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Functionalized graphene-trimethoxyphenyl silane for toluene removal from workplace air by sorbent gas extraction method

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A B S T R A C T
Inhalation exposure to toluene in the environment and workplace causes that some concerns about its adverse health effects on public and workers raise. So the implementation of high-performance methods to control toluene emission in industrial and environment settings is very important. Moreover, a new synthesized sorbent based on functionalizing graphene with N-Phenyl-3-aminopropyl trimethoxy silane (G-PhAPTMS, $C_{12}H_{21}NO_3Si$) was developed as a novel sorbent for removal of toluene from air by sorbent gas extraction procedure (SGEP). By proposed method, the removal efficiency of G-PhAPTMS was compared with other sorbents such as activated carbon (AC), graphene (G), and graphene oxide (GO). In addition, the standard gas of toluene generated in pure air with different concentrations, and the effects of parameters such as temperature (10-90 °C), flow rate (50-500 mL min^{-1}) and the amount of sorbent (2-30 mg) were investigated. According to the results, increasing the flow rate and temperature had negative effects on the removal efficiency of all sorbents. The highest removal efficiency of G-PhAPTMS was obtained up to 35 °C and less than 250 mL min^{-1} (>95%). In optimized conditions, the amount of sorbent for toluene removal from air was achieved more than 10 mg of G-PhAPTMS. Finally, the results indicate that the G-PhAPTMS has high removal efficiency and surface area as compared to the AC, G, and GO. Furthermore, functionalizing graphene with N-Phenyl-3-aminopropyl trimethoxy silane improved the absorption of toluene due to chemical bonding (π–π electron donor–acceptor) and introduced an environmentally friendly sorbent.

1. Introduction

Toluene is one of the well-known air contaminants and widely used as an organic solvent in various industries such as petroleum refining, shipping, rubber manufacturing, automobile repairing, and shoe manufacturing [1]. It is estimated that toluene is consumed about 2.3 million tons in worldwide annually [2]. Moreover, public and occupational exposure to toluene can occur through the inhalation of toluene fumes from cigarette smoking and vehicle emission [3]. In addition, it is likely to release from indoor sources such as paints, paint thinners, and adhesives [4].The studies have been shown that chronic exposure to toluene can cause a wide variety of health problems including neurotoxic effects (from headache and fatigue to narcosis with increasing exposure level) and mucosal irritation [5, 6]. Because of the harmful effects of toluene, the implementation of high-performance methods to control toluene emission in industrial and environment settings is inevitable [7]. There are some different methods such as including adsorption, condensation, thermal

oxidation, catalytic oxidation, photo catalytic oxidation and bio filtration that can be applied to reduce the concentration of toluene in air [8-11]. It seems that adsorption as a low operating cost and effective method can be used to remove toluene from air at low concentration[12, 13]. Adsorption is a process in which the molecules of pollutants are trapped at the surface of porous materials such as zeolites, silica gel and activated carbons by physical adsorption [14-16].

Among the different adsorbents, carbon adsorbing materials such as graphene oxide, activated carbons, carbon nanotubes, and porous carbon have demonstrated more advantage due to their low density, chemical stability and variety of structural forms [17-20]. The founding of new carbon materials is always one of the favorite subjects in the process of adsorption and sequestration [21]. Graphene, new two-dimensional carbon nanomaterial, as a new member of the carbon family with desirable properties such as low weight, small size, high surface area, and superior electrical, thermal and mechanical properties has attracted much attention [22-24]. The more advantage of graphene is the adsorption ability of chemicals with benzene rings like toluene through strong π-π interaction [25, 26]. In addition, some functional groups has turned graphene into an excellent adsorbent [27].

On the other hand, graphene has high theoretic surface area up to 2620 m^2 g^{-1} that it become an ideal adsorption [28, 29]. Furthermore, graphene can be easily obtained from the cheap natural graphite in large scale [29, 30]. In this regard, the high adsorption capacity of graphene and its derivatives was confirmed for dyes [31], pharmaceutical antibiotics [32], heavy metals, and VOCs in water [33, 34]. However, the studies on toluene adsorption characteristics and behaviors onto graphene from air are limited [35].

