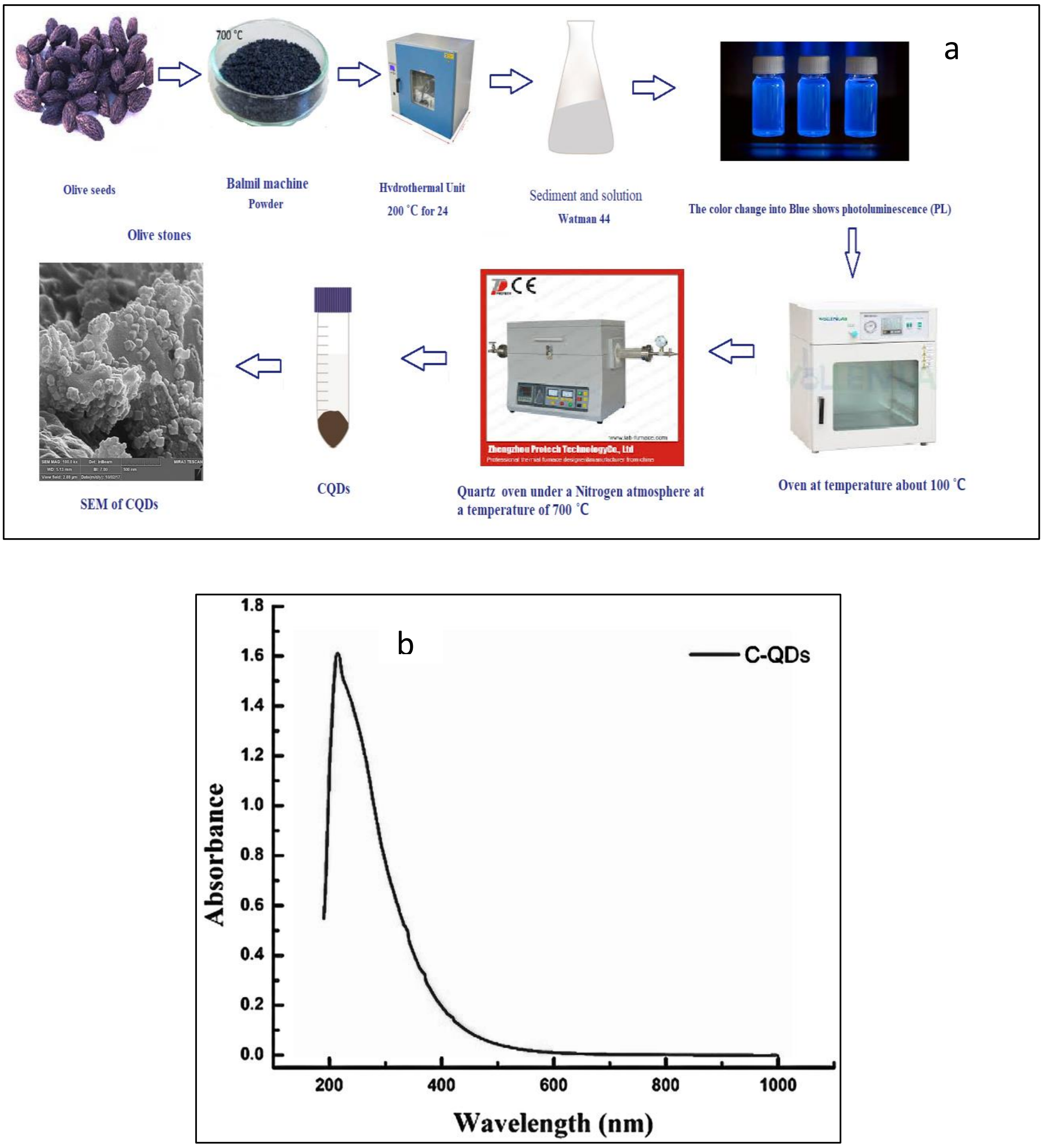


Fig. 2. a) The primary steps of synthesizing CQD b) UV irradiation absorbed by CQDs products

after stones are washed and dried in the environment temperature. The ground powder is sifted by mesh number 45(345 microns) to get equal powder which is used for synthesizing carbon quantum dots.

First of all, 500 grams of powder is put in 8 Liters of water in the hydrothermal unit. The unit is firmly closed and set the temperature at 200 °C for 24 hours and let it take time; then the unit gets inactive for 12-24 hours to reach environment temperature and gets cool. The sediment and solution are emptied from the valve in the lower part of the unit in a container. The sediments are completely separated in a compact Watman 44 by filter paper with the help of the vacuum pump and a shining brown material is extracted (Fig. 2a).

In the next step, the solution was studied under UV 365 Micrometer. The color change into Blue shows photoluminescence (PL) specification on property. The color changing means that the material has been synthesized correctly and consists of quantum dot particles which are semi-conductors. The results showed that the UV irradiation can be absorbed by CQDs products at 220 nm as Fig. 2b. The extracted liquid is poured in the beaker after it is filtered and put in the oven at temperature about 100 °C until it dries completely and converted into powder. The powder is put in a glass type container and put in a quartz type oven under a Nitrogen atmosphere at a temperature of 700 °C for 1 hour to be carbonized. In this situation the compound gets carbonized structure and all impurities get out.

Three prepared below compounds with the prime CQDs made of olive stone and effects of temperature and moisture in different benzene concentrations were studied. The adsorbents were placed in filters by dip-coating method and testing were carried out in the pilot environment. Three forms of CQDs were generated by process, A) The activated sample by CQDs-HNO3 B) The activated sample by CQDs-KOH C) The activated sample by CQDs-Ionic liquid. Then the research is continued by studying the covered filters with three kinds of adsorbents to eliminate benzene in different conditions.

To activate with KOH (CQDs-KOH)

The powder acquired from carbonized step with potassium hydroxide which is smashed well and gets equal mixture will be added by 2 grams of KOH compound for each gram of carbonized powder. The combined mixture is put in the oven for 1 hour at temperature of 800 °C under nitrogen atmosphere. In the next step, the produced powder compound is poured into a beaker and some HCL is added and put in a stirrer at a temperature of 80 °C. The acquired solution is filtered by paper and set the solution PH at neutral and continue the process by putting it at 100 °C in the oven to dry and gets equal soft powder.

To activate with Nitric Acid (CQDs-HNO_3)

In this sample, acid nitric vapor was used. 1.5 gram activated material by potassium hydroxide was put into the system area and nitric acid is added in the lower part and let the system for 24 hours at a temperature of 125 °C to activate. The nitric acid vapor which contains amino activation was passed over the powder and this formed a link and consequently carbon quantum dot powder gets activated.

To activate with Ionic liquid (CQDs-Ion)

0.5 gram activation powder by KOH is poured in a beaker and 0.5 ml acetone are added to it so the powder gets softer and then it is put in stirrer and 120 ml/g Ethyl Methylimidazolium bis-1 is added to it and the temperature begins with 20 °C and every 3 minutes temperature is increased up to 50 °C. This condition causes acetone to steam and gets out of the compound and material gets converted into powder very light and porous. The powder has the hydrophobic compound and not solvable in water. This Ionic composition causes to produce Ionic bonds and forming anion and cation and better links for eliminating benzene compounds, and it has more resistance against temperature.

