



Removal of ethylbenzene from air by graphene quantum dots and multi wall carbon nanotubes in present of UV radiation

Maling Gou^{a,b} and Baharak Bahrami Yarahmadi^{c,*}

^a State Key Laboratory of Biotherapy and Cancer Center, West China Hospital, Sichuan University and Collaborative Innovation Center for Biotherapy, Chengdu 610041, China

^b Department of Thoracic Oncology, Cancer Center, West China Hospital, Medical School, Sichuan University, Chengdu 610041, China

^{c,*} Occupational Health Engineering Department, School of Public Health, Kerman University of Medical Sciences, Kerman, Iran

ARTICLE INFO:

Received 12 Sep 2019

Revised form 15 Nov 2019

Accepted 5 Dec 2019

Available online 28 Dec 2019

Keywords:

Graphene quantum dots,
Multi wall carbon nanotubes,
Ethylbenzene,
Air removal,
UV-radiation,
Solid gas removal

ABSTRACT

Luminescent graphene quantum dots (GQDs) and multi wall carbon nanotubes (MWCNTs) as photocatalytic sorbent based on was used for removal of toxic ethylbenzene from air in present of UV-radiation. A novel method based on solid gas removal (SGR) based on GQDs and MWCNTs as an efficient adsorbent was used for ethylbenzene removal from air in Robson quartz tubes (RGT). After synthesized and purified of GQDs and MWCNTs, a system was designed for generation of ethylbenzene in air with difference concentrations, and then the mixture was moved to quartz tubes with UV radiation in optimized conditions. The ethylbenzene in air was absorbed on the 25 mg of GQDs or MWCNTs, desorbed from sorbent at 146°C and determined by GC-FID. The main parameters such as, temperature, ethylbenzene concentration, amount of GQDs / MWCNTs and flow rate were studied and optimized. The recovery of ethylbenzene removal from air (more than 95%) and absorption capacity of adsorbent (186.4 mg g⁻¹) were achieved in present of UV radiation at room temperature by GQDs. The flow rate and temperature were obtained at 300 mL min⁻¹ and less than 42 °C, respectively. Based on results, the special surface area and favorite porosity of GQDs caused to efficient removal of ethylbenzene from air in present of UV as compared to other carbon compounds such as MWCNTs, and graphene.

1. Introduction

One of the most important issues facing human beings today and even endangering their health is air pollution. Volatile organic compounds (VOCs) are one of the most important pollutants, and these compounds are listed as toxic [1, 2]. Global warming, ozone depletion, photochemical smog, and contributor of haze is the effect of this material [3, 4]. The boiling point range of volatile organic compounds is from 50 to 250 °C and because of

high vapor pressure creates a notable amount of the molecules to evaporate and release in the air [5, 6]. Their health effects on humans are very important, these compounds can irritate the respiratory system and eyes, cause headaches and nausea, damage the kidneys, liver, the central nervous system and even in chronic exposure cause cancer [7-10]. Some of the major industries producing volatile organic compounds include petroleum refineries, chemical industries, automotive industries, paint industry, pharmaceuticals, cable and wire industries, printing, aerospace, textile, etc. [1, 11]. BTEX (Benzene, toluene, ethylbenzene, and xylene) are the most common VOCs and usually used in the

*Corresponding Author: Baharak Bahrami Yarahmadi

Email: baharakb72@gmail.com

DOI: <https://doi.org/10.24200/amecj.v2.i04.82>

petrochemical industry and as reagents for the synthesis of multiple C-based products [11-13]. Among BTEX, ethylbenzene is mainly used in the manufacture of styrene. The release of Ethylbenzene into the air could be carcinogenic, cause secondary aerosol and photochemical smog. Ethylbenzene is a colorless liquid that smells like gasoline. The odor threshold for ethylbenzene is 2.3 parts per million (ppm). The chemical formula for ethylbenzene is C_8H_{10} , and the molecular weight is $106.16 \text{ g mol}^{-1}$. The vapor pressure for ethylbenzene is 9.53 mm Hg at $25 \text{ }^\circ\text{C}$, and its octanol/water partition coefficient is 3.13. In petrochemical factories, BTEX and mercury vapor released in air and can be absorbed in humans via the inhalation and dermal routes of exposure. So determination BTEX and mercury in air, water and human matrixes is very important [14-17]. Previous study reported the carcinogenic effects of ethylbenzene in humans. EPA has classified ethylbenzene as a Group D, not classifiable as to human carcinogenicity. ACGIH recommends a TLV-TWA of 100 ppm and STEL/C of 125 ppm for ethylbenzene based on irritation and central nervous system effects [18-20]. Acute (short-term) exposure to ethylbenzene in humans results in respiratory effects, such as throat irritation and chest constriction, irritation of the eyes, and neurological effects such as dizziness. Chronic (long-term) exposure to ethylbenzene by inhalation in humans has shown conflicting results regarding its effects on the blood. Animal studies have reported effects on the blood, liver, and kidneys from chronic inhalation exposure to ethylbenzene [21-23]. There are many successful techniques which have been developed and applied to control the VOCs emission, such as condensation, membrane, absorption, adsorption, thermal combustion, catalytic, photocatalytic oxidation, non-thermal plasma, and biofiltration [24-27]. Photocatalytic oxidation (PCO) as the most current generation of air cleaning technology has a magnificent potential to eliminate vaporous pollutants even at low concentrations [28]. Exceptional features of this method are operating at ambient temperature without notable energy supply, environmentally

friendly final products (CO_2 and H_2O), and applicable for various pollutants [29]. PCO implemented using photocatalyst, ultraviolet (UV) light and oxygen to decay chemical pollutants[30]. Numerous researchers have reviewed the materials for the removal of VOCs [27, 31]. Most sources have been reviewed based on a particular kind of material, such as TiO_2 [32], graphene-based materials [33], zinc indium sulfide [34] and silica-nanosphere-based materials, etc., or concentrating on the catalytic oxidation processes in a specific condition such as low-temperature, visible light, or based on a review of the aspect of different VOCs[35].

