

ORIGINAL ARTICLE

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

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Received September 27, 2013; Revised December 19, 2013; Accepted December 27, 2013

This paper is available on-line at <http://ijoh.tums.ac.ir>

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 of 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 mm Hg 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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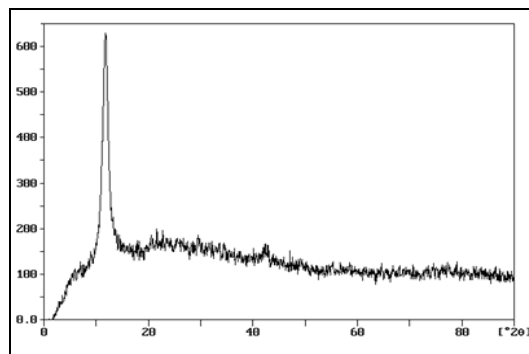


Fig 1. X-ray diffractions of grapheme

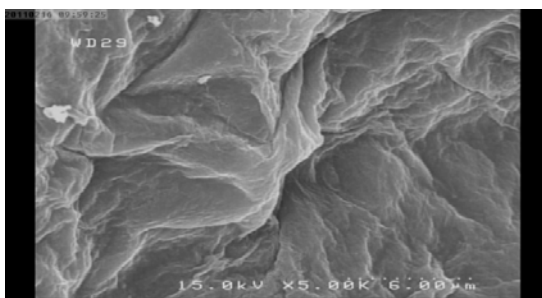


Fig 2. SEM of Graphene

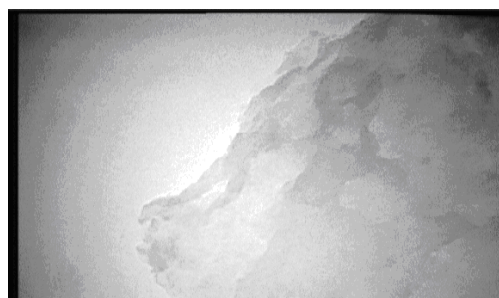


Fig 3. TEM of Graphene

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

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

66 MATERIALS AND METHODS

67 Apparatus

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

75 Synthesis of grapheme

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

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

100 Characterization methods

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

$$106 \quad \text{Eq. 1} \quad n = 2d_{(hkl)} \sin(\Theta)$$

107 λ , θ , n , d and hkl are wavelength, scattering angle,
108 integer order of the diffraction peak, distance of lattices
109 and miller indices respectively. The scherrer equation
110 can obtain the mean crystallite size of powder composed
111 of crystalline particle (Equation 2):

$$112 \quad \text{Eq. 2} \quad n = K \lambda / \beta_0 \cos\Theta$$

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

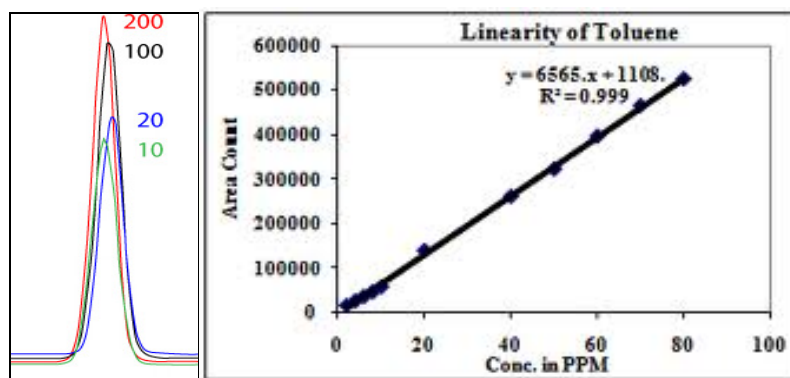


Fig 4. Calibration curve for the toluene in the solution (mg/L)