In this study, toluene removed from air based on G-PhAPTMS by SGEP. The different experimental conditions such as mass, flow rate, and temperature were investigated and optimized. By proposed procedure, the chemically adsorption

mechanism of toluene was achieved based on π-π interaction between toluene and the surface of the G-PhAPTMS.

2. Experimental procedure
2.1. Material and Instruments
Toluene was purchased from Fluka (Germany) with purity above 99.5%. In addition, standard gas was obtained by injecting a certain amount of toluene into a 10 ml glass vial with PTFE cap to determine absorption capacity. In this study, helium and pure air were used as the dilution gas. Standard gas was prepared with a relative humidity of 32±5% for simulating the humidity in the workplace air. Thus, before filling the vial, the dilution gas was passed through deionized water. The concentrations of toluene in the standard gas were prepared from 9 to 75 mg L^{-1} (in batch system, high concentration up to 400 mg L^{-1}).

In addition, a dynamic standard gas generation was designed to measure removal efficiency. This system consisted of impinger, adsorption tube, micro compressor, and sampling Tedlar bag (SKC Inc., USA). A certain amount of toluene was injected to the impinger, and then the dilution gas with a certain flow was passed through the adsorption tube. At the end of the system, unabsorbed toluene was collected into the Tedlar bag. The concentration of toluene in the Tedlar bag was measured by gas chromatography equipped with flame ionization detector (GC-FID) and air sample loop injection (Agilent GC, 7890A, FID, Netherland). Also, GC-MS was used for validation toluene concentration in air.

The crystal structure studies of the solids were carried out by X-ray diffractions (PW 1840, Phillips X-ray diffractmeter, Netherland) with Cu-K$_\alpha$ radiation source. Raman spectroscopy was performed using an Almega Thermo Nicolet and 532 nm Ar-ion laser excitation source. The Fourier transform infrared (FT-IR) spectrum was recorded on Bruker IFS 88 spectrometer (Bruker Optik GmbH, Ettlingen, Germany) with KBr pelleting method in the 4000–400 cm^{-1}. The morphology of the sorbent was examined using scanning electron

microscopy (SEM, Phillips, PW3710, Netherland) and transmission electron microscopy (TEM, CM30, Philips, Netherland).