In this study, a novel analytical method based on UV- GQDs or UV-MWCNTs was used for ethylbenzene removal from air by SGR technology. All of important parameter for photocatalytic process were optimized and the results validated by spiking standard concentration of ethylbenzene to real samples. The mixture of ethylbenzene vapor in air was generated and storage in polyethylene bags and its concentration determined by GC-MS before moved to quartz tubes. The removal efficiencies were calculated in UV- GQDs, GQDs and MWCNT_s by SGR procedure.

2. Experimental

2.1. Gas Chromatography (GC-FID)

The gas chromatography with flame ionization detector (GC-FID) based on air sample loop injection was used for ethylbenzene determination in gas phase (Agilent GC, 7890A, FID, Netherland). Before injection to GC-FID, Slide the plunger carrier down and tighten. An air sample introduced into the carrier gas by sampling valves which was used to sample gases or liquids. Air sampling bags were used by valve and septum port (Tedlar, Germany). GC with a split injector (200°C), flame ionization detector (250°C), and a column with methylsiloxane was used. The oven temperature was adjusted from 25°C to 250°C which was held for 15 min. The carrier gas of hydrogen with flow rate of 1.2 mL min^{-1} were tuned. For batch system, the vials (PTFE) with air-tight cap (parker) were

prepared. TGS 2180 (China) and Dräger 3500 (Lübeck, Germany) as gas detectors was used for determination of H₂O vapor and O₂ in air. The ethylbenzene was evaporated and mixed with purified air at 135°C in chamber.

2.2. Reagents

The ultra-pure chemicals were purchased from Merck and Sigma Aldrich (Germany). The Deionized Distilled water (DDW) was prepared by (Millipore, CAS 7732-18-5). The standard of ethylbenzene (C₆H₅C₂H₅) was generated with ultra-pure air in chamber. The accuracy and precision of the pilot was investigated by injecting a concentration of ethylbenzene in chamber and determination of ethylbenzene in air bags by GC-MS before moved to RGT which was filled with GQDs or MWCNTs. The high purity of ethylbenzene was purchased from Merck (CAS N: 100-41-4, EC N: 202-849-4, Germany) and the calibration solutions of 0.1, 0.2, 0.5, 1.0, 1.5 and 2.0 % (v/v) were prepared. The GQDs and MWCNTs were synthesized by RIPI.

2.3. Pilot of gas generation

By pilot design, the purified air was prepared based on HEPA filter *and* activated carbon (HEPA-AC) with *electro air cleaner (EAC, Canada)*. The HEPA-AC removed VOCs and the particles dust from 200 to 300 nm. The pure air passed through

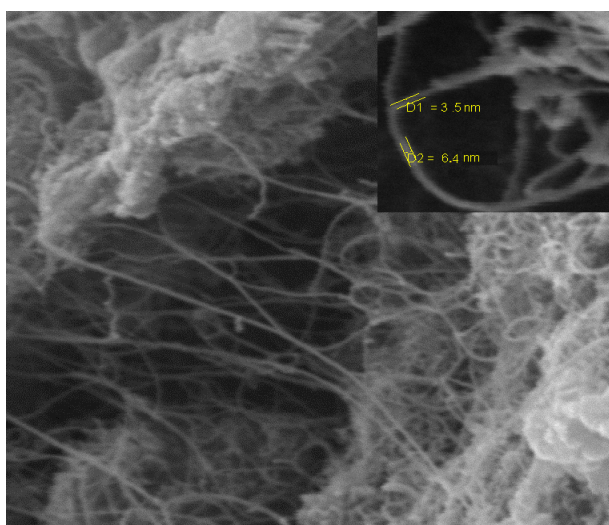


Fig. 1a. SEM of MWCNTs

connection of PVC tubes and storage in 1-5 liter of bulk bag. After adjusting of H₂O, the mixture moved to GQDs or MWCNTs in optimized flow rate and temperature. All of lines and bags were covered with heating jackets capable of controlling the temperature up to 70 °C to prevent condensing.

2.4. Synthesis of LGQDs and MWCNTs

High-purity MWCNTs were synthesized by use of camphor, an environment-friendly hydrocarbon as a carbon source using chemical vapor deposition (CVD) method on Co-Mo/MgO Nano-catalysts [36]. We prepared GO from graphite adopting a modified Hummers' method [37, 38]. The GO was used for synthesizing of GQDs by Dong et al. Firstly, the amount of GO was refluxed with HNO₃ (10 M) at 120°C for one day. When the reaction was completed the color of solvent darkened. Then, the suspension was centrifuged for 15 min after being cooled at 25°C. The suspension was collected after washing of product with DW and then centrifuged. Secondly, the obtained GO was dispersed in 20 mL DW, heated hydrothermally in a Teflon-lined stainless steel at 220°C for 10 hours and centrifuged (3500) for 20 min (brown color). So, GQDs were obtained in this procedure by green fluorescence under 365 nm UV light irradiation [39].

