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Adsorption characteristics of 1,2,4-trichlorobenzene, 2,4,6-trichlorophenol, 2-naphthol and naphthalene on graphene and graphene oxide

Zhiguo Pei ^{a,*}, Lingyun Li ^b, Lixiang Sun ^c, Shuzhen Zhang ^a, Xiao-quan Shan ^a,
Shuang Yang ^a, Bei Wen ^a

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

^b Supervision and Testing Center for Vegetable Quality, Ministry of Agriculture, The Institute of Vegetables and Flowers, Chinese Academy of Agricultural Sciences, Beijing, China

^c College of Chemistry and Materials Science, Ludong University, Yantai 264025, China

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ABSTRACT

Adsorption of 1,2,4-trichlorobenzene (TCB), 2,4,6-trichlorophenol (TCP), 2-naphthol and naphthalene (NAPH) on graphene (G) and graphene oxide (GO) was investigated using a batch equilibration method and micro-Fourier transform infrared spectroscopy. All adsorption isotherms of four aromatics on G and GO were nonlinear, indicating that except for hydrophobic interaction, some specific interactions were involved in adsorption. For G, four aromatics had similar adsorption capacity at pH 5.0 in despite of their different chemical properties. A series of pH-dependent experimental results showed that 2-naphthol had higher adsorption capacity on G at alkaline pH than that at acidic pH. Theoretical calculation ascribed this to higher π -electron density of anionic 2-naphthol than that of neutral 2-naphthol, which facilitated the π - π interaction formation with G. For GO, the adsorption affinity of four aromatics increased in the order: NAPH < TCB < TCP < 2-naphthol. FTIR results revealed that TCB, TCP and 2-naphthol were adsorbed on G mainly via π - π interaction. In contrast, high adsorption of TCP and 2-naphthol on GO was attributed to the formation of H-bonding between hydroxyl groups of TCP and 2-naphthol and O-containing functional groups on GO.

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1. Introduction

Industrialization and urbanization result in discharge of toxic chemicals in natural surface water bodies [1], including persistent aromatic pollutants, which are widely detected in the effluents of pharmaceutical, petrochemical, dyestuff, pesticide, and other industries. Numerous studies focused on the efficient removal of these toxic pollutants from aqueous solutions such as by photocatalysis [2], adsorption [3], and elec-

trolysis [4]. Among these approaches, adsorption has been found to be superior to other techniques due to its low-cost, high efficiency and easy of operation.

Graphene (G) is a two-dimensional structure consisting of sp^2 hybridized carbons with only one atomic thickness, and has attracted considerable attention since the report of Novoselov et al. [5]. Due to their large theoretical specific surface area, remarkable electronic properties and high ability of modification, potential environmental applications of G as

* Corresponding author. Fax: +86 10 62923563.

E-mail address: peizg@rcees.ac.cn (Z. Pei).

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superior adsorbent have been recognized for removal of organic and inorganic contaminants from water and gases [6–14]. For example, it was found that sulfonated G was one of the most effective adsorbents for naphthalene and 1-naphthol [6,7]. Wu et al. [8] revealed the high adsorption of acrylonitrile, *p*-toluenesulfonic acid, 1-naphthalenesulfonic acid and methyl blue on G nanosheets. Ramesha et al. [9] found that exfoliated graphene oxide (GO) and reduced GO are effective adsorbents for anionic and cationic dyes. In addition, G nanosheets also have high adsorption affinity for heavy metals, where the amount of active surface sites on G is an important factor influencing the adsorption of heavy metal ions. Previous works on arsenic adsorption onto magnetite reduced GO composites and G sheets [10,11], and on Hg(II) adsorption to polypyrrole-reduced GO composites showed that G composites have a strong adsorption affinity for metal ions [12,13].

It should be noted that G is a good model adsorbent for understanding phenomena occurring at carbon/solution interface due to its knowable structures. However, to our knowledge, most of previous adsorption studies about G nanosheets were limited to phenomenon description and/or to their potential application for water cleaning. Questions on the underlying adsorption mechanisms of organic contaminants on G have not been addressed although several theoretical calculation or simulation studies assumed that charge transfer process and π - π interaction were possibly responsible for the adsorption of aromatics to G [15–17]. These simulation studies were only limited to G with <204 carbon atoms and 40 hydrogen atoms to simplify the adsorption system and to make the calculation or simulation practical [16]. Current knowledge believes that real synthesized G is not ideal, which often has some defect sites and there is a small portion of O-containing functional groups on the outermost surface [18]. In addition, solvent effects on adsorption were not considered in the theoretical calculations. Therefore, detailed experimental studies, especially spectroscopic evidences for the relevant mechanisms of adsorption, are strongly needed to characterize the interactions between G and aromatics with different structures.

