

## ORIGINAL ARTICLE

# Nobel Method for Toluene Removal from Air Based on Ionic Liquid Modified Nano-Graphen

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## ABSTRACT

The aim of this study was to investigate the removal of toluene from air through Nano-graphene modified by ionic liquid (NG-IL). The batch adsorption experiments in glass bottle of gas chromatography equipped with flame ionization detector (GC-FID) were used. Graphene ultrahigh-quality synthesized by substrate-free gas-phase method in a single step and graphene sheets were deposited with ionic- liquid by thermal adsorption in acetone blank solution. Various conditions including contact time, amount of adsorbent, adsorbate concentration, humidity, and temperature were studied and optimized. NG-IL adsorbent was used for the adsorption of toluene vapor from gaseous media and the effect of different conditions such as; toluene concentration, humidity, and temperature on the adsorption were investigated. The Langmuir adsorption isotherms were employed for toluene by NG-IL adsorbent. The adsorption capacity was decreased by raising the sorbent humidity above 50 percent. The toluene capture capacity for NG-IL was 126 mg/g. The results of SEM, XRD, and TEM showed that, the NG-IL have beneficial surfaces for toluene removal. NG-IL as a novel adsorbent has not previously been used for the adsorption of pollutants.

**Keywords:** *Toluene, Air, Nano graphene, Ionic liquid, Gas chromatography mass spectrometry*

## INTRODUCTION

Environmental pollution has created many problems in the recent years. Volatile organic compounds (VOCs) such as are the major pollutants being released from various industrial processes [1]. VOCs such as toluene, benzene, and o, m, p-xylenes existing in gasoline, diesel, and waste vegetable oil are widely used in chemical solvents [2]. Toluene vapors are released into air as gases from some solids or liquids. Toluene can be absorbed by respiratory and gastrointestinal tracts. The exposure to VOCs caused many problems in human

body such as, neurological effects, eye irritation, headaches, dizziness, fatigue, tremors, mental depression, bronchitis, asthma, and cancer [3,4]. The US Environmental Protection Agency (USEPA) has considered toluene as a major pollutant. Toluene is a volatile liquid (vapor pressure, 22 mmHg at 20°C), and is released into the atmosphere from industrial and consumer uses. The largest sources of toluene release are the evaporation from gasoline, which is 5-7% toluene, and release through car exhaust [5].

Various techniques including biofilter, biotrickling filter, bioscrubber, and adsorption have been successfully adopted to remove toluene vapors from gaseous media [6-7]. Many adsorbents including zeolites [8], metal oxides [9], compost [6,10],

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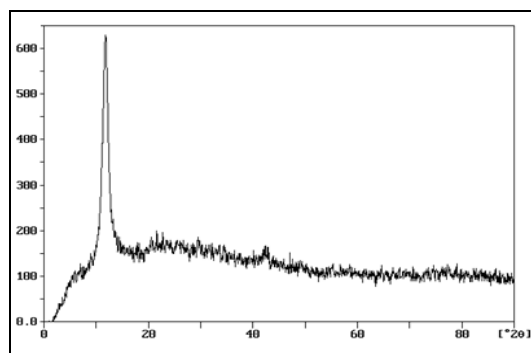