2.5 Characteristics

After hydrothermal method for synthesis nano

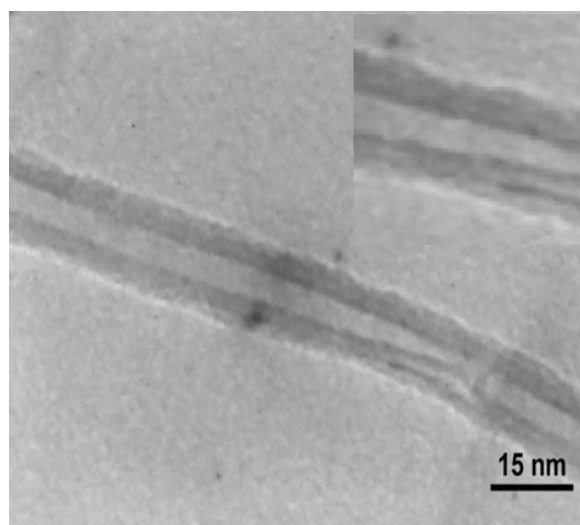


Fig. 1b. TEM of MWCNTs

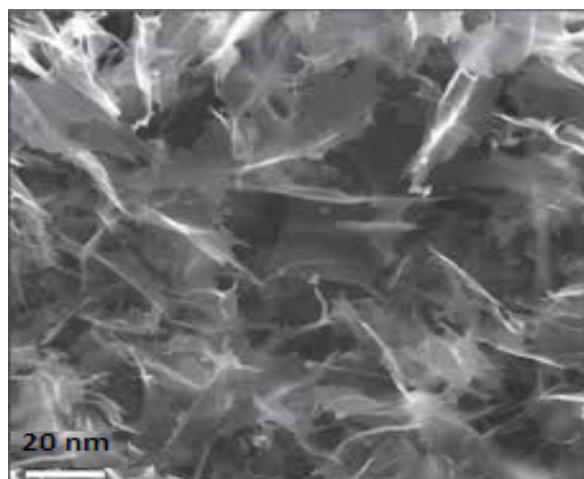


Fig. 2a. SEM of GQDs

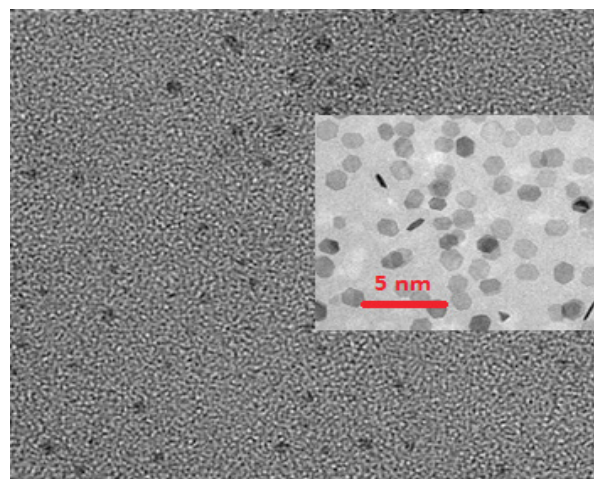


Fig. 2b. TEM of GQDs

materials, the SEM and TEM images of the MWCNTs and GQDs were shown in Figure 1 (a, b) and 2(a, b). The surface area and pore size of GQDs and MWCNTs based on nitrogen adsorption was evaluated by Brunauer-Emmett-Teller (BET) method. The surface area and porosity of the MWCNTs and GQDs, before and after heat treatment were similar values. Raman spectra of GQDs and MWCNTs show the G and D bands that are characteristic for carbon structures. Raman spectra show quality of nanostructure which was deepened on I_G/I_D (Fig. 3). The pore size, length, BET surface area and textural properties of GQDs and MWCNTs were shown in Table 1 and 2.

2.6. Removal Procedure

The 25 mg of different GQDs and MWCNTs, was used as sorbents for removal of ethylbenzene from air in optimized conditions (flow rate 300 mL min⁻¹, 42 °C). The different concentration of ethylbenzene in air (bulk bag) was passed through the GQDs and MWCNTs sorbents. After efficient adsorption in present of UV radiation, the ethylbenzene concentration in air was determined by GC-FID. Also, the removal efficiency calculated after desorption of ethylbenzene from GQDs and MWCNTs by thermal accessory at 150 °C. For sample blank, 1 mL of air in bulk bag was injected

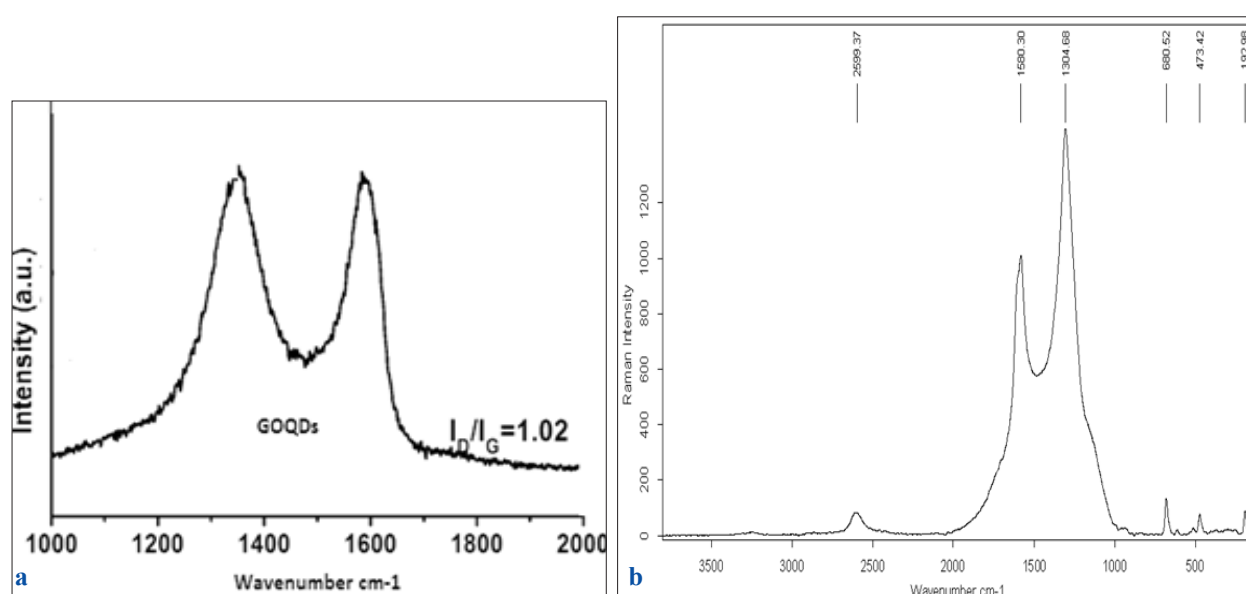


Fig. 3. Raman spectroscopy of a) GQDs and b) MWCNTs

Table 1. Textural properties of GQDs and MWCNTs

Carbon	S_{BET}^a (m ² /g)	d_{sp}^b (nm)	d_p^c (nm)	V_{sp}^d (cm ³ /g)	V_{lp}^e (cm ³ /g)	PA (A)
MWCNT	375	5.54	15.08	0.51	1.04	117.52
GQDs	343	4.65	14.17	0.53	0.89	101.18

^aBET specific surface area, ^bdiameter of small pores, ^cdiameter of large pores, ^dVolume of small pores, ^eVolume of large pores, pore Diameter (PA)