2.2. Synthesis of functionalized graphene with N-Phenyl-3-aminopropyl trimethoxy silane

Graphene (G) was prepared by our special CVD (chemical vapor deposition) method by an electrical furnace consisting of a quartz tube. The furnace heating tuned up to 1000 ºC for 25 min. The reaction between methane and hydrogen (4:1) was obtained. In order to pure grapheme without any metals, the product was stirred in HCl solution (ultra-trace) for about 20 h. The sample was then washed repeatedly with ultra-pure water until the solution became neutral. The treated product was finally dried in oven at 120 ºC. For carboxylation process, 1 g of the as-prepared G was first mixed with a 200 mL mixture of concentrated H_2SO_4 and HNO_3 (3:1 v/v) and stirred for 20 min at room temperature followed by sonication at 55 ºC for 4 hours in an ultrasonic bath (50 kHz and 100 W). After cooling to room temperature, the reaction mixture was diluted with 500 ml of deionized water and then vacuum-filtered through a filter paper (0.2 µm). Finally, G-COOH was dried in oven at 70 °C. In order to the formation of the free hydroxyl group, 0.5 g of filtered G-COOH was added to a methanolic solution of sodium borohydride. Then, the G bearing –OH group were allowed to disperse in xylene followed by addition of N-Phenyl-3-aminopropyl trimethoxy silane (PhAPTMS) to synthesize functionalized G in refluxing. After washing with xylene to remove the unreacted excess PhAPTMS, the product was dried for 10 h at 90 °C under reduced pressure. Morphology of the G-PhAPTMS was studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Graphite powder (5 g) and $NaNO_3$ (2.5 g) were mixed with 120 mL of concentrated H_2SO_4 and stirred for 30 min in an ice bath (0-5 °C). $KMnO_4$ (15 g) was gradually added to the vigorously stirred suspension and the temperature of the mixture was kept to be below 15 °C. The ice bath was then removed, and the mixture was stirred at 35 °C until it gradually became
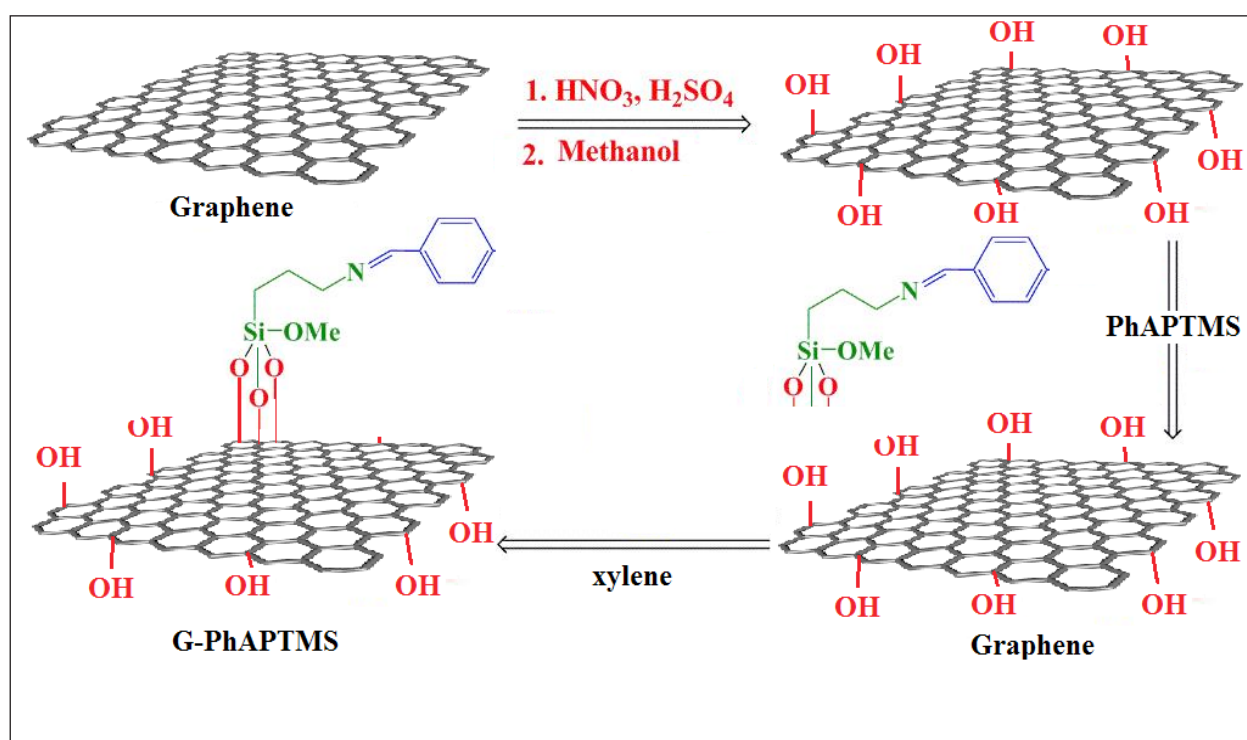
Scheme 1. Synthesis of functionalized graphene with N-Phenyl-3-aminopropyl trimethoxy silane

brownish slurry, and then it was diluted slowly with 250 mL of water. The reaction temperature was rapidly increased to 98 °C with effervescence, and the color changed to brown color. Later, H_2O_2 solution (30%) was added to stop the oxidation process, and the color of the mixture changed to bright yellow, indicating fully oxidized graphite. The graphite oxide formed was washed by rinsing and centrifugation with diluted HCl solution and then repeatedly with deionized water until the filtrated solution became neutral. Graphene oxide nanosheets were obtained by ultra-sonication of the filtered graphite oxide suspension followed by centrifugation for 15 min at 3000 rpm to remove any un-exfoliated graphite oxide (Scheme 1). Finally, it was air-dried at 60 °C for 12 h. In this study, graphene oxide and activated carbon commercially were purchased from RIPI, Iran.