Fig 1. X-ray diffractions of grapheme

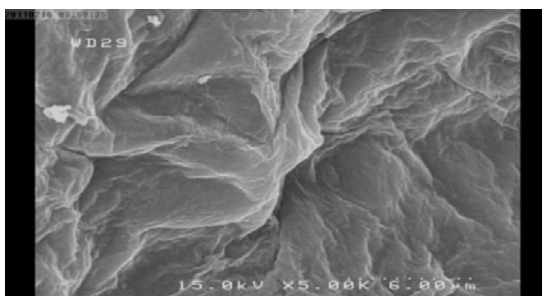


Fig 2. SEM of Graphene

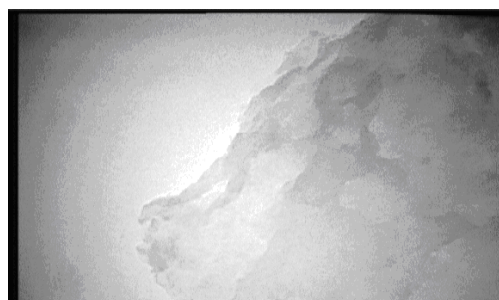


Fig 3. TEM of Graphene

diatomaceous earth, chaff [10], ground tire rubber [6], and activated carbon [11-12] have been used for the removal of toluene vapors.

In this study, the Nano-graphene modified by ionic liquid (NG-IL) were, as a novel sorbent, used to remove toluene from air. Experimental parameters were studied and optimized. The performance of the proposed method was evaluated.

## MATERIALS AND METHODS

### Apparatus

Gas chromatography equipped with flame ionization detector and air sample loop injection was used (Agilent GC, 7890A, FID, Netherland). Gas sampling bags with valve and septum port (Tedlar) and air sampling apparatus (Bucket brigade) with liquid nitrogen were used. Vials with PTFE air-tight cap (parker) and mixed by a rotary shaker (RSB-12).

### Synthesis of grapheme

Graphene is a single atomic layer of carbon atoms tightly packed in a two-dimensional honeycomb lattice. This novel material is atomically thin, chemically inert, consists of light atoms, and possesses a highly ordered structure. Graphene is electrically and thermally conductive, and is the strongest material ever measured. These remarkable properties make graphene the ideal support film for electron microscopy. The substrate-free gas-phase method is the first and only process that can synthesize ultrahigh-quality graphene in a single step, without the use of substrates or graphite. Graphene sheets are created through the delivery of liquid alcohol

droplets directly into atmospheric-pressure microwave generated plasmas. The substrate-free gas-phase method is the first and only process that can synthesize ultrahigh-quality graphene in a single step, without the use of substrates or graphite. Graphene sheets are created through the delivery of liquid alcohol droplets directly into atmospheric-pressure microwave generated plasmas. Extensive characterization of the synthesized graphene has proven that the sheets are oxygen-free and exhibit a highly ordered structure. Graphene sheets are deposited with ionic-liquid by thermal adsorption in acetone blank solution [13-14].

### Characterization methods

A X-ray diffractions (Phillips PW 1840 x-ray diffractometer with Cu-K radiation source) was utilized for the crystal structure of the solids (Fig 1). The graphene distance layer can be calculated based on Bragg's law (Equation 1):

$$\text{Eq. 1 } n = 2d_{(hkl)} \sin(\Theta)$$

$\lambda$ ,  $\theta$ ,  $n$ ,  $d$  and  $hkl$  are wavelength, scattering angle, integer order of the diffraction peak, distance of lattices and miller indices respectively. The scherrer equation can obtain the mean crystallite size of powder composed of crystalline particle (Equation 2):

$$\text{Eq. 2 } n = K \lambda / \beta_0 \cos\Theta$$

Physisorption of Nitrogen was measured at 77 K using a BEL-SORP-mini porosimeter. Surface area, pore size and volume values were calculated from nitrogen adsorption-desorption isotherms (Sorptometer Kelvin 1042, Italy). The concentration of toluene (purity of 99.5%, Merck, Germany) in the solution was quantified by a gas chromatography equipped with