Table 2. Pore size, length and BET surface area of GQDs and MWCNTs

Carbon	Diameter (nm)	Length (um)	I_G/I_D	Surface Area (m ² /gr)
MWCNT	4-20	8-14	0.77	375
GQDs	3-15	8-12	0.68	346

*(IG/ID): LG band originates from ordered, well-graphitized carbon, D band is the disorder-activated band

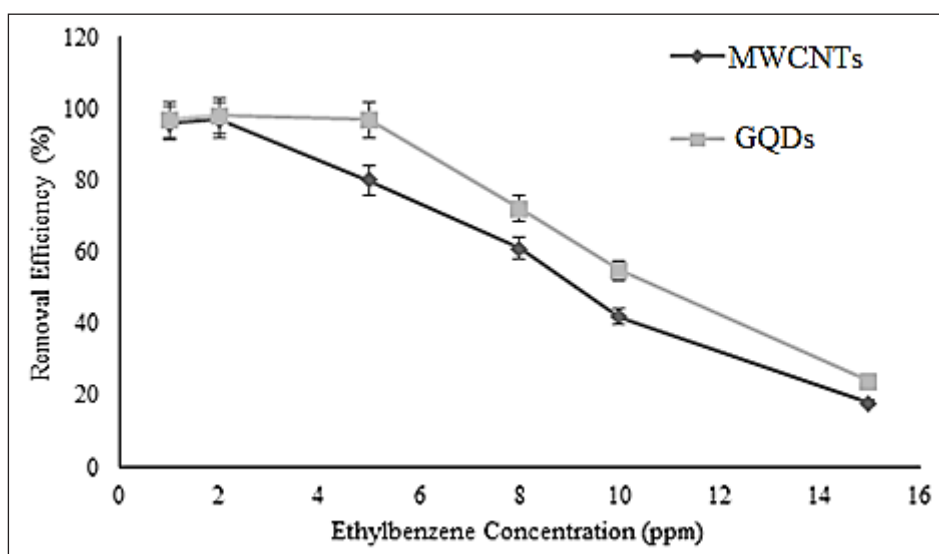
to injector of GC-FID by Hamilton syringes and the concentration of ethylbenzene was determined by GC-FID and GC-MS (Agilent 7890A, USA). So, SGR procedure based on GQDs can be efficiently removed ethylbenzene from air.

2. Results and Discussion

3. 1. Optimizing of parameters

In optimized conditions, the adsorption capacity of ethylbenzene in an air is the amount of adsorbate ethylbenzene (mg) on GQDs sorbent (g). The removal efficiency of GQDs is the ratio of removed ethylbenzene to initial ethylbenzene concentration in air. The removal efficiency and adsorption capacity are depended on the important parameters

such as; kind of sorbent, size of nanoparticles, temperature, flow rate, ethylbenzene concentration and humidity which were optimized. The effect of ethylbenzene concentration was investigated by SGR method from 1.0 to 100 ppm. The results showed us, high concentration of ethylbenzene, based on the GQDs was saturated early graphene dot sites. In optimized conditions, the ethylbenzene concentration for 25 mg of GQDs and MWCNTs was achieved, 4.66 ppm and 2.54 ppm, respectively in 25°C (Fig. 4). So, the absorption capacity was achieved 186.4 mg g⁻¹ and 102.4 mg g⁻¹, respectively (Fig. 5). For ethylbenzene removal from air, the effects of humidity on removal efficiency of GQDs and MWCNTs were studied between 10% - 70%.

**Fig. 4.** The effect of ethylbenzene concentration on air removal

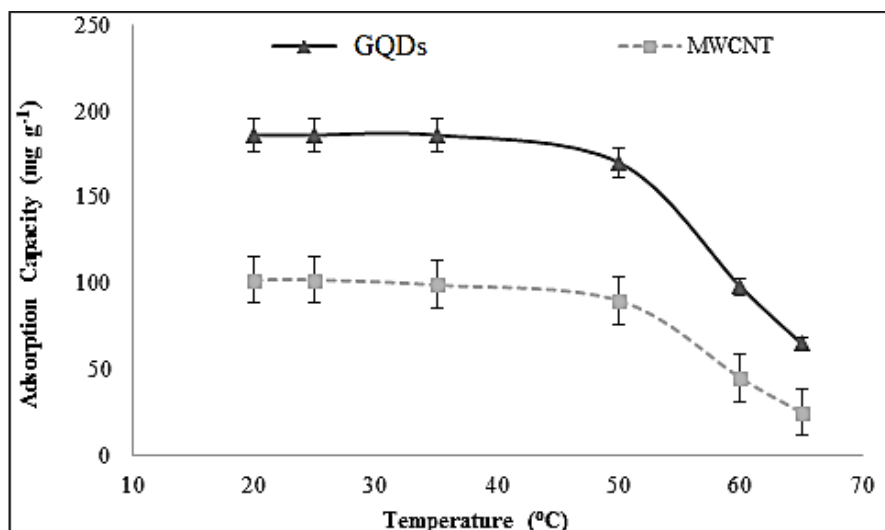


Fig. 5. The effect of temperature on adsorption capacity for ethylbenzene removal from air by GQDs

The results showed, by increasing of humidity up to 10%, the removal efficiency wasn't decreased. The temperature has effected on adsorption capacity and recovery of GQDs for ethylbenzene removal from air. The effect of temperature was studied between 25–150 °C. The results showed us, the adsorption efficiency of ethylbenzene by GQDs was achieved under 420 °C and desorption was obtained at 146°C (Fig. 6). In optimized flow rate value, the maximum recovery was happened by GQDs by SGR procedure. So, the effect of different flow rates between 50 to 800 mL min⁻¹ was evaluated

based on GQDs for ethylbenzene removal from air. The results showed, the recovery of removal was decreased in more than 350 mL min⁻¹. Therefore, 300 mL min⁻¹ was selected as optimum flow rate (Fig. 7). The inside of quartz tubes was filled with GQDs and MWCNTs as a sorbent for ethylbenzene removal from air. Diameter and length of quartz tubes and physical and chemical properties of GQDs and MWCNTs is important factor for adsorption efficiency of ethylbenzene which must be optimized. Based on results, 0.3 cm of diameter and 5 cm of length selected as optimum column for

