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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
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 C₈H₁₀ and the molecular weight is 106.16 g mol⁻¹. The vapor pressure for ethylbenzene is 9.53 mm Hg at 25 °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 (CO₂ and H₂O), 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 TiO₂ [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 MWCNTs 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 H$_2$O vapor and O$_2$ 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 (C$_6$H$_5$C$_2$H$_5$) 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 connection of PVC tubes and storage in 1-5 liter of bulk bag. After adjusting of H$_2$O, 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 HNO$_3$ (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

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**Fig. 1a.** SEM of MWCNTs

**Fig. 1b.** TEM of MWCNTs
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.
to inject 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](image.png)

**Fig. 4.** The effect of ethylbenzene concentration on air removal
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 absorption 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. 5.** The effect of temperature on absorption capacity for ethylbenzene removal from air by GQDs

![Absorption Capacity vs Temperature](image)

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

![Removal Efficiency vs Temperature](image)
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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 * | Recovery (%) |
|------|-------|-------|--------------|-----------|--------------|
| 1.38 ± 0.08 | ------ | 1.0 | 1.34 ± 0.09 | 97.1 |
| 5.58 ± 0.31 | ------ | 5.0 | 2.32 ± 0.12 | 98.0 |
| 10.43 ± 0.44 | ------ | 10.0 | 5.51 ± 0.32 | 98.7 |
| 20.65 ± 1.02 | ------ | 20.0 | 10.38 ± 0.47 | 97.4 |
| 80.48 ± 3.88 | ------ | 80.0 | 19.07 ± 0.52 | 96.5 |

*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)

Fig. 7. The effect of flow rate on ethylbenzene removal from air by GQDs
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 Fe\(_3\)O\(_4\) nanoparticles (NPs) at different relative humidities (RH) as adsorption for removal of gaseous benzene, toluene, ethylbenzene and m-xylene (BTEX) and sulfur dioxide (SO\(_2\)). 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 TiO\(_2\) 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 g m\(^{-3}\) (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 g m\(^{-3}\) (about 25 ppm) at 3 min residence time, which is lower than this article\[44\]. Hadi et al. used nano-magnetic particles (Fe\(_3\)O\(_4\)) 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 L g\(^{-1}\) 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 g L\(^{-1}\)\[45\]. 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 absorbent 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.

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