Filter preparation Method

Iranian manufactured auto filers have been used in this research (cabin filter for Renault Sandro cars) and coated by a dip coating. The main filter consists of small parts and washed up with acetic acid, ethanol to eliminate primary pollutants and coating afterwards. In this method it takes 48 hours to adsorb the solution completely by filters and then gets dry in 48 hours at normal temperature of the environment.

Study the benzene adsorption on the adsorbents and assigning adsorption capacity

As mentioned before, a volume of 100 ml

samples (Erlenmeyer empty) were considered. The adsorption capacity or the amount of benzene adsorption is assigned by q_e (mg/g) formula. The capacity was calculated by three different adsorbents (1-1 and 1-2) formulas. In this equation, adsorbent adsorbing capacity q_e (mg/g), prime benzene concentration C_0(mg/L), benzene balance concentration in the container C_e (mg/L), the amount of adsorbent mg, the desorption efficiency (R) and the volume of the container V(lit) are shown.

$$R = \left(\frac{(C0 - Ce)}{C0}\right) \times 100 \quad (1)$$

$$qe = \frac{(c0 - ce) \times V}{M} \quad (2)$$

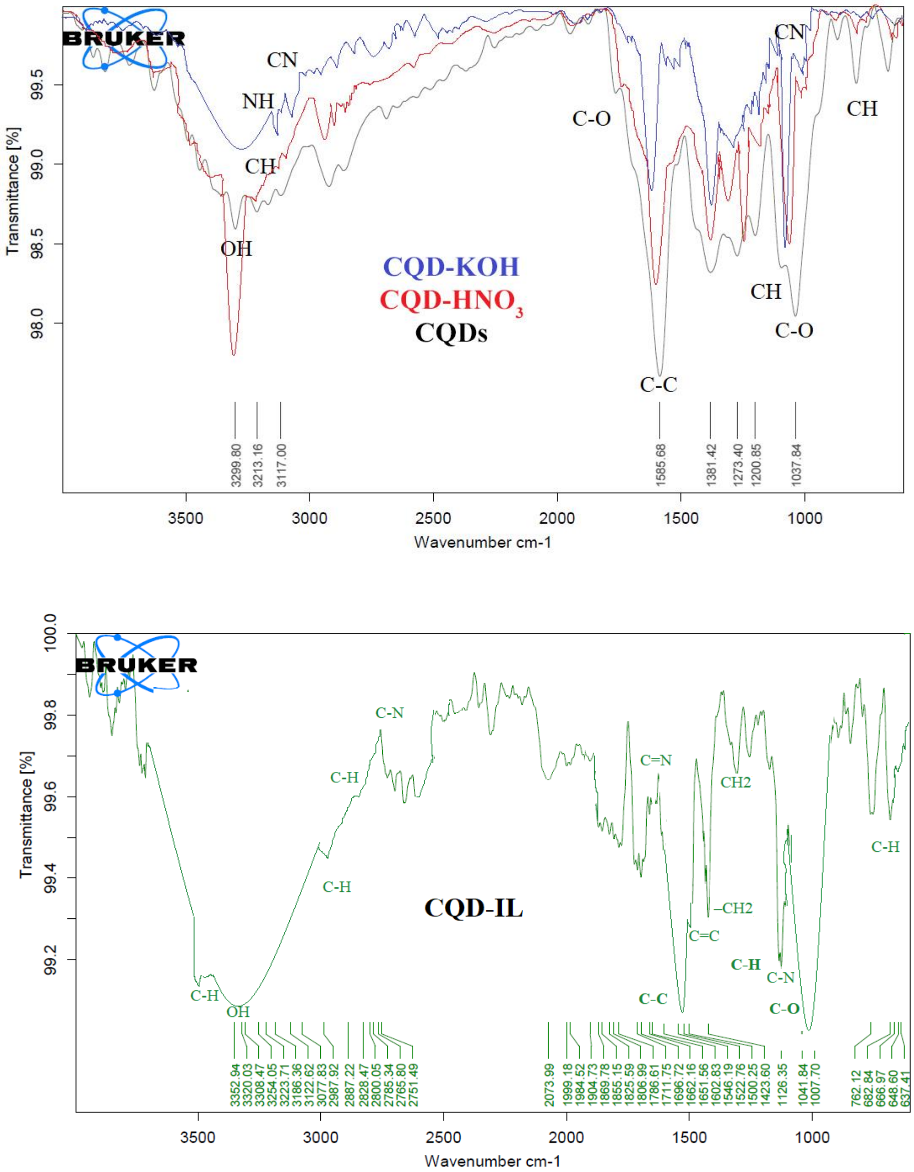


Fig. 3. The Fourier-transform infrared spectroscopy. Black lines are FTIR spectrums of primary CQDs sample and blue lines activated samples with KOH and red line samples of activated with nitric acid vapor and green lines is CQD- Ionic liquid solution.

RESULTS AND DİSCUSSİONS

Fourier-transform infrared spectroscopy (FTIR)

FTIR in the synthesized samples are shown in Fig 3. In this figure, the prime spectrum of FTIR of CQDs is shown in black with peaks at different wavenumbers. These numbers were observed 1037 cm^{-1},1200 cm^{-1} ,1273 cm^{-1} to C-O bond and the peak 1381 cm^{-1} shows the formation of C-H bond. Further, a peak was observed in the wavenumber 1585 cm-1, which can be attributed to the C = C bond, and the last peak appeared in 3299 cm-1, which indicates the formation of the C-H bond. In Fig. 3, the red graph is the sample activated with nitric acid vapor. In the spectrum of activation with acid vapor, there are peaks of 1313 cm^{-1} and 1404 cm^{-1} which is an indication of N-O and C-O bonds. The other common peaks with CQDs were formed in the samples. Meanwhile other peaks of 3377 and 3448 cm^{-1} wavenumbers were observed showing C-H and O-H bonds. This shows a successful process of activation with Nitric Acid vapors, and nitrogen and oxygen compounds mixed well in this sample. The spectrum of KOH sample which is shown in blue color in this figure shows that this sample has C-H and C-O bonds. Peaks of 1041 and 1007 cm^{-1} were formed in the Ion activated sample which shows C-F bonds .The usage of the Ionic solution to activate CQDs causes fluorine atom penetration into the structure (green color). The other peaks of the spectrum

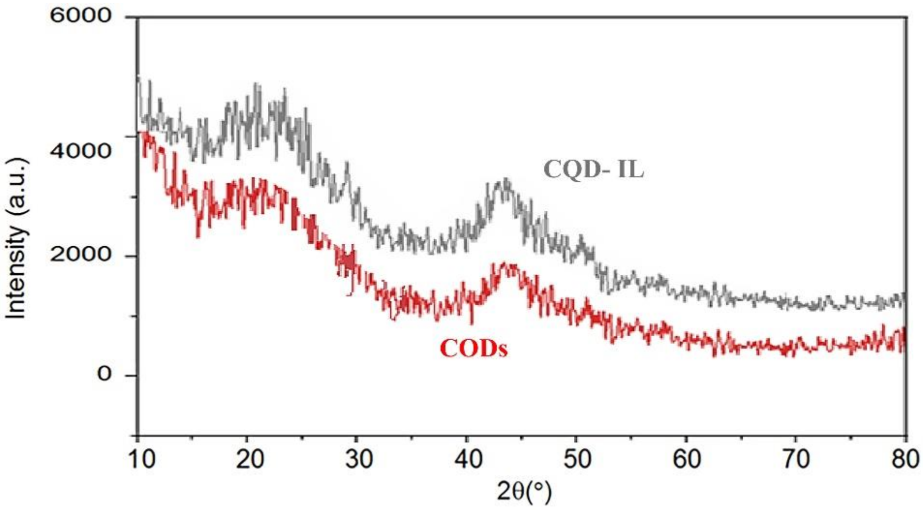


Fig. 4. XRD spectra of a (CQDs-IL and b) CQDs and similar forms of acidic and basic