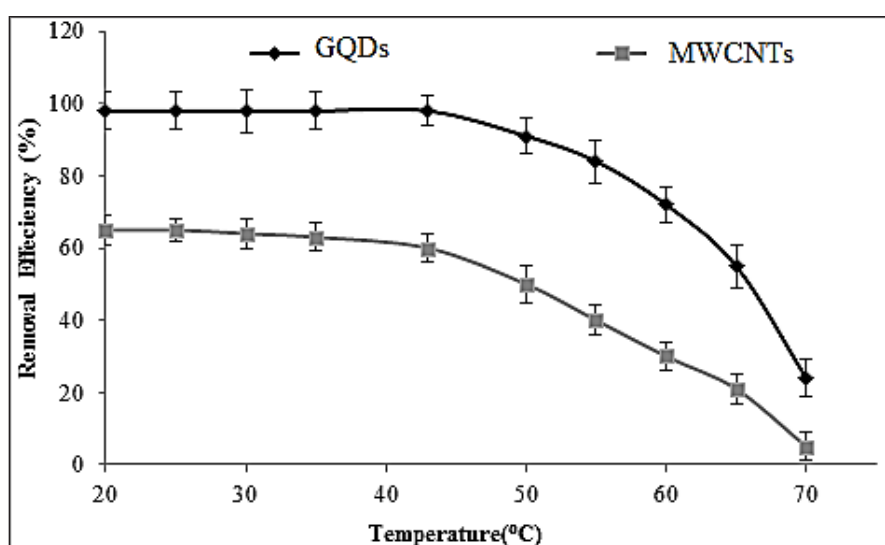


Fig. 6. The effect of temperature on ethylbenzene removal from air by GQDs

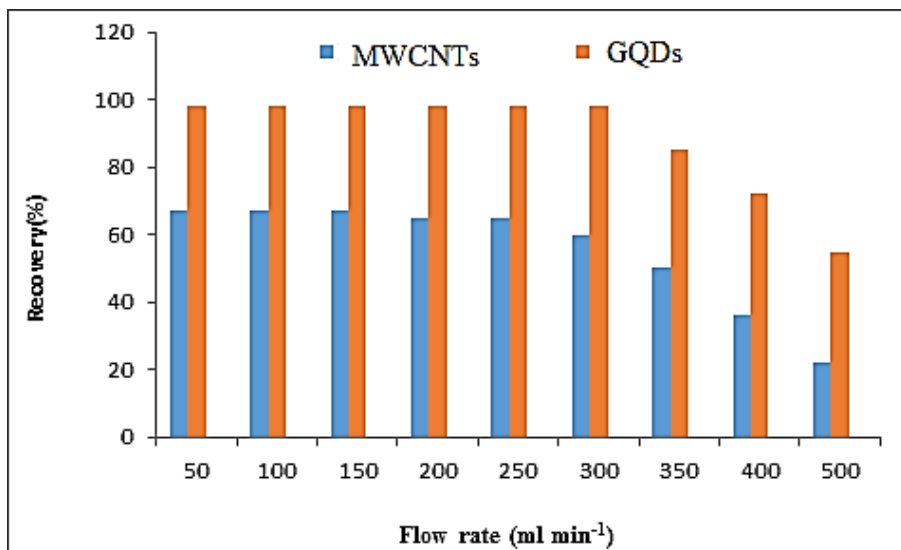


Fig.7. The effect of flow rate on ethylbenzene removal from air by GQDs

further study.

3.2. Analyzing and Validation

The GQDs was selected as a novel sorbent for removal of ethylbenzene vapor from air in present of UV radiation by SGR method. By procedure, a mixture of 1–100 ppm of ethylbenzene in air which was generated in chamber was validated by GC-MS and then, passed through GQDs. After absorption ethylbenzene on GQDs at room temperature, the ethylbenzene desorbed from it at 146°C and determined by GC-FID. Since, the standard reference material (SRM) for ethylbenzene in air aren't available, the standard ethylbenzene concentration was generated in a bag (5 Li) by

chamber and used for validation by spiking of real samples (Table 3).

3.3. Discussion

Fei Yu et al. investigated the removal of TEX from aqueous system by the functionalized magnetic nanoparticle-carbon nanotubes composites that were synthesized, characterized and applied. The APCNTs-KOH composites exhibited high adsorption capacity for TEX onto APCNTs-KOH in a decrease order of ethylbenzene > m-xylene > o-xylene > p-xylene > toluene (227.05, 138.04, 63.34, 249.44, and 105.59 mg g⁻¹), which was higher than current study [40]. In another research,

Table 3. Validation of methodology with GC-FID/SGR for ethylbenzene removal from air by UV-GQDs (ppm)

* Bag GC-MS	Added Ethylbenzene	UV-GQDs ^a	Recovery (%)
1.38 ± 0.08	-----	1.34 ± 0.09	97.1
	1.0	2.32 ± 0.12	98.0
5.58 ± 0.31	-----	5.51 ± 0.32	98.7
	5.0	10.38 ± 0.47	97.4
10.43 ± 0.44	-----	10.07 ± 0.52	96.5
	10.0	19.96 ± 0.93	98.9
20.65 ± 1.02	-----	19.89 ± 1.13	96.3
	20.0	40.11 ± 2.15	101.1
80.48 ± 3.88	-----	78.65 ± 4.23	97.7
	80.0	157.33 ± 7.86	98.4

^a Mean of three determinations ± confidence interval (P = 0.95, n = 5)

* (Air bag; 1-80 ppm in 5 Li bag, 300 mL min⁻¹ air flow rate, Peak Area, 25 mg, T=25°C)