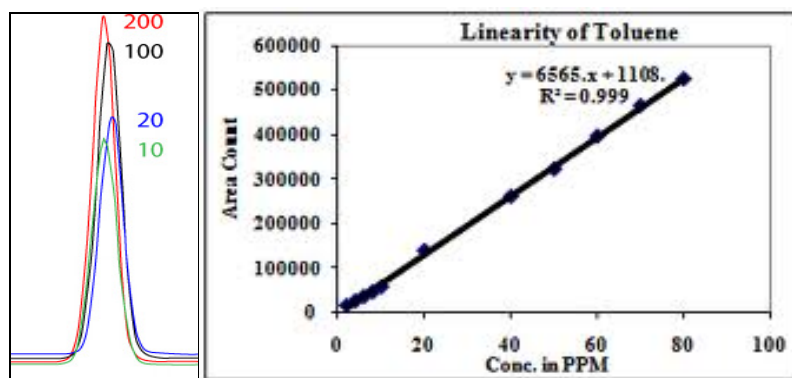


Fig 4. Calibration curve for the toluene in the solution (mg/L)

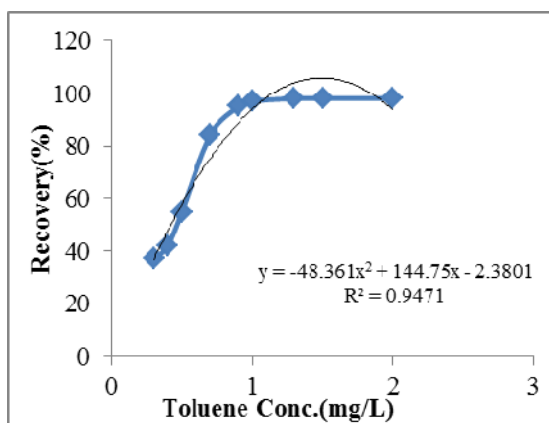


Fig 5. Effect of toluene concentration

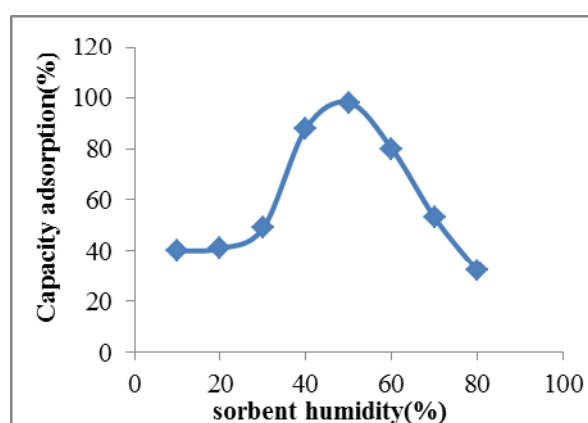


Fig 6. Effect of sorbent humidity

flame ionization detector (Agilent GC, 7890A, Netherland). The GC-FID procedure was optimized as follows. The amount of 100  $\mu$ L of gaseous sample was injected into the instrument by 1 mL gastight syringes (Hamilton series). Helium (1.11 mL/min) and H<sub>2</sub> (30 mL/min) were used as carrier gas and fuel gas, respectively. The characteristic of GC column was Agilent CP Sil 5: 30 m  $\times$  250  $\mu$ m  $\times$  0.25  $\mu$ m. The temperatures of the oven, injector, and detector were fixed at 100, 230, and 250  $^{\circ}$ C, respectively. The synthesis of graphene was characterized by scanning electron microscopy (SEM) by S4160-Hitachi Japan and transmission electron microscopy (TEM) by CM30-Philips (Figs 2 and 3).

#### General Procedure

The experiments including adsorbent humidity (0–50%), contact time (0–12 h), and adsorbate concentration (10 mg/L) were carried out at room temperature (25  $^{\circ}$ C) in the 250 mL vials (with PTFE airtight cap) and mixed by a rotary shaker (250 rpm for 12 h). The effect of temperature (25–60  $^{\circ}$ C) on the adsorption was also determined as described above. After agitation period, 100  $\mu$ L of the polluted gas was analyzed for toluene by GC-FID. Calibration curve for determination of the toluene concentration was prepared

according to the standard method [15]. The adsorbent capacity of NG-IL for toluene was calculated by equation 3, where  $q_e$  (mg/g) is the adsorption capacity of NG-IL,  $C_0$  (mg/L) is the initial concentration of toluene,  $C_e$  (mg/L) is the equilibrium concentration of the toluene in the solution,  $m$  (g) is the mass of the adsorbent, and  $V$  (L) is the volume of the polluted gas (or volume of the vial).

