



## Sorption of 1-naphthol by plant cuticular fractions

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### Abstract

The contribution of aliphatic-rich plant biopolymer to sorption of hydrophobic organic compounds is significantly important because of their preservation and accumulation in the soil environment, but sorption mechanism is still not fully understood. In this study, sorption of 1-naphthol by plant cuticular fractions was examined to better understand the contributions of respective fraction. Toward this end, cuticular materials were isolated from the fruits of tomato by chemical method. The tomato cuticle sheet consisted of waxes (6.5 wt%), cuticular monomer (69.5 wt%), and polysaccharide (24.0 wt%). Isotherms of 1-naphthol to the cuticular fractions were nonlinear ( $N$  value (0.82 – 0.90)) at the whole tested concentration ranges. The  $K_{oc}/K_{ow}$  ratios for bulk cuticle (TC1), dewaxed cuticle (TC2), cutin (TC4), and desugared cuticle (TC5) were larger than unity, suggested that tomato bulk cuticle and cutin are much powerful sorption medium. Sorption capability of cutin (TC4) was 2.4 times higher than the nonsaponifiable fraction (TC3). The 1-naphthol interactions with tomato cuticular materials were governed by both hydrophobic-type interactions and polar (H-bonding) interactions. Removal of the wax and polysaccharide materials from the bulk tomato cuticle caused a significant increase in the sorption ability of the cuticular material. There was a linear negative trend between  $K_{oc}$  values and the amount of polysaccharides or fraction's polarities ( $(N+O)/C$ ); while a linear positive relationship between  $K_{oc}$  values and the content of cutin monomer (linear  $R^2 = 0.993$ ) was observed for present in the cuticular fractions. Predominant sorbent of the hydrophobic organic compounds (HOCs) in the plant cuticular fraction was the cutin monomer, contributing to 91.7% of the total sorption of tomato bulk cuticle.

**Key words:** plant cuticle; 1-naphthol; sorption; cutin monomer

### Introduction

Sorption and desorption are the major processes influencing the fate of hydrophobic organic compounds (HOCs) in the environment and their risk assessment. The predominant sorbent of HOCs in soils is the soil organic matter (SOM) (Chin *et al.*, 1997; Chiou *et al.*, 1998; Perminova *et al.*, 1999; Chefetz *et al.*, 2000; Salloum *et al.*, 2002; Kang and Xing, 2005). In both forest and agricultural soils, plant derived cuticular materials can constitute a significant part of soil organic matter (Kögel-Knabner *et al.*, 1992; Nierop, 1998). Many researches suggested that the chemical natures and physical conformation of SOM were the major factors controlling its sorption mechanism and affinity (Chin *et al.*, 1997; Chiou *et al.*, 1998; Kang and Xing, 2005). Most of these studies suggested a positive correlation between the amount of HOC sorption and the aromatic carbon content of the sample (Chin *et al.*, 1997; Chiou *et al.*, 1998; Perminova *et al.*, 1999). However, recently several studies demonstrated aliphatic-rich SOM also has a high sorption affinity (Chefetz *et al.*, 2000; Salloum *et al.*, 2002; Kang and Xing, 2005). The main

sources of aliphatic compounds for SOM are derived from microbial lipids, plant waxes, and above- and below-ground plant biopolymers, such as cutin, cutan and suberin (Nierop, 1998; Heredia, 2003). These aliphatic-rich SOM structure have been reported to show selective preservation in the soil, with little or no alteration (Kögel-Knabner *et al.*, 1992, 1994; Nierop, 1998). Hence the contribution of aliphatic-rich plant biopolymer (SOM precursors) to the overall sorption and sequestration of HOCs becomes quite important because of their accumulation in the soil environment (Chefetz, 2003; Stimler *et al.*, 2006).