In order to better understand the adsorption mechanisms we choose G and GO with different π -electron density and O-containing functional groups as adsorbents and 1,2,4-trichlorobenzene (TCB), 2,4,6-trichlorophenol (TCP), 2-naphthol and naphthalene (NAPH) as common representatives of aromatics with different structures. NAPH and TCB are structurally similar to 2-naphthol and TCP, but contain no polar hydroxyl group. The aims of this study were (i) to elucidate the adsorption of aromatics with different structures on G and GO with different physicochemical properties; and (ii) to provide an insight to the relevant adsorption mechanisms using a batch equilibration method and micro-Fourier transform infrared spectroscopy (μ -FTIR).

2. Experimental section

2.1. Chemicals

TCP (97.4%), TCB (98%), 2-naphthol (98%), and NAPH (98%) were purchased from Aldrich Chemical Co. Inc. (Milwaukee,

WI), and used as-received. Their selected properties are listed in Table 1. NaNO_3 , NaOH and HNO_3 were of guarantee reagent grade. Methanol was of HPLC grade.

2.2. Materials

G and GO were synthesized by a modified Hummers method [19]. Briefly, graphite powder (10 g) and sodium nitrate (5 g) were mixed with sulfuric acid (230 mL) in an ice bath, and potassium permanganate (30 g) was slowly added, and the mixture was kept at 274 K for 2 h with continuous agitation. The reaction was kept at 308 ± 2 K for 30 min with gas release, and then 460 mL of deionized water was gradually added, bringing about violent effervescence. The temperature of the water bath was increased to 371 K and the reaction was maintained at this temperature for 40 min in order to increase the oxidation degree of GO product. The resultant bright-yellow suspension was further treated with a H_2O_2 solution (30 mL, 30%) followed by centrifugation and careful washing to clean out remnant salt. The wet GO was dewatered by vacuum drying at 323 K. G was achieved by a low-temperature expansion under high vacuum. The above prepared GO was put into a quartz tube, which was connected to a high vacuum pump. The tube temperature was increased to 473 K at a rate of 50 K/min, and kept at this temperature for 5 h under a high vacuum (<1 Pa). After that the tube was cool down to room temperature and uninstalled from the vacuum pump, the produced G was obtained.

The surface functional groups on G and GO were determined by μ -FTIR and X-ray photoelectron spectroscopy (XPS). Nitrogen specific surface areas of G and GO were estimated using an accelerated surface area system and Brunauer–Emmett–Teller (BET) equation to adsorption of N_2 at 77 K.

2.3. Adsorption experiments

All adsorption experiments were conducted in triplicates using a batch equilibration technique at 23 ± 1 °C. Adsorption of TCB (1.0, 2.0, 5.0, 10.0, 15.0, 20.0, and 27.0 mg/L), TCP (1.0, 2.0, 5.0, 10.0, 15.0, 20.0, and 27.0 mg/L), 2-naphthol (1.0, 2.0, 5.0, 10.0, 15.0, 20.0, and 30.0 mg/L), and NAPH (2.0, 5.0, 10.0, 15.0, 20.0, and 25.0 mg/L) were carried out by mixing a certain amount of G and GO with 0.01 M NaNO_3 solution in 50 mL glass centrifuge tubes sealed with Teflon-lined screw caps. The suspended solution pH was adjusted to 5.0 ± 0.1 by addition of 0.1 M HNO_3 or 0.1 M NaOH to assure these adsorbates present in neutral species during adsorption process. The suspension was stirred continuously for 24 h to ensure complete adsorption (apparent equilibrium was reached before this time). The suspension was centrifuged at 1667g for 20 min to separate liquid from solid phases, and the concentrations of solutes in the supernatant phase were determined by HPLC. Controls were also prepared identically but contained no adsorbents, which were simultaneously run to assess loss of solutes. Results showed that no significant loss of solutes was observed (recoveries always >99–101%), indicating that microbial degradation, volatilization, or adsorption to the glass walls were negligible during the adsorption experiments.