2.3. General procedure

Because the removal efficiency is highly affected by the amount of sorbent, the effects of amount of sorbents were studied in 1, 2, 4, 5, 10, 15, 20, 25, and 30 mg of different sorbents including G-PhAPTMS, G, GO and AC. The flow rate of the dilution gas was set from 50 to 500 ml min^{-1}. The effects of temperature on the absorption of toluene were investigated in different temperature from 10 to 90 °C. The same concentration of standard gas of toluene was passed through the adsorption tube containing different amount of each sorbents in various thermal and flow rate conditions. The concentration of unabsorbed toluene collected in the Tedlar bag was analyzed by gas chromatography equipped with flame ionization detector. Removal efficiency was calculated as seen in Equation 1. The removal of toluene was evaluated in present of pure air in different flow rate by G-PhAPTMS, G, GO and AC as nanosorbents. In optimized conditions, the static and dynamic system was used by SGEP. The air was purified with electro air cleaner (EAC) and mixed with toluene in pilot. By proposed pilot, the pure air with and without toluene gas based on SGEP method was measured (5 times) by GC-FID and validated by GC-MS. The novel

G-PhAPTMS sorbent had chemical and physical adsorption between G and N-Phenyl with toluene, respectively. The mechanism of chemical adsorption was occurred based on π–π interaction of N-Phenyl with toluene. Moreover, the G-PhAPTMS was more interaction than G for toluene removal from air. By new synthesis, G was functioned by PhAPTMS and improved the compatibility between toluene and surface of sorbent in optimized conditions as compared to G, Go, and AC.

$$Removal\ Efficiency = C_{in}\text{-}C_{out}/C_{in} \times 100 \qquad Eq\ 1$$

C_{in} (mg L^{-1}) and C_{out} (mg L^{-1}) were the concentration of toluene before and after adsorption respectively.

3. Results and discussion

Morphology of the G-PhAPTMS has been studied by SEM and TEM (Figure 1 and 2). After functionalizing of graphene with N-Phenyl-3-aminopropyl trimethoxy silane, it seems that the graphene has much more active surface to absorb toluene.

3.1. Effect of Temperature

The removal efficiency of G-PhAPTMS, G, GO and AC in temperature from 10 to 90 °C are shown in Figure 3. Functionalizing graphene could improve the properties of graphene in absorption of toluene from the air by increasing temperature. In addition, activated carbon had more removal efficiency rather than graphene oxide in the same conditions. The removal efficiency of G-PhAPTMS decreased
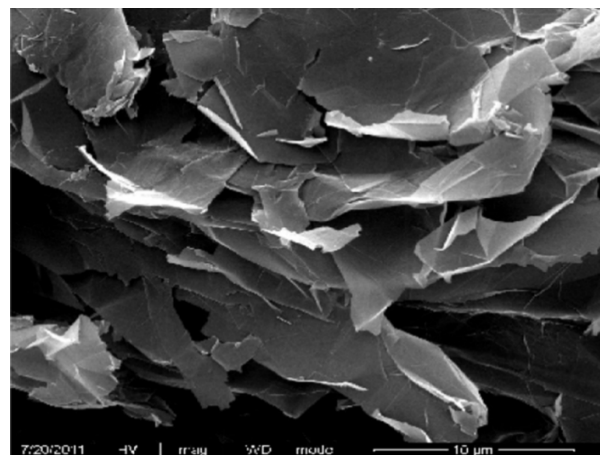

Fig. 1. SEM images of the G-PhAPTMS.

studies, the removal efficiency with increasing temperature was reported in other studies [36]. For instance, Sone et al. (2008) reported that absorption of VOCs can be highly influenced by increasing temperature. They found that when temperature was increased from 50 °C to 80 °C, the percentage of recovery of toluene decreased from 105.04 to 96.86 for charcoal [37]. Furthermore, it has been found out by Shih an Li in 2008 that lower temperature is a favorite condition for absorbing VOCs into the surface of carbon nanotube [38]. Overall, it can be argued the negative relation between increasing temperature and decreasing removal efficiency indicates that the sorption is an exothermic process, and decreasing temperature can improve the absorption properties of all investigated sorbents.