Natarajan et al. used the biofiltration method for the removal of the ethylbenzene-xylene mixture while the total inlet loading rate range was 25.408 g m⁻³ per hour. The maximum removal capacities attained for ethylbenzene and toluene were 85.63 and 63.2 g m⁻³ per hour respectively, which was lower than our proposed method. The elimination capacities were evaluated at different loading rates and found to vary in a linear pattern. Based on result removal capacities was lower than this study [41]. Ye and Ariya used Fe₃O₄ nanoparticles (NPs) at different relative humidities (RH) as adsorption for removal of gaseous benzene, toluene, ethylbenzene and m-xylene (BTEX) and sulfur dioxide (SO₂). X-ray diffraction, Brunauer–Emmett–Teller, and transmission electron microscopy were deployed for nanoparticle surface characterization. Using gas chromatography equipped with flame ionization detection, Adsorption experiments of BTEX on NPs were measured, which under dry conditions indicated high removal efficiencies (up to (95 ± 2)%), which are similar to our result [42]. Bina et al. used multi-walled, single-walled, and hybrid carbon nanotubes (MWCNTs, SWCNTs, and HCNTs) for removal of ethylbenzene (EB) from aqueous solution. Ethylbenzene has a higher adsorption tendency on CNTs so that more than 98% of it adsorbed in the first 14 min, which is related to the low water solubility and the high molecular weight. Isotherm's study indicates that the BET isotherm expression provides the best fit for ethylbenzene sorption by SWCNTs [43]. Kamaei et al. used nitrogen-doped commercial TiO₂ nano-catalysts for photocatalytic decomposition of ethylbenzene in the air using a packed-bed annular photoreactor. The removal efficiency of ethylbenzene under UV irradiation using N-doped catalyst was more than 90% for the initial concentrations up to 0.586 gm⁻³ (135 ppm) at 1 min residence time. Moreover the removal efficiency under visible light radiation could be obtained for the initial concentrations up to 0.1 gm⁻³ (about 25 ppm) at 3 min residence time,

which is lower than this article[44]. Hadi et al. used nano-magnetic particles (Fe₃O₄) as an adsorbent to eliminate ethylbenzene from aqueous solutions.

The characterization of the adsorbent was investigated by transmission electronic microscope (TEM) and X-ray diffraction (XRD) pattern. The results showed that the most amounts of ethylbenzene adsorption and distribution ratio in optimum condition were 49.9 mg g⁻¹(which was lower than our method) and, 261.9 Lg⁻¹ respectively. The results explained that the removal rate of ethylbenzene was higher in batch (99.8 %) rather than continuous (97.4%) conditions [8]. Ahmed et al. used nZVI for eliminating benzene, toluene, ethylbenzene, and xylene (BTEX) contaminants from aqueous solutions. X-ray diffraction (XRD), UV spectrophotometry, and scanning electron microscopy (SEM) were used for nZVI characterization. The effects of contact time, initial BTEX mixture concentration, adsorbent dose, temperature, and pH on the amount of BTEX absorbed were studied. The highest removal efficiency of 97% for the BTEX mixture was achieved at a stirring rate of 100 rpm, the temperature of 60°C, and pH 7, which is higher than our study. The minimum effective time for efficient removal was 30 min, while the effective dose for BTEX compounds removal was 0.22 gL⁻¹[45]. Yan et al. used CuMgFe layered double hydroxide (CuMgFe-LDH), for the degradation of ethylbenzene. the degradation efficiency of 0.08 mmol L⁻¹ ethylbenzene was 93.7% under the optimized conditions at 0.2 g L⁻¹, CuMgFe-LDH and 4.0 mmol L⁻¹ persulfate at pH 7.6, which is lower than our result [46]. Azizi et al. used the graphene oxide grafted with polymethyl vinyl ketone and aniline (GO-MVK-ANI), for the elimination of ethylbenzene. The synthesized material was characterized via FTIR, SEM, energy-dispersive X-ray spectroscopy and Brunauer–Emmett–Teller analysis.

Based on the result with initial ethylbenzene concentration of 20 mg g⁻¹ under the optimum

conditions (the contact time of 11 min, pH of 5.64 and adsorbent dose of 3.75 g L^{-1}), ethylbenzene could be adsorbed (73%), which is lower than our result [47]. Samarghandi et al. investigated Catalytic Ozonation Process (COP) to treat polluted air streams containing ethylbenzene. Respectively at 50 ppm of this pollutant, for single ozonation and single modified pumice, the best removal efficiency of ethylbenzene was 58–80%, while the maximum removal efficiency of ethylbenzene was 90% for COP (6 L min^{-1} of flow rate of inlet air, 15 g of the adsorbent, and 50 ppm of ethylbenzene), which is lower than this study [48]. Also samarghandi et al. used ozone and carbosieve in the catalytic removal of ethylbenzene from the polluted airstream. GC – FID was used for sampling and analysis. The results of this study showed that the removal effectiveness of a single ozonation process is averagely less than 25%. Also, with the concentration increase of ethylbenzene the efficiency of adsorbent decreased. The increase ratio of the efficiency in the catalytic ozonation process to the efficiency of carbosieve adsorbent was averagely 45% which is lower than the current study [49].

4. Conclusions

In this study, the GQDs and MWCNTs as nano sorbents were used for ethylbenzene removal from air in present of UV-radiation by SGR method. According to experimental procedure, the simple, reliable and sensitive method based on GQDs was demonstrated in real samples. In optimized conditions, the concentration of ethylbenzene, air flow rate, amount of GQDs and MWCNTs, temperature, and humidity were studied. The results showed, the flow rate (300 ml L^{-1}) can more effected on capacity adsorption by GQDs as physical adsorption. However, in optimized conditions, the removal efficiency and adsorption capacity of GQDs were obtained more than 95% and 186.4 mg g^{-1} , respectively as compared to MWCNTs.

5. Acknowledgments

We are thankful to Kerman University of Medical Sciences (KUMS) and Iranian Petroleum Industry Health Research Institute (IPIHRI).