The pH effect experiments were conducted using a batch adsorption approach as mentioned above. Both initial concen-

Table 1 – Selected properties of TCB, TCP, 2-naphthol, and NAPH.^a

Organic chemicals	Structures	MW (g/mol)	S (mg/L)	Log K_{ow}	pKa
CP		197.45	434.0	3.72	6.15
TCB		181.5	31.0	4.25	–
2-Naphthol		144.16	999.03	2.70	9.51
NAPH		128	32.13	3.33	–

^a MW: molecular weight, g/mol; S: aqueous solubility at room temperature, mg/L; K_{ow} octanol–water partition coefficient; pKa, dissociation constant.

trations of four adsorbates were 5.0 mg/L. After equilibrium was reached, the suspension was centrifuged, and the adsorbate concentrations in the supernatant were determined by HPLC. The adsorbed mass was calculated from the differences between the initial and final equilibrium concentrations.

2.4. μ -FTIR measurements and Raman spectra measurements

μ -FTIR spectra were recorded on NICOLET iN 10 MX (Thermo Scientific). Samples for μ -FTIR analysis were prepared with identical conditions to that used in the adsorption experiments. TCB-, TCP- or 2-naphthol-adsorbed G and GO were washed with 0.01 M NaNO₃ solution, and then freeze-dried overnight. Microsamples were pressed on a diamond bracket and μ -FTIR spectra were measured. The resolution for FTIR spectra was 16 cm⁻¹, and a total of 100 scans were collected for each spectrum. Difference spectra of adsorbed samples are obtained by subtracting adsorbate free spectra of G or GO from the corresponding spectra of adsorbate adsorbed G or GO.

Raman spectra were recorded with a Renishaw inVia Raman spectrometer (Renishaw plc, UK). The laser excitation was provided by an argon ion laser operated at wavelength of 514 nm.

2.5. Analysis

Solutes in the supernatants were determined by an Agilent 1200 reversed-phase HPLC (Atlantis-dC18 ODS HPLC column, 4.6 i.d. × 150 mm, 5 μ m) equipped with UV and fluorescence detectors. The determination wavelengths were set at 230 nm for TCB and TCP, the fluorescence wavelengths for

measurements of 2-naphthol and NAPH were at excitation wavelengths of 275 and 225 nm, and at emission wavelengths of 394 and 335 nm, respectively. The mobile phase was methanol:water (80:20, v:v) for TCB, TCP, and NAPH, and methanol:water (60:40, v:v) for 2-naphthol at a flow rate of 1.0 mL min⁻¹.

2.6. Data analysis

Adsorption data were fitted to the Freundlich equation using software Origin 7.5, and nonlinear regression analyses were conducted by the least-squares method. Freundlich equation can be expressed as $Q = K_f C^n$, where Q (mg/g) is the amount of adsorbed organic compounds by G and GO, C (mg/L) is the equilibrium concentration in solution, K_f is an empirical constant related to adsorption capacity (mg⁽¹⁻ⁿ⁾ g⁻¹ Lⁿ), and n is the Freundlich exponent or a site energy heterogeneity factor, often used as an indicator of isotherm nonlinearity.

3. Results and discussion

3.1. Characterization of G and GO

Selected physical and chemical properties of G and GO are given in Table S1. The BET specific surface area of G and GO were found to be 239.1 and 65.0 m² g⁻¹, respectively. The discrepancy of the obtained surface area of G and theoretical value (2620 m² g⁻¹) is attributed to the incomplete exfoliation and aggregation during reduction process because of unavoidable van der Waals force between each single layer of G. Transmission electron microscopy (TEM) shows that both G and GO had typically wrinkled, sheet-like structures (Supplementary Fig. S1).

In Fig. S2, Raman spectrum of G displays two prominent peaks at 1360 and 1593 cm^{-1} , which correspond to the well documented D band and G band, respectively. It is well known that G band corresponds to first-order scattering of E_{2g} mode observed for sp^2 carbon domains, and pronounced D band is associated with structural defects, amorphous carbon, or edges that can break symmetry and selection rule. Defect content is given by the ratio of D band to G band intensity (ID/IG). Compared to GO, the ID/IG of G decreased from 0.79 to 0.68, indicating decrease of amorphous carbon and structural defects on G layer (Fig. S2).