Plant cuticular materials play an important role in sorption of polar and nonpolar pollutants in soils (Chen *et al.*, 2005; Stimler *et al.*, 2006). Sluszny *et al.* (1998) found that incubation of soils in the presence or absence of organic matter amendments did not affect the organic-normalized sorption coefficient ( $K_{oc}$ ). Stimler *et al.* (2006) suggested that the decomposition of the cuticular materials of tomato and pummelo fruit during incubation had only a minor effect on the sorption-desorption behavior of the PAHs, while the sorption of triazines were significantly affected by the decomposition of the cuticles from pummelo leaves. Stimler *et al.* (2006) suggested that the more condensed structure of the cutin and mainly the cutan biopolymer govern sorption of the cuticle residues with decomposition. Recently, many researchers focused on the sorption by the

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plant cuticles or other persistent biopolymer. Studies have shown high sorption capacity by these aliphatic fractions (Chefetz, 2003; Chen *et al.*, 2005; Chen and Xing, 2005; Shechter *et al.*, 2006). Chefetz (2003) concluded that long aliphatic chains in cutin and aliphatic substituents of polyester are more effective than aromatic moieties in binding pyrene. Chen and Xing (2005) demonstrated the markedly high sorption capacity of various plant cuticular fractions, and highlight the polarity and accessibility of organic matter in uptake of nonpolar and polar organic pollutants.

Plant cuticles are highly complex membranes that cover the outer surface of the aerial parts of terrestrial plants, acting not only as a primary barrier but also as a gateway between the plant and its environment (Heredia, 2003). Plant cuticular material occurs in considerable amounts in both natural and agricultural areas (180 and 1500 kg/hm<sup>2</sup>, respectively). The main compositions of plant cuticles are soluble cuticular waxes, insoluble cutin, nondegradable cutan. In addition, amounts of polysaccharides, phenols, and amino acids may also present (Heredia, 2003). The nature of each composition is different, which may result in different sorption capabilities. However, the characteristics of such sorption by plant cuticular fractions are still not well-understood.

The main objective of this study was to examine sorption of 1-naphthol by isolated plant cuticular fractions to better understand their sorption activity and their individual contribution to the sorption. Tomato fruit cuticle was chosen as a model plant cuticle. 1-naphthol was used since it is a metabolite of naphthalene, and a component in pesticides (napropamide and carbaryl).

## 1 Materials and methods

### 1.1 Isolation of plant cuticular fractions

Cuticular fractions were isolated from the fruits of ripe tomato using a modified version of the method reported by Kögel-Knabner *et al.* (1994). The flowchart of the isolation processes of cuticular fractions is displayed in Fig. 1.

Briefly, cuticle sheets were manually peeled from fresh tomato fruits. The sheets were boiled in water for 1 h, and the pulp was removed manually as much as possible. Then the bulk cuticle sheets were treated with a solution of oxalic acid (4 g/L) and ammonium oxalate (16 g/L) at 40°C for

24 h and washed with deionized stiller water to remove any residual fruit pulp materials and the used chemicals. This procedure yielded the bulk cuticle sheets (TC1). Waxy materials were removed from TC1 fraction by Soxhlet extraction with chloroform/methanol (1:1, v/v) at 70°C for 6 h to yield a dewaxed cuticle fraction (TC2). To remove the cutin monomer, TC2 fraction were saponified with 1% potassium hydroxide in methanol for 3 h at 70°C under refluxing and stirrer spinning conditions, producing the nonsaponifiable fraction (TC3). To obtain the cutin biopolymer (TC4), the dewaxed tomato cuticles (TC2) were hydrolyzed with 6 mol/L HCl solution with refluxing for 6 h at 100°C to remove carbohydrates components. TC1 were also hydrolyzed with 6 mol/L HCl solution with refluxing for 6 h at 100°C, gaining desugared cuticles (TC5). The resulting fractions of TC3, TC4, and TC5 were separated from the basic or acidic solution by filtration, and then the residues were washed with a mixed solution of methanol and deionized distilled water (1:1, v/v) 5 times to adjust these fractions to neutral conditions at the end and to remove dissolved organic matter (e.g., cutin monomer and carbohydrates) sorbed by these residues. All isolated fractions were dried, ground, and sieved (<0.15 mm) before analysis and sorption experiments. Based on mass balance, the yields of TC2, TC3, TC4, and TC5 were calculated to the percentage contents of TC1.