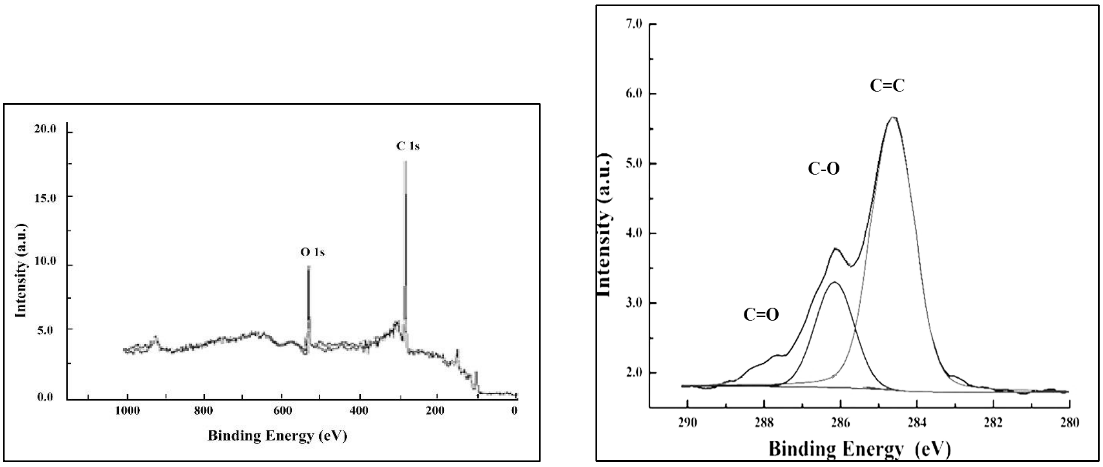
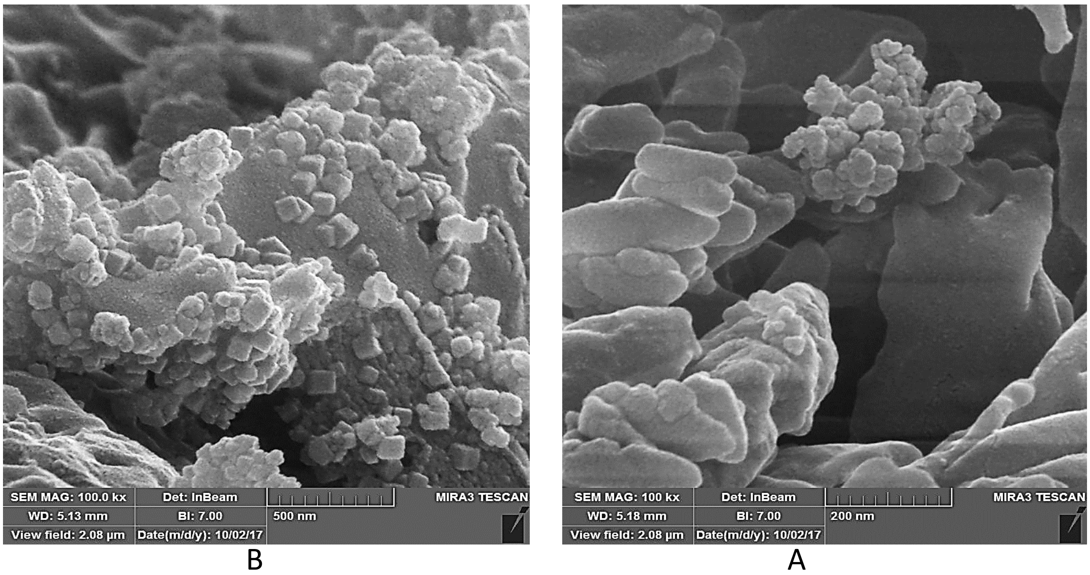


Fig. 5. XPS analysis of CQDs and ground olive power.

FTIR were 1000-1600 cm^{-1} and 2073 cm^{-1} which have C-O, N=O, C=O, C=N bonds. This proves that ionic liquid solution can enter the nitrogen groups into the structure of CQDs plus formation of carbon groups.

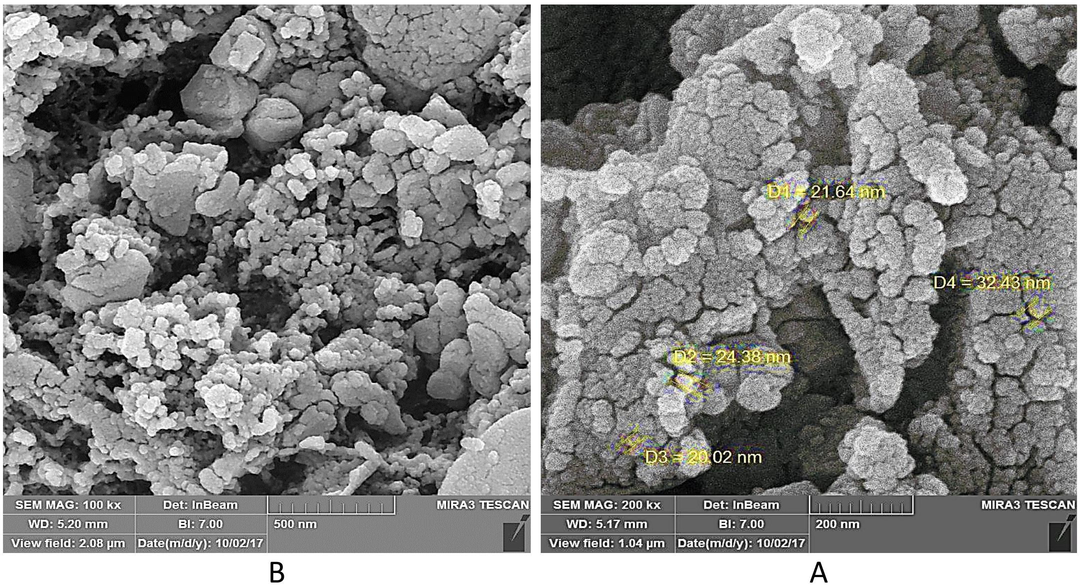
XRD spectra of CQD

In Fig. 4, the X-ray diagram was shown for carbon quantum dots(CQDs) and carbon quantum dots modified with task-specific ionic liquid (CQD-IL). This XRD curve of CQD-KOH and acidic form is similar to CQDs due to previous reported references. In this pattern two main peaks in 2 is equal to 23 degrees and 44 degrees were observed. The observed wide peak is in the intensity of 23 degrees in peak 002 relates to the graphite. The width peak can be interpreted to minor graphitization and small size of carbon quantum dots. The observed CQD-IL peak in 44 degrees angle relate to (101) which indicates similar to



B A

Fig. 6. A field emission scanning electron microscope Fig. of CQDs



B A

Fig. 7. A field emission SEM of sample CQDs activated with nitric acid vapor

graphene formed by quantum dot particles. The XRD pattern for CQDs is similar to CQD-IL which was indicated that carbon quantum dots modified with task-specific ionic liquid did not have worse effect on the structural order of CQDs.