$$\text{Eq. 3 } q_e = (C_0 - C_e)V/m$$

After the pre-concentration a sample valve similar to those used in liquid chromatography is used to inject the volatile contents of the sample loop onto the column for separation and eventual detection and measurement by a flame ionization detector (FID). Calibration curve for 10, 20, 100, 200 mg/L were obtained (Fig 4).

#### RESULTS

**The Effect of Contact Time:** Fig 2 shows the effect of contact time (0–1 h) on the adsorption of toluene by NG-IL. The adsorption as can be seen in the figure reached its maximum capacity by the elapse of time (20 min). The effect of contact time on the removal of toluene by NG-IL (adsorbent dose=1 g, temperature =25  $^{\circ}$ C, adsorbent humidity =50%, and toluene conc. =7 mg/L).

**Table 1.** The value of Langmuir isotherm model constants in NG-IL adsorbent

Temperature (°K)	Langmuir isotherm			
	$Q_{max}$	Max $C_e/q_e$	$R^2$	$T_{effective}$ (min)
323	180.3	2.13	0.9952	100
343	162.4	2.96	0.9958	88
358	131.2	3.55	0.9946	83

**Table 2.** Comparison NG-IL with other natural sorbents

mg/g	NG	NG-IL	SWCNT	Nano-ZNS	Carbon active
Adsorption Capacity	91	126	54	63	74

**The effect of toluene concentration and adsorbent humidity:** The effect of initial toluene concentration in the range of 0.5 to 2 mg/L is presented in Fig 5. The effect of adsorbent humidity (0–90%) on the sorption was determined. As can be seen, adsorption capacity was expanded by increasing the sorbent humidity up to 50 percent (Fig 6).

#### Dynamic adsorptive of NG-IL

The adsorption capacity of NG-IL was determined for toluene by using column technique. Toluene concentration (10 mg/L) was carried out at room temperature (25°C) in the 250 mL vials (with PTFE airtight cap) and mixed by a rotary shaker (250 rpm for 12 h). The effect of temperature (25–60°C) on the adsorption was also determined as described above. After adsorption of toluene by NG-IL at a flow rate of 0.5–5 ml min<sup>-1</sup>, 100 µL of the polluted gas was analyzed for toluene by GC-FID. After toluene was eluted from nano sorbent with 1 mL of ethanol (95%), the concentration of toluene in eluate was determined by GC-FID. In order to successfully represent the dynamic adsorptive behavior, it is important to have a satisfactory description of the equation state between the two phases composing the adsorption system. In this study the Langmuir adsorption isotherms were employed for toluene by NG-IL adsorbent. The Langmuir model assumes uniform energies of adsorption onto the surface of NG-IL. The Langmuir equation may be written as Eq. 1:

$$\frac{C_e}{q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}} \quad (\text{Eq. 1})$$

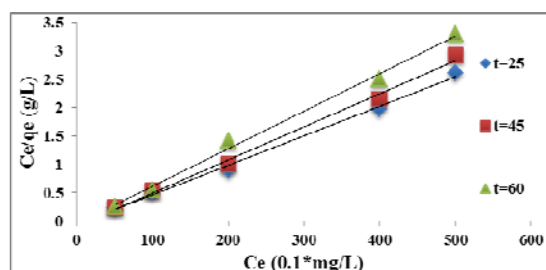
$C_e$  is the equilibrium concentration (mg L<sup>-1</sup>) and  $q_e$  is the amount adsorbed at surface equilibrium mg g<sup>-1</sup> and  $Q_{max}$  and  $b$  is Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The Langmuir model provided a good fit throughout the concentration range. The applicability of the isotherm models and the high values of the correlation coefficients ( $R^2 = 0.995$ ) for NG-IL suggest favorable adsorption by toluene at 25°C. The value of  $Q_{max}$  in