### 1.2 Elemental analysis

The C, H, and N content of the cuticular fractions were determined using an EA 1112 CHN elemental analyzer (Thermo Finnigan), while the oxygen content was calculated by the mass difference. The H/C, O/C and (O+N)/C atomic ratios were calculated to evaluate the structure and polarity of the isolated cuticular fractions.

### 1.3 Batch sorption experiment

A polar aromatic organic compound, 1-naphthol, was chosen as a sorbate. The selected properties of 1-naphthol, such as the aqueous solubility, octanol-water partition coefficient and dissociation constant ( $pK_a$ ), are 866 µg/ml (25°C), 501 and 9.34, respectively. The organic compound with analytical-grade was purchased from Shanghai Chemical Co. and used without further purification. 1-Naphthol is common organic contaminant in soil and sediment and has often been used in environmental research.

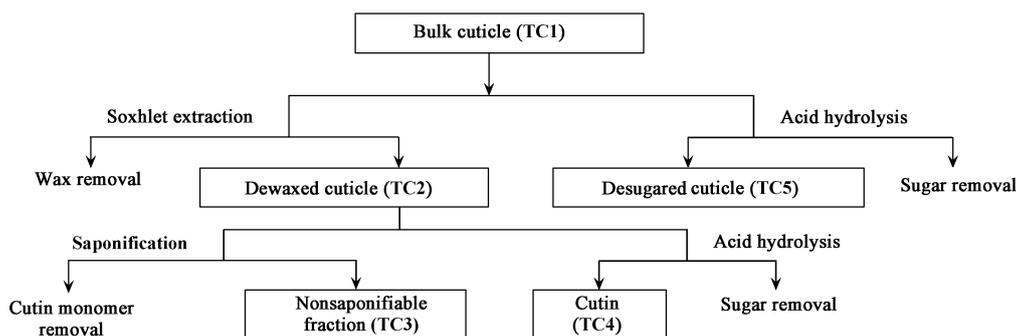


Fig. 1 Flowchart of the isolation processes of tomato cuticular fractions.

All sorption isotherms of the isolated cuticular fractions were obtained using a batch equilibration technique in screw cap vials with aluminum foil liners. 1-Naphthol was dissolved in the background solution including 0.01 mol/L  $\text{CaCl}_2$  to maintain a constant ionic strength, and 200 mg/L  $\text{NaN}_3$  to prevent biological degradation of sorbate. To have the tested organic compound at a neutral state, the pH value of the background solution was controlled at 7. The solid-to-solution ratios were adjusted to achieve to 30%–80% sorption of organic compound at apparent equilibrium. For each sample, nine different initial concentrations were used ranging from 10 to 600 mg/L; each point, including the blank, was run in duplicate, and resulted in 18 data points for each isotherm. Preliminary tests indicated apparent equilibrium of 1-naphthol was reached before 2 d. The vials were sealed with aluminum foil-lined Teflon screw caps and then placed on a rotating shaker and agitated in the dark at 20 r/min for 3 d at  $25 \pm 0.5^\circ\text{C}$ . The solution was separated from remaining solids by centrifugation at 4500 r/min for 30 min. An aliquot amount of the supernatant was removed, diluted with deionized stiller water. To further enhance determination sensitivity, the analyzed solution was basified to a pH of 12 with 0.1 mol/L NaOH solution to make sure 1-naphthol present in dissociation state. The equilibrium concentration of 1-naphthol was measured by using UV-2550 spectrophotometer at 332 nm. Because of little sorption by vials and no biodegradation, the sorbed amount by sorbent was calculated by mass difference (Chen *et al.*, 2005).