The FTIR spectra of G and GO are shown in Fig. S3. For G, peak at 1574 cm^{-1} was assigned to benzene ring C=C stretching vibration. Peaks appeared at 1734 and 1240 cm^{-1} were the results of carboxyl C=O and epoxy C–O stretching vibrations, respectively. For GO, FTIR spectrum shows a broad peak at 3399 cm^{-1} , which corresponds to –OH stretching vibration. In low wavenumbers range, FTIR spectra of GO shows C=O (1731 cm^{-1}), aromatic C=C (1626 cm^{-1}), carboxyl O=C–O (1378 cm^{-1}), and alkoxy C–O (1073 cm^{-1}) stretching vibrations, respectively [10]. FTIR spectra indicated that not only GO but also G has some O-containing functional groups on their outermost surface and defect sites.

XPS provides useful information on the nature of functional groups and on the defects on the G and GO surface. In Fig. 1a the XPS C1s peak of G is presented. Deconvolution of the C1s peak resolved a main peak of sp^2 C=C (284.2 eV) and several small peaks of the carbon in C–O (286.2 eV), the carbonyl carbon in C=O (288.3 eV), and the carboxylate carbon in O–C=O (290.0 eV). The spectrum of GO showed four types of carbon bonds: the carbon sp^2 C=C (284.8 eV) in the basal plane of GO, the carbon in C–O (286.8 eV), the carbonyl carbon in C=O (288.3 eV), and the carboxylate carbon in O–C=O (290.2 eV) (Fig. 1b) [8,20,21]. These results indicated that the surface of GO had large numbers of functional groups. Compared to G, the C–O peak at 286.8 eV and the C=O peak at 288.3 eV related to the oxidized carbon species were greatly strengthened, indicating that GO contained more O-containing functional groups than G.

3.2. Effect of pH on adsorption

Fig. 2 shows the effect of solution pH on the adsorption of TCB, TCP, 2-naphthol, and NAPH on G and GO. Generally, solu-

Fig. 2 – Effect of pH on the adsorption of TCP, TCB, 2-naphthol, and NAPH on G (a) and GO (b).

tion pH had different effects on the adsorption of different solutes.

For TCB and NAPH, as shown in Fig. 2a and b, their adsorption on G and GO were almost independent of solution pH over the investigated pH range because both TCB and NAPH were nonionizable [3]. The adsorption of TCP decreased slightly over pH 2.0–6.0, and decreased rapidly at pH > 6.0, consistent to the adsorption of TCP on soil and peat [22]. Considering pK_a value of TCP (6.15), it appears that the greater adsorption at low pH may be due to higher content of neutral TCP. An increase in solution pH increased the fraction of negatively charged TCP species. Therefore, electrostatic repulsion of anionic TCP with negatively charged surfaces of G and GO makes adsorption unfavorable.

A striking observation shown in Fig. 2 is that 2-naphthol exhibited remarkably different trends on G and GO when solution pH changed. As shown in Fig. 2a, adsorption of 2-naphthol on G was almost pH-independent from pH 2.0–8.0, followed by a significant increase of adsorption capacity over pH range of 8.0–9.2, and then decreased slightly (Fig. 2a) [3,6]. In fact, even at pH 10.2, 2-naphthol still had considerably higher adsorption capacity on G than that at acidic pHs. Considering pK_a value (9.51) of 2-naphthol, the predominant fraction of 2-naphthol was in anion form at pH above 9.51. The high adsorption capacity of 2-naphthol at higher pH suggested that specific adsorption-enhancement interaction

Fig. 1 – The C1s XPS spectra of G (a) and GO (b).