6. Reference

- [1] R.K. Nath, M.F.M. Zain, M. Jamil, An environment-friendly solution for indoor air purification by using renewable photocatalysts in concrete: A review, *Renew. Sust. Energ. Rev.*, 62 (2016) 1184-1194.
- [2] J. Yan, Y. Chen, W. Gao, Y. Chen, L. Qian, L. Han, M. Chen, Catalysis of hydrogen peroxide with Cu layered double hydroxide for the degradation of ethylbenzene, *Chem.*, 225 (2019) 157-165.
- [3] M. Li, Z. Huang, F. Kang, Progress of volatile organic compounds control technology, *Chem. Ind. Eng.*, 32 (2015) 2-9.
- [4] H. Wang, Z. Xiang, L. Wang, S. Jing, S. Lou, S. Tao, J. Liu, M. Yu, L. Li, L. Lin, Emissions of volatile organic compounds (VOCs) from cooking and their speciation: A case study for Shanghai with implications for China, *Sci. Total Environ.*, 621 (2018) 1300-1309.
- [5] M. Feiz-Arefi, F. Ghorbani-Shahna, A. Bahrami, H. Ebrahimi, A. Mahjub, Photocatalytic Removal of Methylbenzene Vapors by $\text{MnO}_2/\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ Nano composite, *Iran. J. Health Safe. Environ.*, 6 (2019) 1158-1166.
- [6] S. Zhang, J. You, C. Kennes, Z. Cheng, J. Ye, D. Chen, J. Chen, L. Wang, Current advances of VOCs degradation by bioelectrochemical systems: a review, *Chem. Eng. J.*, 334 (2018) 2625-2637.
- [7] A.N. Baghani, A. Sorooshian, M. Heydari, R. Sheikhi, S. Golbaz, Q. Ashournejad, M. Kermani, F. Golkhorshidi, A. Barkhordari, A.J. Jafari, A case study of BTEX characteristics and health effects by major point sources of pollution during winter in Iran, *Environ. pollut.*, 247 (2019) 607-617.
- [8] M. Hadei, M. Aalipour, N. Mengli Zadeh, H. Pourzamani, Ethylbenzene removal from aqueous solutions by nano magnetic particles, *Arch. Hyg. Sci.*, 5 (2016) 22-32.

- [9] A. Masih, A.S. Lall, A. Taneja, R. Singhvi, Exposure levels and health risk assessment of ambient BTEX at urban and rural environments of a terai region of northern India, *Environ. Pollut.*, 242 (2018) 1678-1683.
- [10] L. Wang, C. Yang, Y. Cheng, J. Huang, H. Yang, G. Zeng, L. Lu, S. He, Enhanced removal of ethylbenzene from gas streams in biotrickling filters by Tween-20 and Zn (II), *J. Environ. Sci.*, 26 (2014) 2500-2507.
- [11] A. Carvajal, I. Akmirza, D. Navia, R. Pérez, R. Muñoz, R. Lebrero, Anoxic denitrification of BTEX: Biodegradation kinetics and pollutant interactions, *J. environ. manage.*, 214 (2018) 125-136.
- [12] M.H. El-Naas, J.A. Acio, A.E. El Telib, Aerobic biodegradation of BTEX: progresses and prospects, *J. Environ. Chem. Eng.*, 2 (2014) 1104-1122.
- [13] R. Moolla, C.J. Curtis, J. Knight, Assessment of occupational exposure to BTEX compounds at a bus diesel-refueling bay: A case study in Johannesburg, South Africa, *Sci. Environ.*, 537 (2015) 51-57.
- [14] H.Z. Mousavi, A. Asghari, H. Shir Khanloo, Determination of Hg in water and wastewater samples by CV-AAS following on-line preconcentration with silver trap, *J. Anal. Chem.*, 65 (2010) 935-939.
- [15] H. Shir Khanloo, A. Khaligh, H.Z. Mousavi, M.M. Eskandari, A.A. Miran-Beigi, Ultra-trace arsenic and mercury speciation and determination in blood samples by ionic liquid-based dispersive liquid-liquid microextraction combined with flow injection-hydride generation/cold vapor atomic absorption spectroscopy, *Chem. Paper.*, 69 (2015) 779-790.
- [16] H. Shir Khanloo, M. Osanloo, M. Ghazaghi, H. Hassani, Validation of a new and cost-effective method for mercury vapor removal based on silver nanoparticles coating on micro glassy balls, *Atmos. Pollut. Res.*, 8 (2017) 359-365.
- [17] L. Zhao, X. Qin, X. Hou, Y. Li, K. Zhang, W. Gong, J. Nie, T. Wang, Research on determination of BTEX in human whole blood using purge and trap gas chromatography-mass spectrometry combined with isotope internal standard, *Microchem. J.*, 145 (2019) 308-312.
- [18] Ethylbenzene, International Agency for Research on Cancer (IARC), 77 (2000) 227-266.
- [19] Threshold limit values for chemical substances and physical agents and biological exposure indices, in, American Conference of Governmental Industrial Hygienists (ACGIH), 1995.
- [20] S. Wilbur, S. Bosch, Interaction profile for: benzene, toluene, ethylbenzene, and xylenes (BTEX), Agency for Toxic Substances & Disease Registry (ATSDR), 2004.
- [21] M. Delikhoon, M. Fazlzadeh, A. Sorooshian, A.N. Baghani, M. Golaki, Q. Ashournejad, A. Barkhordari, Characteristics and health effects of formaldehyde and acetaldehyde in an urban area in Iran, *Environ. pollut.*, 242 (2018) 938-951.
- [22] F. Golkhorshidi, A. Sorooshian, A.J. Jafari, A.N. Baghani, M. Kermani, R.R. Kalantary, Q. Ashournejad, M. Delikhoon, On the nature and health impacts of BTEX in a populated middle eastern city: Tehran, Iran, *Atmos. Pollut. Res.*, 10 (2019) 921-930.
- [23] S. Hazrati, R. Rostami, M. Fazlzadeh, F. Pourfarzi, Benzene, toluene, ethylbenzene and xylene concentrations in atmospheric ambient air of gasoline and CNG refueling stations, *Air Qual. Atmos. Health*, 9 (2016) 403-409.
- [24] M. Bahri, F. Haghigat, Plasma-based indoor air cleaning technologies: the state of the art-Review, *Clean Soil Air Water*, 42 (2014) 1667-1680.
- [25] M. Sansotera, S.G.M. Kheyli, A. Baggioli, C.L. Bianchi, M.P. Pedferri, M.V. Diamanti, W. Navarrini, Absorption and photocatalytic degradation of VOCs by perfluorinated ionomeric coating with TiO₂ nanopowders for air purification, *Chem. Eng. J.*, 361 (2019) 885-896.
- [26] K.W. Shah, W. Li, A Review on Catalytic Nanomaterials for Volatile Organic Compounds VOC Removal and Their Applications for Healthy Buildings, *Nanomaterials.*, 9 (2019) 910.
- [27] C. Yang, G. Miao, Y. Pi, Q. Xia, J. Wu, Z. Li, J.