3.2. Effect of flow rate

The effect of flow rate on removal efficiency in 25 °C was investigated to optimize the flow rate conditions. The flow rate was set on 50 to 500 ml min^{-1} for all sorbents. The results are presented in Figure 4.

The removal efficiency of G-PhAPTMS, G, GO, and AC decreased by increasing the flow rate, like temperature. The results showed, the more removal efficiency of G-PhAPTMS as compared to other sorbents, and the removal efficiency of G-PhAPTMS was decreased up to 62% in 500 ml
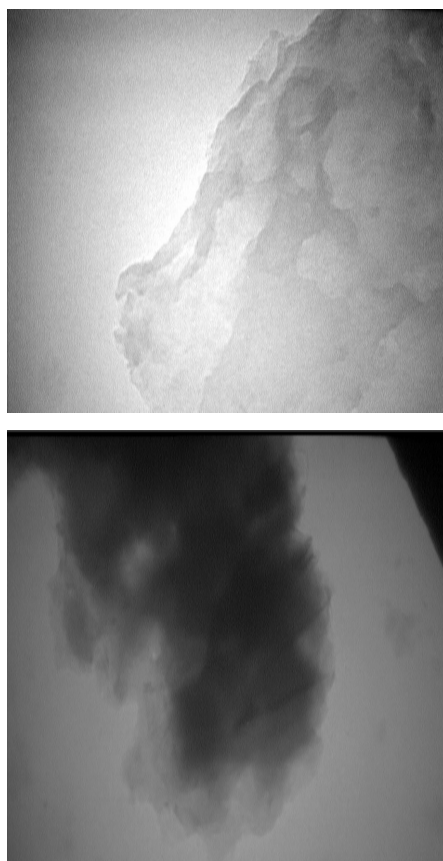

Fig. 2. TEM image of the G-PhAPTMS.

more than 50 °C, while, the removal efficiency of AC and GO decreased sharply from 68% and 40% in 45 °C to 5% and 2% in 90 °C respectively. Based on the results, the temperature can play a main role in removal efficiency of sorbents for toluene removal from air. By paying attention to previous
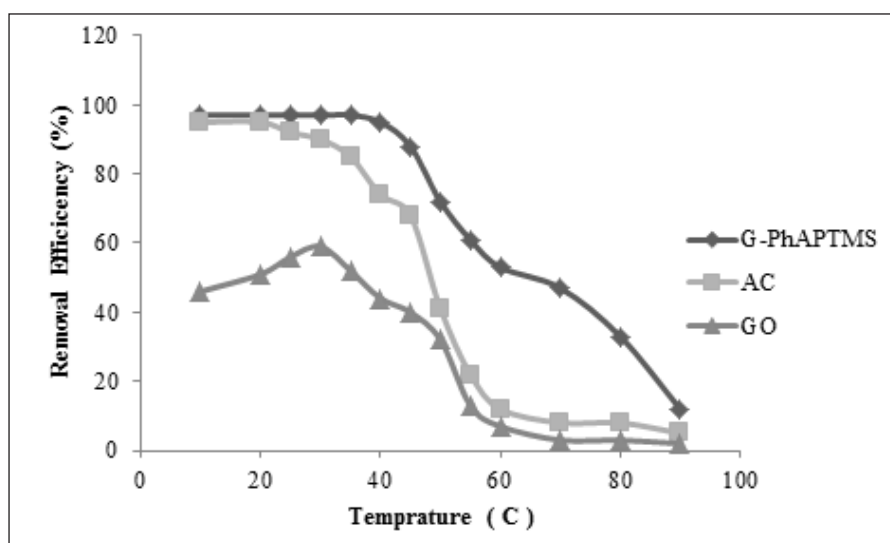