XPS analysis of CQDs and ground olive power is shown in Fig. 5. The XPS of CQDs shows that the CQDs are mainly composed of carbon and oxygen (C1s :67.8 % and O1s:32.2 %), respectively. Due to carbon peak, the main peak at 284.6 eV (70.2 %) related to sp2 graphitic structure and the peaks at 286.16 (20.6 at. %) and 287.2 eV (9.2 at. %) are attributed to C-O and C=O, respectively.

Field emission scanning electron microscope (FESEM)

To specify surface morphology and dispensation of the prepared adsorbent, a field emission scanning electron microscope (FESEM) was employed. The figures of FESEM samples have

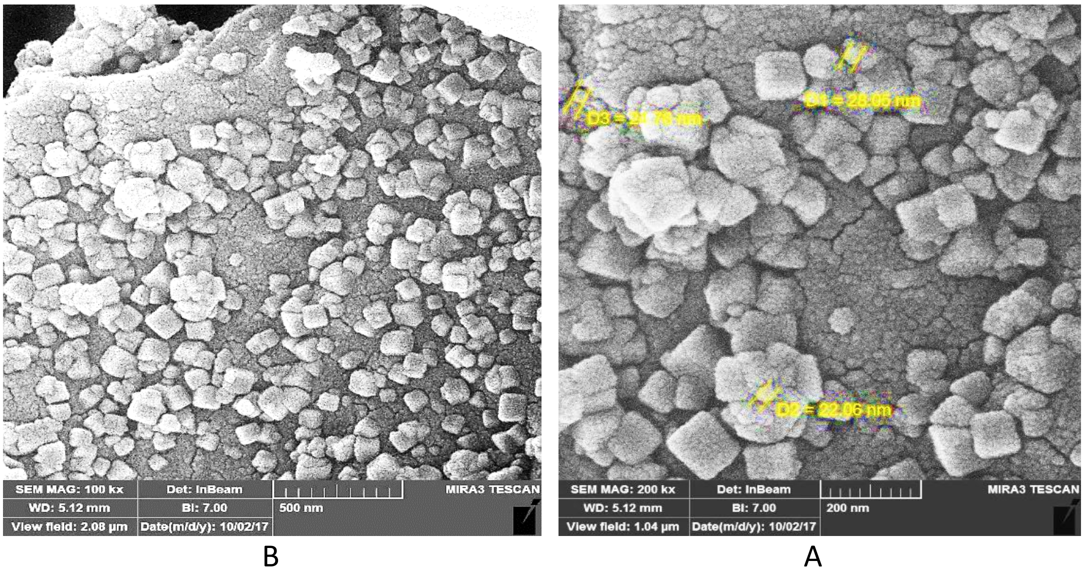


Fig. 8. A field emission SEM of CQDs samples activated with KOH

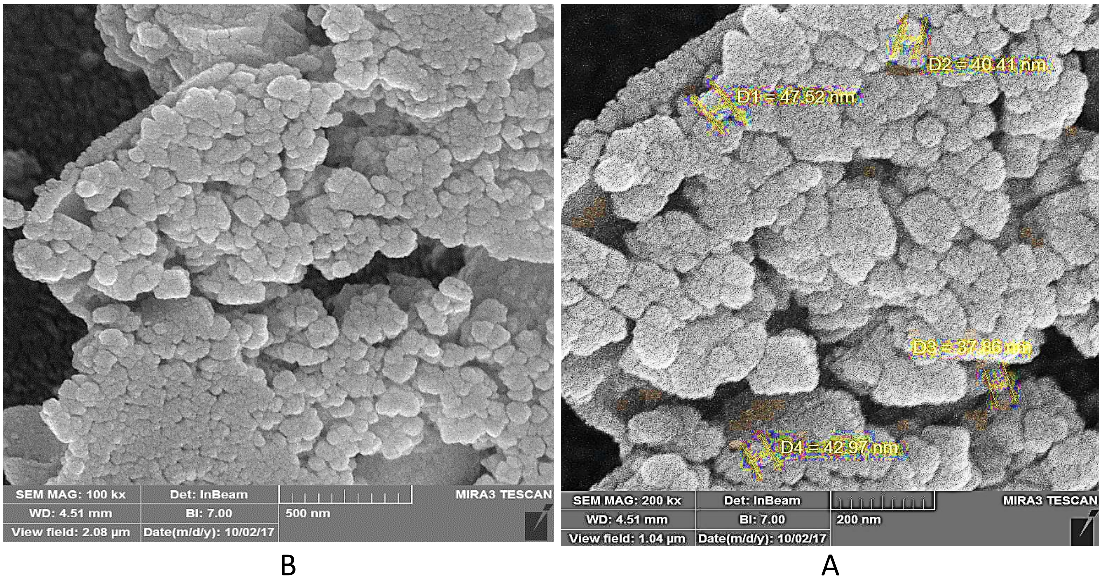


Fig. 9. A field emission SEM of CQDs samples activated with Ionic liquid

been shown in Figs. 6 to 9 in two different magnified figures (Fig. A: at 200 nm scale of magnification and Fig. B: at 500 nm scale of magnification). In Fig. 6, CQDs primary samples were formed as blocks of nanoparticles carbon. The blocks are as a colony and forms big volume of CQDs. The smallest structural units of this sample were among 25 to 35 nanometers which consists of very small particles of CQDs. In the latter figures, the revised sample of CQDs activated with Nitric acid (Fig. 7) CQDs activated with KOH (Fig. 8) and CQDs activated with Ionic Liquid solutions (Fig. 9) can be observed. It’s so clear there are no significant differences between structure and morphology with prime structure of CQDs. Therefore, it can be concluded activation methods and activation of CQDs have no damage to the base structure, but there is a great difference in the last two samples in area and volume of adsorbent pores.

Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was also used due to the importance in studying nanostructure in smaller scales. The microscopic images of the samples have been shown in Figs. 10 to 13. In Fig. 10, the TEM images of the prime samples of CQDs are shown.