occurred to counterbalance electrostatic repulsion between anionic 2-naphthol and G surface. Several possible mechanisms had been considered based on literatures: (1) hydrogen-bonding interaction between $-OH$ group of 2-naphthol and O-containing groups on G; (2) direct anion- π interaction between $-OH$ or $-O^-$ (n-electron donor) groups of 2-naphthol and electron-depleted sites (π -electron acceptor) of G [6]; (3) π - π electron donor-acceptor (EDA) interaction between aromatic ring(s) of 2-naphthol and G surface [8]. Hydrogen-bonding was not likely a primary cause of the enhanced adsorption for following reason. At high pH, both $-OH$ group on 2-naphthol and O-containing groups of G would be ionized, and hydrogen-bonding effect should have been significantly impeded. However, Fig. 2a shows that adsorption affinity of 2-naphthol reached a maximum at pH ~ 9.2 . Zhao et al. [6] pointed out that ionized 1-naphthol might directly interact with the electron-depleted surface of sulfonated graphene via anion- π interaction. But in this study, the anion- π interaction was also excluded because adsorption of TCP was suppressed when its $-O^-$ group prevailed over its $-OH$ group at high pH. On the basis of above analysis, we propose that π - π EDA interaction between π -electron-rich naphthalene ring of 2-naphthol and π -electron-depleted regions of G surface was a primary mechanism for the enhanced adsorption of 2-naphthol, which would be verified in the following FTIR section. For 2-naphthol, its $-OH$ group is a strong electron-donor, makes naphthalene ring of 2-naphthol π -electron rich, thus facilitating π - π EDA interaction between 2-naphthol and G.

When $-OH$ group of 2-naphthol dissociated to $-O^-$ at high pH, it seemed that electron-donating strength would be further improved. The Mulliken electron distribution was calculated employing density functional theory [23–25] (B3LYP) with 6–311++G** basis set as implemented in the Gaussian 98 program [26]. Fig. 3 showed π -electron density of neutral and anionic 2-naphthol. It is found that the total Mulliken electrons on naphthalene ring of neutral 2-naphthol is about -1.038 e. When 2-naphthol is dissociated to anionic 2-naphthol, the total Mulliken electrons on naphthalene ring of 2-naphthol is correspondingly increased to -1.208 e. Undoubtedly, an increase in π -electron density facilitated the adsorption of 2-naphthol to G at higher pH than that at lower pH despite electrostatic repulsion between anionic 2-naphthol and G surface. As for TCP, it has only one benzene ring and, accordingly, has much weaker π -electron-conjugating potential than two-ringed 2-naphthol. The total Mulliken electrons on benzene ring of neutral TCP are -1.572 e (Fig. 3). When TCP was dissociated to anion, the total Mulliken electrons on benzene ring did not increased as the same as 2-naphthol, while decreased (-1.461 e). Possibly, this was one of reasons that TCP adsorption on G decreased at high pH range (Fig. 2a).

It should be noted that, if the same pH value is considered, four solutes has much lower adsorption capacity on GO than that on G (Fig. 2b), which is attributed to smaller surface area and less π -electron density of GO. Another possible reason is that hydrophilic GO surface containing various oxygen groups can bond water molecules, this competitive mechanism af-

Fig. 3 – Mulliken electrons distribution schematics of neutral 2-naphthol (a), anionic 2-naphthol (b), neutral TCP (c), and anionic TCP (d).

Fig. 4 – Adsorption isotherms of TCP, TCB, 2-naphthol, and NAPH on G (a) and GO (b).

fects the adsorption of other organic chemicals on GO. In contrast to G, GO has a markedly different effect on 2-naphthol adsorption as a function of solution pH. Over pH 2.0–8.3, the adsorption of 2-naphthol on GO was pH-independent. At pH > ~8.3, the adsorption capacity of 2-naphthol was not increased as the same as that on G, while decreased rapidly. The different effects of pH on 2-naphthol adsorption are related to different properties of G from GO. Compared to G, GO contained much less π -electron, and more O-containing groups on its surface, which was unfavorable for formation of π - π interaction with 2-naphthol. Thus, 2-naphthol adsorption was not increased accordingly with increasing solution pH as the same as that on G. This result also supported our above hypothesis that π -electron of G played an important role in the enhanced adsorption of 2-naphthol on G, especially at higher pH conditions.

3.3. Adsorption isotherms

The adsorption isotherms of TCB, TCP, 2-naphthanol, and NAPH on G and GO are shown in Fig. 4a and b. All isotherms fitted Freundlich equation well. In general, all adsorption isotherms were highly nonlinear, and the regression parameters are listed in Table 2.