#### 1.4 Data analysis

All sorption data were fitted to the logarithmic form of the Freundlich Equation:

$$\lg Q = \lg K_f + N \lg C_e \quad (1)$$

where,  $Q$  is the solid-phase concentration (mg/kg) and  $C_e$  is the liquid-phase equilibrium concentration (mg/L). The parameters  $K_f$  for the sorption capacity coefficient ((mg/kg)/(mg/L) <sup>$N$</sup> ) and  $N$  (dimensionless) indicating isotherm nonlinearity were determined by linear regression of log-transformed data. Values for the C-normalized capacity coefficient ( $K_{f,OC}$ ) were calculated by normalizing  $K_f$  to the C content in each sorbent. Since the  $K_{f,OC}$  value depends on the  $N$  value, it is not possible to compare the  $K_{f,OC}$  values for isotherms with different  $N$  values. Thus,

slopes of sorption isotherms ( $K_d$ ) were calculated from the linear fitting of whole isotherms for 1-naphthol. Values of  $K_{oc}$  were calculated from normalizing  $K_d$  to the carbon level of each cuticular fraction.

## 2 Results and discussion

### 2.1 Characterization of the cuticular fractions

The principal components of the cuticular membrane are soluble and polymerized aliphatic lipids. The yields and elemental compositions of isolated tomato fruit cuticular fractions are presented in Table 1. The amount of waxes in tomato cuticle sheet, removed by Soxhlet extraction, was 6.5 wt%, which was similar to wax fraction content of pepper cuticle (6.2 wt%) (Chen *et al.*, 2005). Similar loss of the total mass was present when the TC1 and TC2 were acid-hydrolyzed (i.e., 24.7 wt% and 23.2 wt% for TC1 and TC2, respectively). In another word, the amount of polysaccharides was about 24.0 wt%. Whereas the fraction removed by saponification was the major part of the tomato fruit cuticle (i.e., cutin monomer), corresponding to 70.4 wt% (i.e., TC4). Due to tomato cuticle is cutan-free (Shechter *et al.*, 2006; Osman *et al.*, 1999; Tegelaar *et al.*, 1991), TC3 fraction (28.8 wt%) should contain 24.0 wt% of pectin or polysaccharide and 4.8 wt% cutin monomer, suggested that cutin monomer was not removed completely by saponification process from TC2 to TC3. These data were consistent with the literature results (Osman *et al.*, 1999; Stimler *et al.*, 2006). The major structural component of the cuticle is cutin, a biopolyester mainly composed of interesterified hydroxyl and epoxy-hydroxy fatty acids with a chain length of 16 and/or 18 carbons ( $\text{C}_{16}$  and  $\text{C}_{18}$  class) (Osman *et al.*, 1999; Heredia, 2003). Based on mass balance, the elemental compositions of wax, cutin monomer, and polysaccharide were estimated and listed in Table 1.

The organic carbon content of TC5 was the highest (70.16%), while C% of TC3 was the lowest (44.34%). The H/C ratios for TC1, TC2, TC3, TC4 and TC5 samples were 1.6, exhibited a highly aliphatic nature. The polarity index ((N+O)/C) was the highest with TC3, with an order of TC3 (0.84) > TC1 (0.33) = TC2 (0.33) > TC4 (0.23) > TC5 (0.22). Nonsaponifiable fraction (TC3) showed the lowest carbon content, but the highest polarity. That is because the main composition of the nonsaponifiable