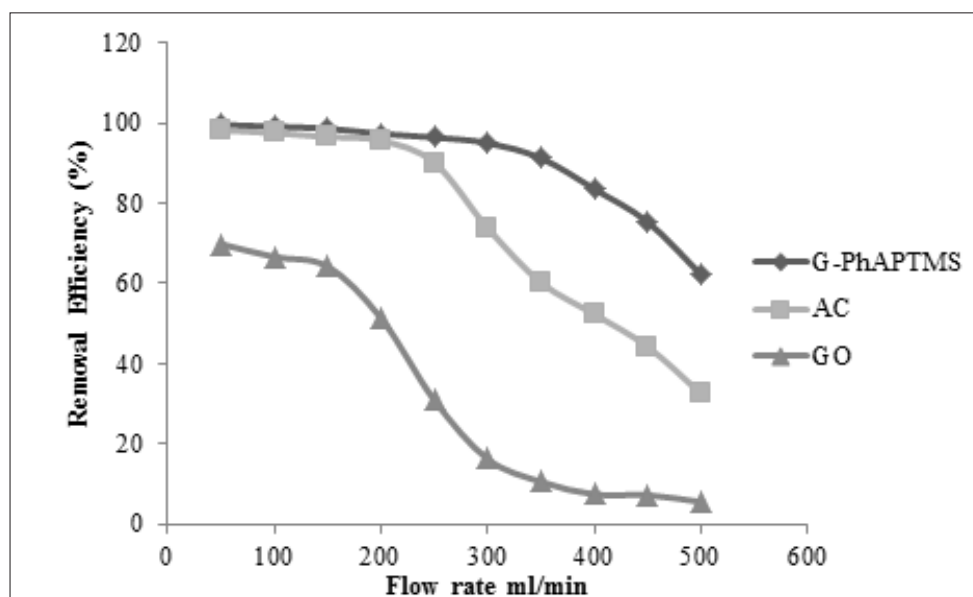**Fig. 3.** the effects of temperature on removal efficiency of G-PhAPTMS, AC, and GO.

Fig. 4. the effects of flow rate on removal efficiency of G-PhAPTMS, AC, and GO.

min^{-1}. However, the removal efficiency of AC and GO in this flow rate was 32% and 5% respectively. Increasing the flow rate affected on the removal efficiency of all sorbents, but this effect was lower for G-PhAPTMS. Similarly, the impact of flow rate (45, 92 and 184 ml min^{-1}) on the removal efficiencies of toluene, limonene and methyl ethyl ketone was investigated by Yao et al in 2009. Their results showed that removal efficiency was decreased from 79% to 21% by increasing the flow rate [39]. Moreover, declining removal efficiency of fluoride by increasing the flow rate from 20 to 30 ml min^{-1} in activated alumina was reported by Ghorai and Pant [40]. The influence of flow rate on removal efficiency may be explained by reaction time. When the flow is high, the molecules of toluene have a little time to interact with the surface of absorbent, so they begin to escape from the end of the sorption tube [41].

3.3. Effect of mass sorbent
The amount of sorbent is another important parameter which was investigated in this study. The absorption tubes were loaded by different amounts of each absorbent from 1 to 30 mg by proposed

method. The temperature and flow rate were set on 25 °C and 200 ml min^{-1}. The results are shown in Figure 5.