These images are shown clearly in two magnified images (Fig. A&B), which the carbon particles are so small. In Fig. 10 (B), nanoparticles

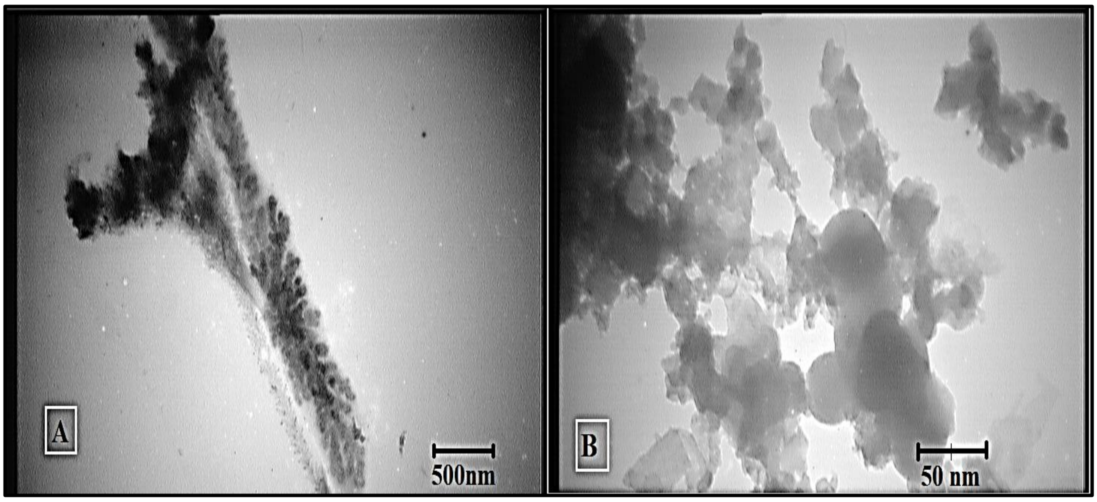


Fig. 10. The TEM images of the prime samples of CQD’s

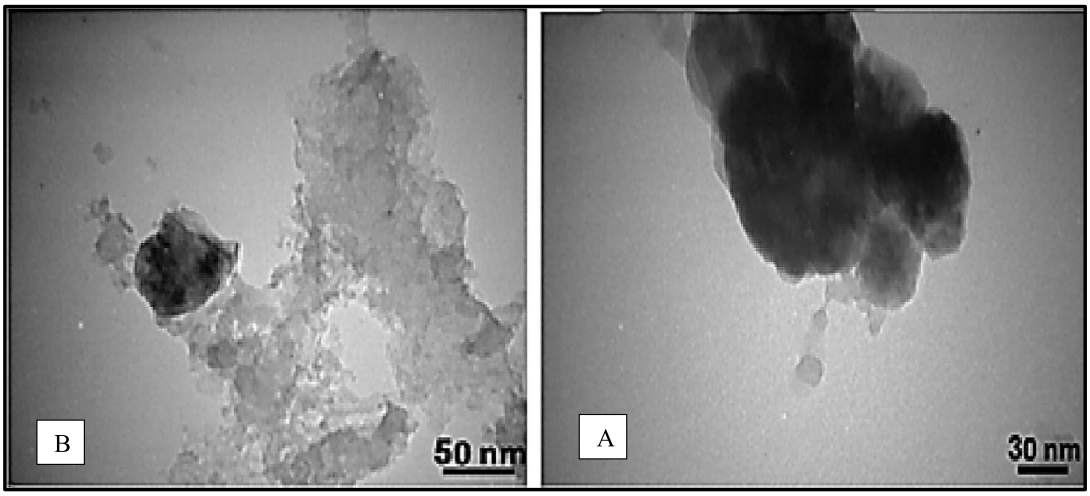


Fig. 11. The TEM images of activated CQD’s with acid vapor

of CQD have formed a mass of carbon and in Fig. 10(A) formation of very small particles of CQD is clearly visible.

TEM images of the activated samples with acid vapor have been shown in two different magnified (Fig.s 11A and 11B); this figure also shows the mass of CQD in great amount in very small size.

In Fig. 12, activated samples with KOH is shown, which indicates the size of CQD to be smaller than 10 nanometers. The TEM image of activated samples with ionic liquid is shown in Fig. 13. The size of nanoparticles of CQD is less than 10 nanometers which is mass of carbon; the particles

TEM images and the data gained from FESEM prove that the particles of CQD were synthesized successfully. The size of nanoparticles of CQD is very small (5 to 10 nanometers), which was developed with the use of the activation process with KOH and ionic liquid. As mentioned before, activation processes and activation had no damage to the prime structure of CQD and only active groups got on the sample area which was proved from FTIR results. The active groups and the area size and distribution of pores are of great importance in the adsorption process.

The study time effect on the amount of benzene elimination

Time is one of the effective factors on the process of adsorption. In this step the effect of