Langmuir plots was 180 mg g<sup>-1</sup> for toluene at 25°C. The values of  $Q_{max}$  and time effective for flow rate depended on temperature of solution. According to results, the maximum capacity of adsorbent in column condition, due to the less amount of contact time, is 12% less than batch system, which is apparently quite expected. The value of Langmuir isotherm model constants are shown in Table 1 and Fig 7. In comparison with other natural sorbents, NG-IL seems to be a cost-effective sorbent in the removal of toluene vapor (Table 2).

#### DISCUSSION

Exhausts chemical gases and work place air contain several types of aromatic hydrocarbons include benzene, toluene, xylenes and need to be removed from gas streams. In order to removal aromatic hydrocarbons many adsorbents were used. The NG sorbent has a physical adsorption of toluene vapor and when ionic liquid pasted on NG, the adsorption capacity increased by chemical adsorption procedure.

In this study, removal of toluene from air has been developed by NG-IL and NG sorbents. Removal efficiency of nano compounds compared with other sorbents. The stationary phase was created by 1g NG-IL that placed in 250 mL PTFE vials. Comparing of specific surface area of NG-IL and NG showed that the BET equation (Brunauer-Emmett-Teller) of NG-IL is lower than NG, but maximum capacity of toluene adsorption in NG-IL was higher than NG or IL. The capacity of toluene adsorption for NG and NG-IL were

**Fig 7.** Langmuir isotherm model for capacity of NG-IL adsorbent

32.7  $\mu\text{g/g}$  and 126.8  $\text{mg/g}$  respectively. In the previous research, removal of toluene was studied. The removal of aromatic hydrocarbons by non-thermal plasmas is under investigation [16]. Yamamoto et al. showed that an efficient removal for toluene can be obtained by using of plasma reactors. Several types of discharge such as dielectric barrier, capillary discharge and various types of packed-bed reactors, have been studied for the treatment of toluene but the removal cost of aromatic hydrocarbons is very high [17,18]. Sorbent materials, such as activated carbon and molecular sieves, are used to remove VOCs from gas streams in industrial applications. Scahill et al. showed that a method for evaluating the toluene removal by sorbent materials. The capacity of toluene adsorption for molecular sieves was 7.5  $\mu\text{g/g}$  which is lower than NG and NG-IL adsorbent. OSHA method (111) was used for sampling of toluene with two options (active and passive sample collection). In both options, samples are extracted with 60/40 (v/v) N, N-dimethyl formamide /carbon disulfide (DMF/CS<sub>2</sub>) and analyzed by gas chromatography using flame ionization detection (50 ml/min) [19]. The proposed method, toluene was extracted without chemical reagents and simply thermal desorption by heating at 80-100°C (0.5-5  $\text{ml min}^{-1}$ , 100  $\mu\text{L}$ ). The NG-IL has high characterization than other sorbets for toluene removal in gas and air. Toluene removal capacity and repeatability of NG-IL has higher than other adsorbents or methods have already been suggested.

## CONCLUSIONS

In this study, NG-IL was used as a novel adsorbent for the adsorption of toluene vapor from gaseous media. The effect of different conditions including contact time, toluene concentration, humidity, and temperature on the adsorption was investigated. The results of the thermodynamic analysis (negative value of obtained  $\Delta H$ ) corroborate that this adsorption process is exothermic. This adsorbent is a waste material with a sorption capacity of 126  $\text{mg/g}$ . According to results, the maximum capacity of adsorbent in column conditions was 12% less than batch system, which is apparently quite expected. NG and IL, both of them is important for toluene vapor extraction in NG-IL sorbent.

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