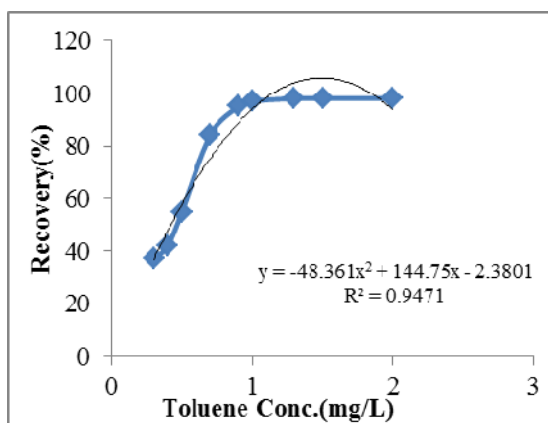


Fig 5. Effect of toluene concentration

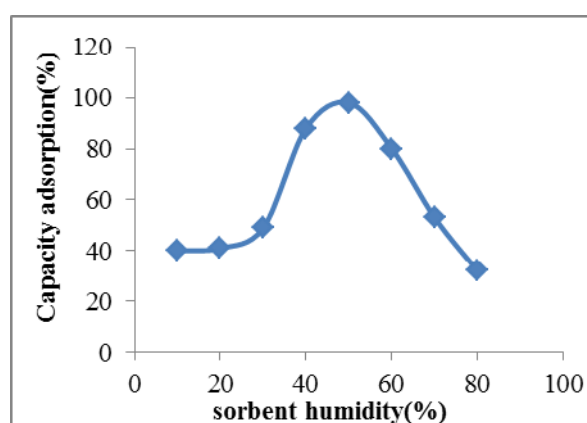


Fig 6. Effect of sorbent humidity

120 flame ionization detector (Agilent GC, 7890A, 145 according to the standard method [15]. The adsorbent
 121 Netherland). The GC-FID procedure was optimized as 146 capacity of NG-IL for toluene was calculated by
 122 follows. The amount of 100 μ L of gaseous sample was 147 equation 3. where q_e (mg/g) is the adsorption capacity of
 123 injected into the instrument by 1 mL gastight syringes 148 NG-IL, C_0 (mg/L) is the initial concentration of toluene,
 124 (Hamilton series). Helium (1.11 mL/min) and H_2 149 C_e (mg/L) is the equilibrium concentration of the
 125 (30 mL/min) were used as carrier gas and fuel gas, 150 toluene in the solution, m (g) is the mass of the
 126 respectively. The characteristic of GC column was 151 adsorbent, and V (L) is the volume of the polluted gas
 127 Agilent CP Sil 5: 30 m \times 250 μ m \times 0.25 μ m. The 152 (or volume of the vial).

128 temperatures of the oven, injector, and detector were 153 Eq. 3 $q_e = (C_0 - C_e)V/m$.

129 fixed at 100, 230, and 250 $^{\circ}$ C, respectively. The 154 After the pre-concentration a sample valve similar
 130 synthesis of graphene was characterized by scanning 155 to those used in liquid chromatography is used to inject
 131 electron microscopy (SEM) by S4160-Hitachi Japan and 156 the volatile contents of the sample loop onto the column
 132 transmission electron microscopy (TEM) by CM30- 157 for separation and eventual detection and measurement
 133 Philips (Figs 2 and 3). 158 by a flame ionization detector (FID). Calibration curve
 159 for 10, 20, 100, 200 mg/L were obtained (Fig 4).

134 General Procedure

135 The experiments including adsorbent humidity (0–

136 50%), contact time (0–12 h), and adsorbate 160 RESULTS

137 concentration (10 mg/L) were carried out at room 161 **The Effect of Contact Time:** Fig 2 shows the effect
 138 temperature (25 $^{\circ}$ C) in the 250 mL vials (with PTFE air- 162 of contact time (0–1 h) on the adsorption of toluene by
 139 tight cap) and mixed by a rotary shaker (250 rpm for 163 NG-IL. The adsorption as can be seen in the figure
 140 12 h). The effect of temperature (25–60 $^{\circ}$ C) on the 164 reached its maximum capacity by the elapse of time (20
 141 adsorption was also determined as described above. 165 min). The effect of contact time on the removal of
 142 After agitation period, 100 μ L of the polluted gas was 166 toluene by NG-IL (adsorbent dose=1 g, temperature
 143 analyzed for toluene by GC-FID. Calibration curve for 167 =25 $^{\circ}$ C, adsorbent humidity =50%, and toluene conc.
 144 determination of the toluene concentration was performed 168 =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 Langmuir plots was 180 mg g⁻¹ for toluene at 25 °C. The effect of initial toluene concentration in values of Q_{max} and time effective for flow rate depended the range of 0.5 to 2 mg/L is presented in Fig 5. The on temperature of solution. According to results, the effect of adsorbent humidity (0–90%) on the sorption maximum capacity of adsorbent in column condition, was determined. As can be seen, adsorption capacity due to the less amount of contact time, is 12% less than was expanded by increasing the sorbent humidity up to batch system, which is apparently quite expected. The value of Langmuir isotherm model constants are shown