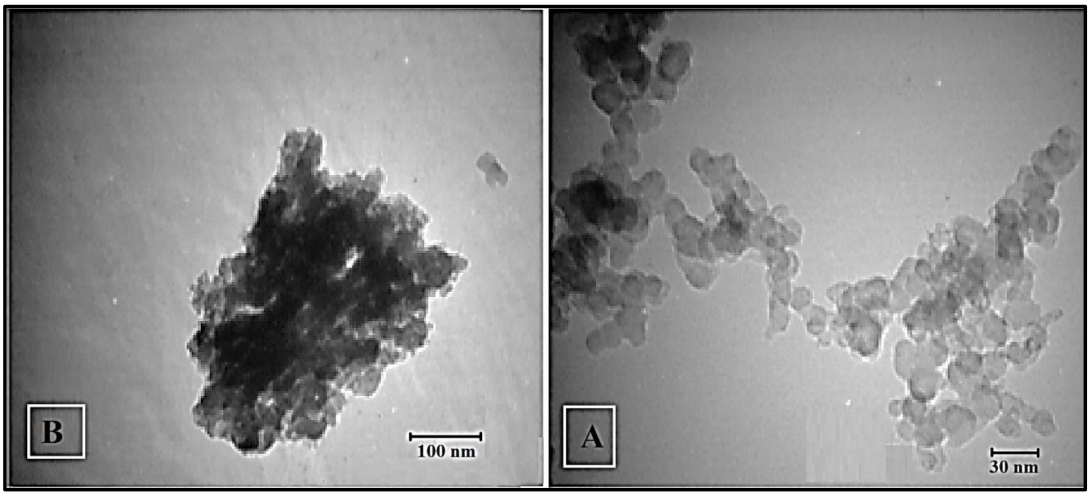


Fig. 12. The TEM images of activated CQD’s with KOH

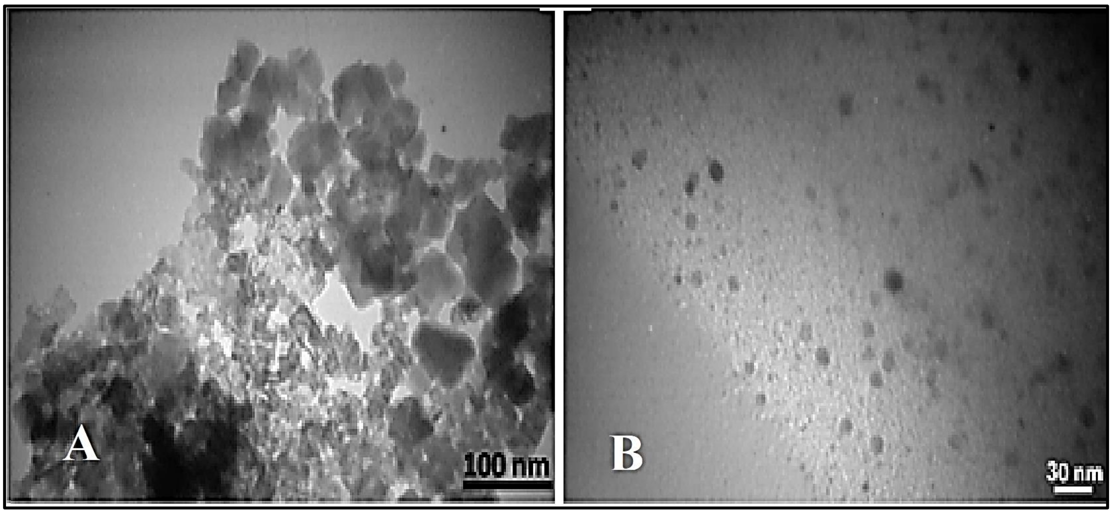


Fig. 13. The TEM images of activated CQD’s with ionic liquid

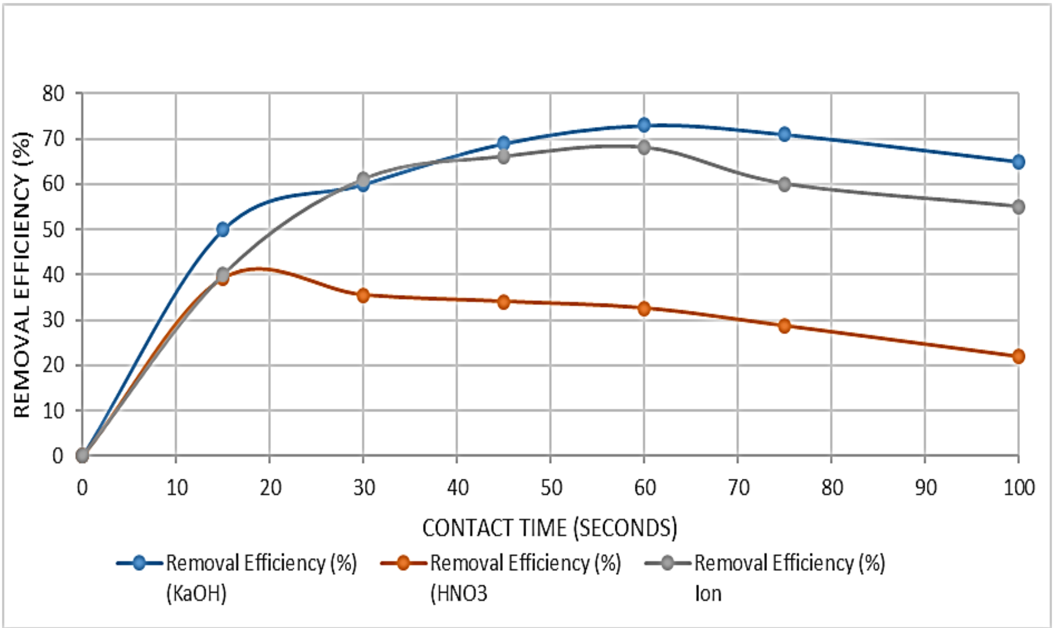


Fig. 14. The effect of contact time on the amount of absorbing benzene by three adsorbents

time on the feedback of benzene adsorption is studied (the adsorbent in contact time of 1 to 100 seconds at the temperature of 35 °C). In CQDs activated with acid nitric and increasing the temperature adsorption is done quickly first 15 seconds and gets to maximum and by passing some time, the adsorption speed decreases gradually. The reason of increasing adsorption in the prime steps is due to chemical bonds available, but it does not go on due to limitations of the specific area and saturation of process which stops after 15 seconds. On the basis of this result, the optimum time of adsorbent was chosen 15 seconds for CQDs activated with nitric acid. In

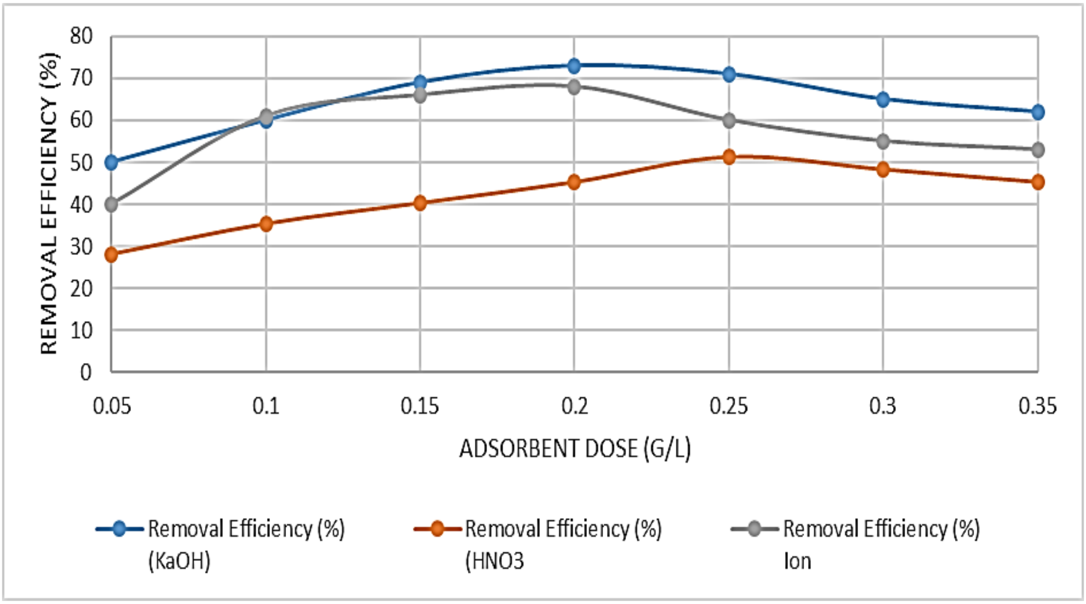


Fig. 15. The effect of the amount of adsorbent on the efficiency process of the benzene elimination by the three adsorbents

CQDs activated with ionic liquid with increasing the time, it started from first 15 seconds and got to 60 seconds to maximum and by passing some time the adsorption speed decreases gradually. In this condition, suitable pores comparing the previous sample didn't get to maximum because of a specific area of the adsorbent and delayed saturation. In the adsorbent of CQDs activated with KOH, increasing the adsorption starts from the first 15 seconds and gets to maximum into 60 seconds and then the speed decreases. On the basis of these tests, the optimum contact time is set to be 60 seconds to prevent the quick saturation of the adsorbents (Fig. 14).

The effect of the amount of adsorbent on the efficiency

To study the effect of adsorbents on the process of elimination of the benzene concentration, different amounts of adsorbents like 0.05 to 0.35 grams with time contact of 60 seconds with a prime concentration of benzene of 0.05 mg/L at the temperature of 35 °C was experimented.

The gained results for three adsorbents were studied. The increase of adsorbent causes percentage of benzene elimination. The adsorbent is the CQDs activated with nitric acid vapor. The amount of adsorbent starts the process up to 0.25 grams and that the efficiency of elimination gets fixed and decreases. The same condition applies to CQDs activated with KOH and ionic liquid as well. Considering the samples, the maximum adsorption at concentration of 0.2 grams is deemed the optimum for experiments. This process can be due to availability activated adsorbent site, with the number of adsorbents. The most percentage of benzene elimination is 70% for CQDs activated adsorbent with KOH and the least elimination will be for CQDs activated with nitric acid vapor equal to 51% (Fig. 15).