The removal efficiency of toluene with G-PhAPTMS increased by increasing the amount of sorbent and reached the highest pint in 5 mg of sorbent. In addition, the removal efficiencies of AC and GO followed the same pattern as the G-PhAPTMS, while reached the highest pint in 15 and 30 mg of sorbents respectively. The GO had the lowest removal efficiency rather than the G-PhAPTMS, G, and AC for all amount of sorbent. The positive impact of amount of sorbent on removal efficiency was reported by Samarghandi et al (2017) in the removal of reactive red from distilled water. They found that the removal efficiency increased when the amount of active carbon and graphene increase from 0.2 to 4 g L^{-1} and 0.02 to 0.4 g L^{-1} respectively [42]. Higher amount of sorbent provides much more chance for the molecule of toluene to react with the available surface of sorbent. So, the removal efficiencies of sorbents increase effectively. Based on the results, the more active absorption sites of g L^{-1} allow the molecules of toluene to absorb rapidly and
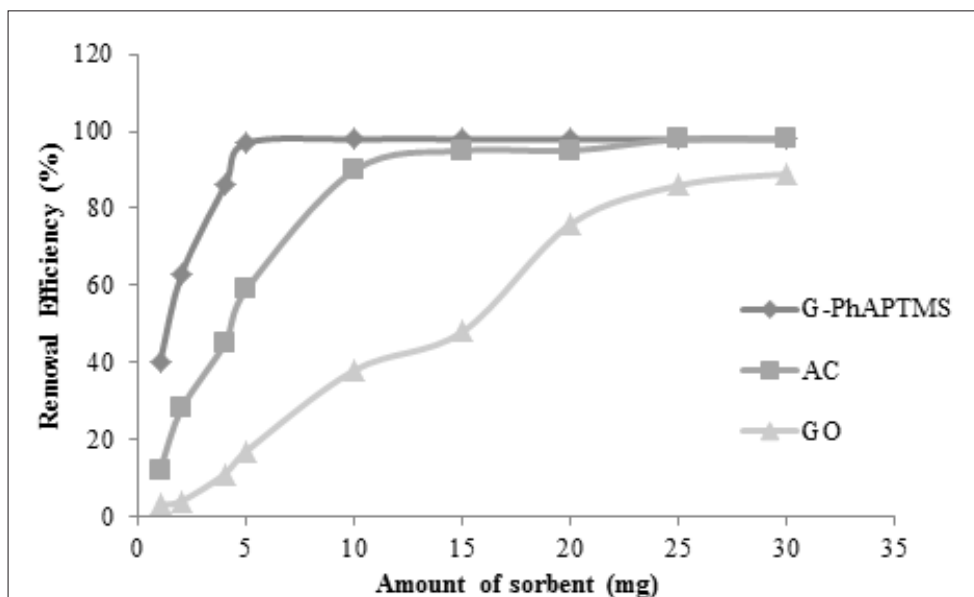
Fig. 5. the effects of amount of sorbent on removal efficiency of G-PhAPTMS, AC, and GO.

functionalizing graphene creates this opportunity that in the lower amount of sorbent, So we have maximum removal efficiency by G-PhAPTMS as compared with other sorbents. Repeatability of the sorbents was investigated in 25 °C, 200 ml min^{-1} and from 2 to 30 mg of each sorbent (Figure 6). Each type of sorbent was used for twenty times and the mean of removal efficiencies were calculated.

The G-PhAPTMS had the highest removal efficiency for all investigated amount of sorbent compared with G, GO and AC sorbents after twenty times absorption and desorption. The mean of removal efficiency of AC experienced a downward pattern from 5 to 30 mg. Decreasing the removal efficiency for the GO happened from 20 mg to 30 mg where the removal efficiency fell from 64 to 42%. According to the results, functionalizing graphene with N-Phenyl-3-aminopropyl trimethoxy silane (G-PhAPTMS) can improve the absorption characteristics of graphene to absorb toluene from air.

3.4. Validation

The G-PhAPTMS was used as a novel and low-cost sorbent for removal of toluene vapor from air. By proposed method, a mixture of 5-100 ppm of toluene vapor in artificial air with argon gas as a carrier gas passed through sorbent (G-PhAPTMS) by a pump. The concentration of toluene in standard gas was validated by highly sensitive and accurate GC-MS instrument in different concentration before using by proposed method. Since standard reference material for toluene in air is not currently available, the spiked of validated toluene concentration in a bag (GC-MS, 50 ppm, bag 5 Li, 0.2 L min^{-1}) were prepared to demonstrate the reliability of the method by G-PhAPTMS. At optimum condition in one minute, 2.0 ppm of toluene vapor in air was almost removed by G-PhAPTMS. The efficient recovery of spiked samples was reasonable and was confirmed using addition method, which it indicates the capability of proposed method for removal of toluene from air (Table 1).