- Xiao, Abatement of various types of VOCs by adsorption/catalytic oxidation: A review, *Chem. Eng. J.*, 370 (2019) 1128-1153.
- [28] L. Zhong, F. Haghghat, Photocatalytic air cleaners and materials technologies—Abilities and limitations, *Buid. Environ.*, 91 (2015) 191-203.
- [29] M. Malayeri, F. Haghghat, C.-S. Lee, Modeling of volatile organic compounds degradation by photocatalytic oxidation reactor in indoor air: A review, *Buid. Environ.*, 154 (2019) 309-323.
- [30] A.H. Mamaghani, F. Haghghat, C.-S. Lee, Photocatalytic oxidation technology for indoor environment air purification: the state-of-the-art, *App. Catal. B: Environ.*, 203 (2017) 247-269.
- [31] M. Hussain, P. Akhter, J. Iqbal, Z. Ali, W. Yang, N. Shehzad, K. Majeed, R. Sheikh, N. Russo, VOCs photocatalytic abatement using nanostructured titania-silica catalysts, *J. Environ. Chem. Eng.*, 5 (2017) 3100-3107.
- [32] C.H.A. Tsang, K. Li, Y. Zeng, W. Zhao, T. Zhang, Y. Zhan, R. Xie, D.Y. Leung, H. Huang, Titanium oxide based photocatalytic materials development and their role of in the air pollutants degradation: Overview and forecast, *Environ. int.*, 125 (2019) 200-228.
- [33] M. Hu, Z. Yao, X. Wang, Graphene-based nanomaterials for catalysis, *Ind. Eng. Chem. Res.*, 56 (2017) 3477-3502.
- [34] Y. Pan, X. Yuan, L. Jiang, H. Yu, J. Zhang, H. Wang, R. Guan, G. Zeng, Recent advances in synthesis, modification and photocatalytic applications of micro/nano-structured zinc indium sulfide, *Chem. Eng. J.*, 354 (2018) 407-431.
- [35] A. Truppi, F. Petronella, T. Placido, M. Striccoli, A. Agostiano, M.L. Curri, R. Comparelli, Visible-light-active TiO₂-based hybrid nanocatalysts for environmental applications, *Catal.*, 7 (2017) 100.
- [36] A. Rashidi, M. Akbarnejad, A. Khodadadi, Y. Mortazavi, A. Ahmadpour, Single-wall carbon nanotubes synthesized using organic additives to Co–Mo catalysts supported on nanoporous MgO, *Nanotech.*, 18 (2007) 315605.
- [37] Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets, *J. Am. Chem. Soc.*, 130 (2008) 5856-5857.
- [38] N.I. Kovtyukhova, P.J. Ollivier, B.R. Martin, T.E. Mallouk, S.A. Chizhik, E.V. Buzaneva, A.D. Gorchinskiy, Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations, *Chem. mater.*, 11 (1999) 771-778.
- [39] Y. Dong, H. Pang, S. Ren, C. Chen, Y. Chi, T. Yu, Etching single-wall carbon nanotubes into green and yellow single-layer graphene quantum dots, *Carbon*, 64 (2013) 245-251.
- [40] F. Yu, J. Ma, J. Wang, M. Zhang, J. Zheng, Magnetic iron oxide nanoparticles functionalized multi-walled carbon nanotubes for toluene, ethylbenzene and xylene removal from aqueous solution, *Chemosphere*, 146 (2016) 162-172.
- [41] R. Natarajan, J. Al-Sinani, S. Viswanthan, R. Manivasagan, Biodegradation of ethyl benzene and xylene contaminated air in an up flow mixed culture biofilter, *Int. biodet. biodeg.*, 119 (2017): 309-315.
- [42] Z.Y. Connie, P.A. Ariya, Co-adsorption of gaseous benzene, toluene, ethylbenzene, m-xylene (BTEX) and SO₂ on recyclable Fe₃O₄ nanoparticles at 0–101% relative humidities, *J. Environ. Sci.*, 31 (2015) 164-174.
- [43] B. Bina, H. Pourzamani, A. Rashidi, M.M. Amin, Ethylbenzene removal by carbon nanotubes from aqueous solution, *J. environ. pub. health*, 2012 (2012).
- [44] M. Kamaei, H. Rashedi, S.M.M. Dastgheib, S. Tasharrofi, Comparing photocatalytic degradation of gaseous ethylbenzene using N-doped and pure TiO₂ nano-catalysts coated on glass beads under both UV and visible light irradiation, *Catal.*, 8 (2018) 466.
- [45] A.S. Mahmoud, M.K. Mostafa, S.A. Abdel-Gawad, Artificial intelligence for the removal of benzene, toluene, ethyl benzene and xylene (BTEX) from aqueous solutions using iron nanoparticles, *Water Suply.*, 18 (2018) 1650-1663.
- [46] J. Yan, Y. Chen, L. Qian, W. Gao, D. Ouyang,

- M. Chen., Heterogeneously catalyzed persulfate with a CuMgFe layered double hydroxide for the degradation of ethylbenzene. *J. hazard. mater.*, 338 (2017) 372-380.
- [47] A. Azizi, A. Torabian, E. Moniri, A.H. Hassani, H. Ahmad Panahi, Investigating the removal of ethylbenzene from aqueous solutions using modified graphene oxide: application of response surface methodology, *Int. J. Environ. Sci. Tec.*, 15 (2018) 2669-2678.
- [48] M.R. Samarghandi, Z. Daraee, G. Shekher, G. Asgari, A. Reza Rahmani, A. Poormohammadi., Catalytic ozonation of ethyl benzene using modified pumice with magnesium nitrate from polluted air. *Int. J. Environ. Stud*, 74 (2017), 486-499.
- [49] M.R. Samarghandi, G. Asgari, F. Ghorbani, S.A. Babae., The study of effect the combined use of ozone and carbosieve in the catalytic removal of ethylbenzene from the polluted airstream, *J. Neyshabur UN. Medical. Sci.*, 5 (2017) 86-98.