The study of moisture and temperature on adsorbent

Testing was carried out on three adsorbents in 2 conditions of moisture above 50% and below 50% with fixed conditions. As we found out in the previous steps, lower densities of benzene were used to study. The effect of moisture and temperature on the adsorbent are due to quick saturation of adsorbent CQD activated with nitric acid vapor. The result showed that the amount of adsorption for adsorbent CQD activated with KOH decreases, but this amount is less than the activated adsorbent with nitric acid and the reason is due to solubility of both two adsorbents in water which causes the decrease in benzene adsorption capacity.

In the sample of CQD activated with ionic liquid at moisture of more than 50%, the amount of adsorption reduces but this amount is much less than two other adsorbents and the reason is due to resistance of the ionic liquid compound against

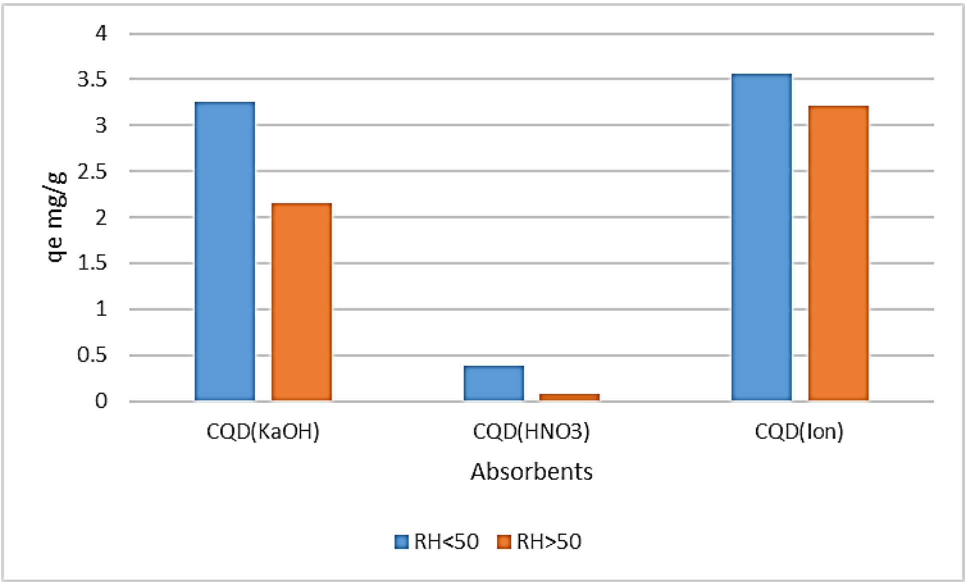


Fig. 16. The effect of moisture on the amount of benzene adsorption by adsorbent

the solubility in water (Fig. 16).

Then, the effect of temperature changes under a constant condition was investigated. The amount of adsorption at two temperatures of 10 °C and 35 °C were assessed. The amount of adsorption of CQD activated with nitric acid decreases at above 35 °C. This amount of decrease starts from 10 °C and increases with temperature.

In CQD-IL the amount of adsorption increases and it starts from 10 °C and increases accordingly with temperature. This adsorbent is resistant against temperature changes. The same result was observed for CQD activated with KOH which shows the amount of adsorption at temperatures of 10 °C and 35 °C range were assessed. In this test the amount of adsorption increased proportionally with temperature; but with the increase of temperature above 60 °C the amount of adsorption decreases and it has less resistance to temperature compared with CQD activated by Ionic liquid (Fig. 17).

The comparison of Average pore diameter and coefficient correlation of three revised adsorbents prepared from prime CQDs of olive stones

As it can be observed in the table 1, analysis of Brunauer-Emmett-Teller (BET) was done for three adsorbents; the prime sample of CQD had a very low specific area. Consequently, three different processes were done on them to increase the specific area and porosity which were explained in synthesis part in detail. All three samples had a very good area property than prime CQD which was very effective in the increasing the area, volume of porosity, improving the function of adsorbents. The sample CQD (HNO_3) showed a less

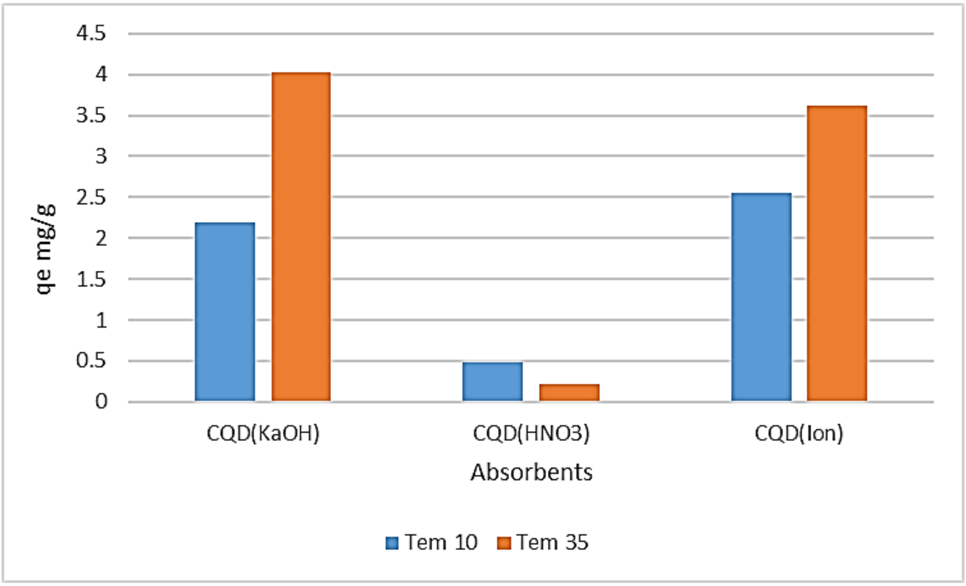


Fig. 17. The effect of temperature on the amount of benzene adsorption by adsorbent

Table 1. The area of samples specification

Average pore diameter (nm)	Total pore volume (cm^3 /g)	specification area (m^2 /g)	
36.927	0.0042	0.464	CQD
3.934	0.114	116.17	CQD-HNO_3
12.622	1.654	524.36	CQD-Ion
3.158	0.434	550.47	CQD (KOH)

specific area -equal to 116 m^2/g; additionally, the total volume of the porosity is 0.11 cm^3/g and the average diagonal is 3.93 nm. The size of adsorbent pores of KOH samples were approx 1.21 to 10 nanometers. CQD (KOH) had the most specific area which was 550 m^2/g and the volume of total porosity was 0.43 cm^3/g. Contrary to activated CQD (HNO_3), the activated sample with ionic liquid had a very large specification area. The specific area was 524 m^2/g and total volume of porosity 1.65 cm^3/g and average size of pores 12.63 nm. The CQD (HNO_3) and CQD (KOH) had the same distributed size of pores despite the difference in specification area. The average diagonal of