Dynamic adsorptive of NG-IL

The adsorption capacity of NG-IL was determined the removal of toluene vapor (Table 2). 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 air-

tight 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 toluene by NG-IL at a flow rate of 0.5–

5 ml min⁻¹, 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 was 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⁻¹) and q_e is

the amount adsorbed at surface equilibrium mg g⁻¹ 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

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

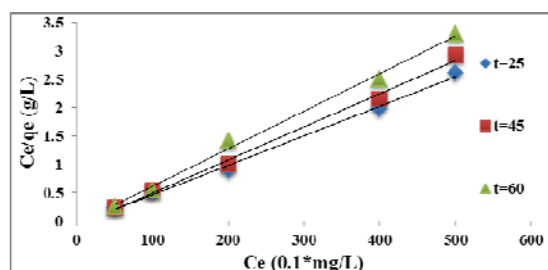
specific surface area of NG-IL and NG showed that the

BET equation (Brunauer-Emmett-Teller) of NG-IL is

lower than NG, but maximum capacity of toluene

absorption 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

237 32.7 $\mu\text{g/g}$ and 126.8 mg/g respectively. In the previous
 238 research, removal of toluene was studied. The removal
 239 of aromatic hydrocarbons by non-thermal plasmas is
 240 under investigation [16]. Yamamoto et al. showed that
 241 an efficient removal for toluene can be obtained by
 242 using of plasma reactors. Several types of discharge
 243 such as dielectric barrier, capillary discharge and
 244 various types of packed-bed reactors, have been studied
 245 for the treatment of toluene but the removal cost of
 246 aromatic hydrocarbons is very high [17,18]. Sorbent
 247 materials, such as activated carbon and molecular
 248 sieves, are used to remove VOCs from gas streams in
 249 industrial applications. Scahill et al. showed that a
 250 method for evaluating the toluene removal by sorbent
 251 materials. The capacity of toluene adsorption for
 252 molecular sieves was 7.5 $\mu\text{g/g}$ which is lower than NG
 253 and NG-IL adsorbent. OSHA method (111) was used
 254 for sampling of toluene with two options (active and
 255 passive sample collection). In both options, samples are
 256 extracted with 60/40 (v/v) N, N-dimethyl formamide
 257 /carbon disulfide (DMF/CS₂) and analyzed by gas
 258 chromatography using flame ionization detection (50
 259 ml/min) [19]. The proposed method, toluene was
 260 extracted without chemical reagents and simply thermal
 261 desorption by heating at 80-100°C (0.5-5 ml min^{-1} ,
 262 100 μL). The NG-IL has high characterization than
 263 other sorbets for toluene removal in gas and air. Toluene
 264 removal capacity and repeatability of NG-IL has higher
 265 than other adsorbents or methods have already been
 266 suggested.

267 CONCLUSIONS

268 In this study, NG-IL was used as a novel adsorbent
 269 for the adsorption of toluene vapor from gaseous media.
 270 The effect of different conditions including contact
 271 time, toluene concentration, humidity, and temperature
 272 on the adsorption was investigated. The results of the
 273 thermodynamic analysis (negative value of obtained
 274 ΔH) corroborate that this adsorption process is
 275 exothermic. This adsorbent is a waste material with a
 276 sorption capacity of 126 mg/g . According to results, the
 277 maximum capacity of adsorbent in column conditions
 278 was 12% less than batch system, which is apparently
 279 quite expected. NG and IL, both of them is important for
 280 toluene vapor extraction in NG-IL sorbent.

281 ACKNOWLEDGEMENTS

282 The authors are thankful to the Iranian Occupational
 283 and Environmental Health Laboratory of IPIHRI
 284 OEHR, PIHO, for their support for this work. The
 285 authors declare that there is no conflict of interests.

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