Fig. 4a compares the adsorption of four adsorbates to G. It was found that, interestingly, adsorption behaviors of four adsorbates to G were similar in despite of their different chemical properties. The adsorption was correlated poorly with hydrophobicity of these chemicals: water solubility (C_{sat})

and *n*-octanol–water partition coefficient (K_{ow}) (Table 1). Similarly, the nonlinear adsorption isotherms of four adsorbates on G also suggested except for hydrophobic interaction, some specific interactions should be responsible for their adsorption on G. As described above, π - π EDA interaction between aromatic ring of four adsorbates and G surface should be a main mechanism responsible for strong adsorption of these adsorbates on G [6–8]. Compared to molecular structures of TCB and NAPH, TCP and 2-naphthol have a more hydroxyl group on their individual molecular structure, while their similar adsorption capacity on G indicated that the presence of hydroxyl group had no substantial contribution to the overall adsorption of TCP and 2-naphthol at the examined pH. These results are consistent to Zhao et al., who also found NAPH and 1-naphthol had similar adsorption capacity on sulfonated graphene [6].

Different from G, adsorption of four adsorbates on GO followed the order of NAPH < TCB < TCP < 2-naphthol, which indicated that different adsorption mechanisms should be responsible for the adsorption on GO (Fig. 4b). The strong adsorption of hydroxyl-substituted 2-naphthol and TCP indicated that their adsorption reaction was related to the presence of hydroxyl group. It was well known that GO has less π -electron and more O-containing groups on its surface. Thus, hydroxyl groups of 2-naphthol and TCP could interact with O-containing groups on GO through H-bonding. Following μ -FTIR spectroscopic study provides a detailed insight to the adsorption mechanisms of these adsorbates on G and GO.

Table 2 – Freundlich constants (K_f and n) and correlation coefficients (r) of TCB, TCP, 2-naphthol, and NAPH adsorption onto G and GO ($n = 3$).

Adsorbents	Adsorbates	K_f	n	r
G	TCP	16.10(1.65)	0.40(0.04)	0.97
	TCB	15.01(1.60)	0.40(0.04)	0.97
	2-Naphthol	22.70(1.65)	0.29(0.03)	0.99
	NAPH	14.17(1.55)	0.47(0.04)	0.97
GO	TCP	3.46(0.16)	0.34(0.02)	0.99
	TCB	1.56(0.16)	0.35(0.04)	0.98
	2-Naphthol	4.20(0.15)	0.53(0.01)	0.99
	NAPH	0.93(0.16)	0.40(0.06)	0.99

Fig. 5 – μ -FTIR spectra of pure TCP, TCB, and 2-naphthol, and adsorbed TCP, TCB, and 2-naphthol on G (a) and GO (b), respectively.

3.4. μ -FTIR analysis

To reveal the adsorption mechanisms of four adsorbates on G and GO, a μ -FTIR study was performed. The μ -FTIR spectra of TCB-G, TCB, TCP-G, TCP, 2-naphthol-G, and 2-naphthol are shown in Fig. 5a. For TCB, the prominent peaks at 1459 cm^{-1} are attributed to benzene ring C=C stretching, and the band at 1127 cm^{-1} is due to strong C–C skeletal vibrations of benzene ring [27]. For TCP, peaks at 1473 , 1400 , and 1167 cm^{-1} are assigned to C=C stretching vibration and C–C skeletal vibrations of benzene ring. Peak at 1280 cm^{-1} is assigned to C–O stretching vibration. Two bands appeared at 1320 and 1222 cm^{-1} are attributed to O–H bending and deformation vibrations [28]. After TCB and TCP were adsorbed on G, peaks of C=C stretching vibration and C–C skeletal vibrations of benzene ring shifted from 1459 and 1127 cm^{-1} to 1455 and 1115 cm^{-1} for TCB, and shifted from 1473 , 1400 , and 1167 cm^{-1} to 1467 , 1390 , and 1154 cm^{-1} for TCP, respectively. Such shifts suggested that benzene rings of TCB and TCP attended the whole adsorption process on G through π – π interaction. It was significant that π – π interaction weakened the double band character of benzene ring and caused red-shift of C=C stretching vibration bands (Fig. 5a). Previous theoretical calculation suggested that benzoic acid adsorption on G was driven primarily by electron transfer process between the G surface and the –COOH group, and to lesser extent by π – π interaction between the G surface and the aromatic core of benzoic acid [16]. However, in this study, for TCP with electron-donating –OH group, different observation was obtained. As shown in Fig. 5a, the C–O stretching vibration (1280 cm^{-1}) and O–H deformation vibration (1320 and 1222 cm^{-1}) of TCP have not been significantly shifted when TCP was adsorbed on G, indicating that hydroxyl group was not involved in the adsorption reaction. It is also the reason why TCB and TCP have similar adsorption capacity on G though they have different molecule structures. As for 2-naphthol standard, peaks