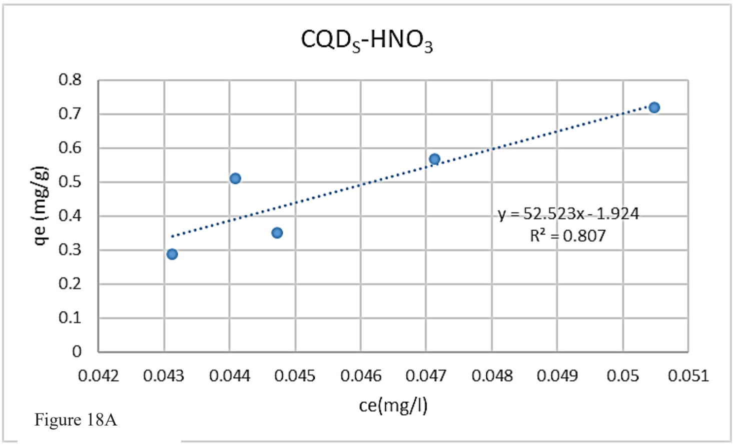


Figure 18A

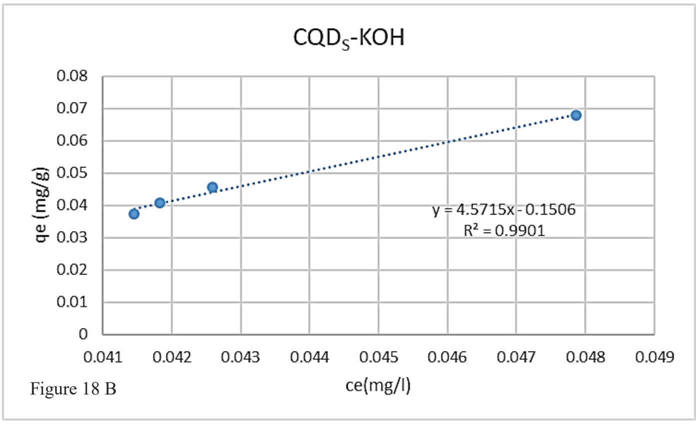


Figure 18 B

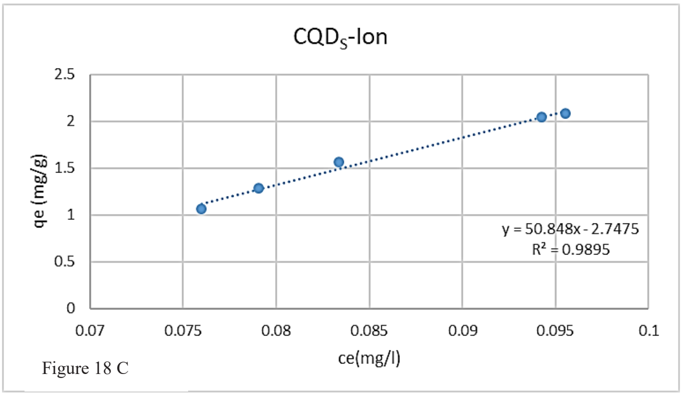


Figure 18 C

Fig. 18. The Comparison of Isotherm and coefficient correlation of three revised adsorbents prepared from prime CQDs of olive stones

Table 2. Comparisons in pollution removal by different adsorbents made from olive stone

Activation method	Pollutant	AC	RE	Area m^2/g	Ref
CQDS-KOH	Benzene	0.02	73	550	This research
CQDs-Ion	Benzene	0.02	68	524	This research
CQDS-HNO_3	Benzene	0.025	51	116	This research
Chemical (KOH)	Toluene	720	Not mentioned	883	(46)
Chemical (HNO_3)	Lead (II)	15.33	Not mentioned	2.45	(41)
Chemical (NaOH)	Lead (II)	16.25	Not mentioned	0.25	(41)
Chemical (H_3PO_4)	Cyanide	57.35	Not mentioned	680	(49)
H_3PO_4+ 3 MHNO₃	Phenol	24.39	Not mentioned	614	(47)
H_3PO_4) + HNO_3	Cobalt (II)	14.08	Not mentioned	173	(50)
Washing (ethanol)	Chloro-phenols	1.09	67-84	78	(51)

CQD (Ion Liquid) had completely different size of pores and completely different from the other two samples and was 12.62 nm. The most volume of porosity in this sample was 1.65 cm^3/g comparing the other samples. This increase was due to activated groups which were caused in revising the adsorbent and caused space in nano-adsorbent.

The graph for benzene adsorption isotherm of the three adsorbents in Fig. 14 and15 showed, the R^2 amounts and equation of isotherms based on benzene adsorption have been drawn. As you may observe the amount of benzene adsorption by CQD-HNO_3 which has the least coefficient of correlation with R^2 and its amount equals to 0.807 (Fig. 18 A); for CQDs-KOH amount of R^2 is 0.990 as the maximum amount (Fig. 18 B). The CQD-Ion coefficient of correlation with R^2 is 0.989 and has little difference with KOH (Fig. 18 C).

The comparison of different adsorbents prepared from olive stones for pollutants adsorption

As mentioned in the introduction of the article, limited research has been done on the carbon adsorbents made of olive stones to eliminate the benzene vapor and this is the first research in its kind. In Ubago-Pérez and his colleague's article, the chemical activation of olive stones with the help of KOH to eliminate Toluene was presented. In this article the elimination efficiency was not specified but the specific area of the adsorbents is 883 m^2/g and focused on KOH which is the cause of increasing the adsorbents area and this is the core of the article (46). In another research by Soudani and colleagues chemical activation with KOH was done to eliminate Phenol and specific areas increased from 13 to 1242 m^2/g (47). In this method, the established area was larger than the similar ones. Blázquez and colleagues activated the olive stone with NaOH but it had a very small area (48). El-Sheikh and colleagues used easier methods like washing with Ethanol to eliminate Nitro phenol, but in this method specific area of the adsorbent was about 78 m^2/g.

All of the methods and specifications can be observed in Table 2-2. The chemical activation of olive stones was done by phosphoric acid, Nitric acid, sulfur acid, KOH and NaOH and even the combination methods. As it is clear the activated carbon in these methods have adsorption, pores and adsorption structure but in most of the articles all adsorbents were used to eliminate pollutants in water area.

CONCLUSIONS

Three revised adsorbents on the basis of CQDs from olive stones to eliminate the benzene area vapor were studied. CQDs-HNO_3 adsorbent had no suitable capacity to absorb benzene in the first 15 seconds and the process 15 mg/L of saturation. The CQDs -KOH has a high efficiency and is the best and suitable adsorbents at 35 °C, moisture below 50% and the most efficient for removal of benzene in 60 seconds with the amount of 20 mg/L adsorption. The maximum percentage of benzene elimination is 70% for CQDs -KOH. CQDs -Ion in comparison to the prime adsorbent has more adsorption capacity to eliminate benzene and by adding more adsorbent more adsorption will result; this process was slower in the prime adsorbent. Considering the results, this adsorbent is the suitable one to eliminate benzene from air at high temperature and moisture. The CQDs -Ion activated sample has a very different pore size compared to other adsorbents. The results show that Ion liquid caused nitrogen groups to enter the CQDs structure in addition to creation of carbon- Fluorine groups. The result of FTIR shows that the process of activation and functionalization have no damage to the prime structure of CQDs and factorial groups lay on the surface of samples. Factorial groups, surface area, pore size distribution is important in the process of adsorption. Having studied the different articles on activation methods of olive stones, the following limitations have been shown and they include temperature of activation, the amount of activation concentration, efficiency, and gas flow speed. Most of the testing in this regard has been in the watery area and little research has been done to eliminate benzene of gas flow. The CQDs -KOH adsorbent has the most efficiency and has the best adsorbent function and the suitable one in adsorption of benzene compounds.

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CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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