4. Conclusions

In this study, different absorbents such as G-PhAPTMS, G, GO, and AC were used to remove toluene from air. The results showed that functionalizing graphene with N-Phenyl-3-aminopropyl trimethoxy silane (G-PhAPTMS)
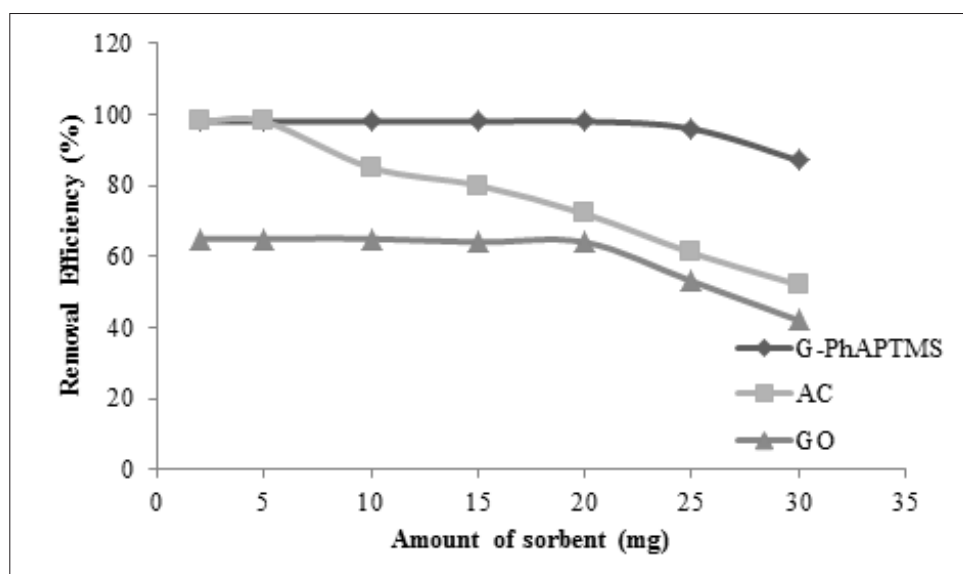
Fig. 6. The removal efficiency of different sorbents after using repeatedly.

Table 1: The recovery of G-PhAPTMS for removing toluene from air.

Samples	Toluene in air (ppm)*	Toluene in sorbent (ppm)**	Sorbent Recovery (%)
Sample A	2.63 ± 0.07	2.57 ± 0.11	97.7
Sample B	6.89 ± 0.14	6.48 ± 0.21	94
Sample C	10.72 ± 0.19	10.51 ± 0.32	98
Sample D	14.08 ± 0.34	13.52 ± 0.84	96
Sample E	18.73 ± 0.17	17.35 ± 0.28	92.6

* Initial concentration in standard gas

** Measured concentration in sorbent

promotes the removal efficiency of graphene by chemical bonding as π–π electron donor–acceptor. Furthermore, increasing temperature and flow rate have negative effects of the removal efficiency of all sorbents, but the results of G-PhAPTMS showed high removal efficiency of toluene compared to the AC, G, and GO. The amount of sorbent was another parameter which was investigated. In optimized conditions, the amount of sorbent for the G-PhAPTMS, AC, and the GO were obtained 5, 5, and 30 mg respectively. This result shows that the G-PhAPTMS has many more available active sites for absorption of toluene. By lower amount of G-PhAPTMS, high removal efficiency was achieved more than 95% by interaction between toluene and N-Ph. The results of repeatability of sorbents also indicate that functionalizing graphene with N-Phenyl-3-aminopropyl trimethoxy silane allows graphene to be used repeatedly, and it can be introduced as an environmentally friendly sorbent.

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