at 1632 , 1602 , 1514 , and 1468 cm^{-1} are attributed to benzene ring C=C stretching, and band at 1279 cm^{-1} is due to C–O stretching vibration, respectively [29,30]. Two peaks at 1325 and 1218 cm^{-1} are attributed to O–H bending and deformation vibrations of 2-naphthol [28]. When 2-naphthol was adsorbed on G (Fig. 5a), it was found that its C=C stretching vibration peaks at 1632 , 1602 , and 1468 cm^{-1} were shifted to 1627 , 1593 , and 1457 cm^{-1} , respectively, suggesting the occurrence of π – π interaction in the form of face-to-face stacking between 2-naphthol and G surface. As for NAPH, no FTIR spectra are provided in Fig. 5a due to its weak FTIR response signal in 1000 – 2000 cm^{-1} . However, according to previous theoretical calculation [6], the main adsorption mechanism of NAPH on G was π – π interaction, where NAPH was adsorbed in a tiled form.

Compared to G, FTIR results revealed that TCP and 2-naphthol have significantly different adsorption mechanism on GO (Fig. 5b). When TCP was adsorbed on GO, it was found that the C–C skeletal vibrations (1167 cm^{-1}) of benzene ring have no shift. And peaks of C=C stretching vibration of benzene ring had very slight shifts from 1473 and 1400 cm^{-1} to 1471 and 1398 cm^{-1} , respectively. Considering the resolution of μ -FTIR, such slight shifts could not be used as evidence for π – π interaction. In contrast, the O–H bending vibration of TCP shifted significantly from 1320 to 1329 cm^{-1} when TCP was adsorbed on GO. This suggested that TCP was adsorbed on GO mainly through H-bonding between hydroxyl group of TCP and O-containing group on GO surface rather than π – π interaction. Similarly, when 2-naphthol was adsorbed on GO, peaks attributable to C=C stretching vibration (1514 and 1468 cm^{-1}) exhibited no shift, suggesting that naphthalene ring of 2-naphthol was not involved in adsorption process on GO (Fig. 5b). However, when C–O stretching vibration of adsorbed 2-naphthol at 1269 cm^{-1} was compared with that of 2-naphthol standard at 1279 cm^{-1} , it appears that a 10 cm^{-1} shift resulted from the formation of H-bonding between hydroxyl group of 2-naphthol and O-containing groups on GO. The shift of O–H bending vibrations from 1325 to 1330 cm^{-1} also verified the presence of H-bonding. This is also the possible reason why TCP and 2-naphthol have higher adsorption capacities on GO than that of TCB and NAPH.

We also tried to give some FTIR evidences for the mechanisms of TCB and NAPH adsorption onto GO. Unfortunately, the obtained FTIR spectra were characterized by broad and overlapping bands that do not provide detailed clues as to identification of adsorption mechanisms due to their low adsorption capacities and/or FTIR response signal. Thus, no FTIR spectra of TCB and NAPH adsorption on GO are shown in Fig. 5b.

4. Conclusions

In view of the foregoing study, it was found that G and GO with different properties have different effects on four aromatics adsorption. On G, four aromatics had similar adsorption capacity at pH 5.0 in despite of their different chemical properties. It was indicated that except for hydrophobic interaction, four aromatics were adsorbed on G mainly via π – π interaction. Compared to G, GO has lesser π -electron density

and more O-containing functional groups. The adsorption affinity of four aromatics increased in the order NAPH < TCB < TCP < 2-naphthol on GO. The higher adsorption of hydroxyl-substituted TCP and 2-naphthol on GO was mainly attributed to the formation of H-bonding between hydroxyl groups of TCP and 2-naphthol and O-containing functional groups on GO.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2012.08.024>.

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