**Table 1** Relative yields of the different tomato cuticle fractions and their elemental analysis and atomic ratios

Sample <sup>a</sup>	Yield (wt%) <sup>b</sup>	C (%)	H (%)	N (%)	O (%) <sup>c</sup>	H/C	O/C	(N+O)/C
TC1	100	63.45	8.78	1.45	26.31	1.65	0.31	0.33
TC2	93.5	63.33	8.66	1.29	26.71	1.63	0.32	0.33
TC3	28.8	44.34	6.21	2.60	46.86	1.67	0.79	0.84
TC4	70.4	69.41	9.45	0.45	20.69	1.62	0.22	0.23
TC5	75.3	70.16	9.59	0.43	19.82	1.63	0.21	0.22
Wax <sup>d</sup>	6.5	65.12	10.60	3.75	20.58	1.93	0.24	0.29
Cutin <sup>d</sup>	69.5	71.81	9.75	0.71	17.73	1.62	0.19	0.19
Sugar <sup>d</sup>	24.0	43.91	6.27	4.23	45.62	1.70	0.78	0.86

<sup>a</sup> TC1: bulk cuticle of tomato; removal of waxy material from TC1 yielded dewaxed cuticle (TC2); saponification of TC2 produced nonsaponifiable fraction (TC3); the TC1 and TC2 samples were hydrolyzed to yield a desugared residue (TC5) and a pure cutin residue (TC4), respectively. <sup>b</sup> The yields of TC2, TC3, TC4, and TC5 were calculated to the percentage contents of TC1. <sup>c</sup> Oxygen content was calculated by the mass difference. <sup>d</sup> Calculated results based on mass balance.

fraction (TC3) was polysaccharide. And polysaccharides have much polar functionalities, such as carboxyl and carbonyl structures, resulting in higher oxygen content and lower carbon content. The results of elemental analysis and atomic ratios of TC1 and TC2 were similar, and the TC4 was close to TC5. The data of bulk cuticle and cutin are consistent with the results of Shechter *et al.* (2006). These elemental composition data indicate that the cuticular fractions were mainly aliphatic components with a wide range. The plant cuticle is chemically heterogeneous in nature. The heterogeneous structure and components would affect sorption characteristics of the cuticular fractions.

## 2.2 Sorption of 1-naphthol with tomato cuticular fractions

Sorption isotherms of 1-naphthol by the cuticular fractions are displayed in Fig.2. The sorption isotherms fit well to the Freundlich equation; the Freundlich model parameters are listed in Table 2. The sorption isotherms were nonlinear exhibiting a Freundlich  $N$  value of 0.82–0.90. Similar results were observed for 1-naphthol to the pepper cuticular fractions (Chen *et al.*, 2005) and atrazine to tomato bulk cuticle and cutin fractions (Shechter *et al.*, 2006). However, precise comparison cannot be made between  $K_f$  values because of their different units as a result of nonlinearity. Therefore, the sorption coefficients ( $K_d$ ,  $K_{oc}$ ) were calculated (see Materials and Methods) (Table 2). According to Table 2, the calculated ratios of  $K_{oc}/K_{ow}$  for TC1, TC2, TC4, and TC5 were larger than unity, suggested that tomato bulk cuticle and cutin are much powerful sorption medium, which attributed to tomato cuticle constructed of hydroxy-fatty acids with chain lengths of  $C_{16}$  and  $C_{18}$  (Osman *et al.*, 1999). The

1-naphthol interactions with tomato cuticular materials are governed by both hydrophobic-type interactions and polar (H-bonding) interactions.

Carbon-normalized capacity coefficients ( $K_{f,OC}$ ) of 1-naphthol with tomato bulk cuticle (TC1), dewaxed cuticle (TC2), nonsaponifiable cuticle (TC3), cutin (TC4), and desugared cuticle (TC5) were 1288, 1517, 908, 1756, and 1915 (mg/kg OC)/(mg/L) <sup>$N$</sup> , respectively. As previously reported, the  $K_{f,OC}$  values for atrazine with tomato bulk cuticle and the cutin biopolymer were 284 and 760 (mg/kg OC)/(mg/L) <sup>$N$</sup>  ( $N = 0.74$  for bulk cuticle, and  $N = 0.94$  for cutin), respectively (Shechter *et al.*, 2006). The octanol-water partition coefficient of 1-naphthol and atrazine are same ( $K_{ow} = 501$ ), but sorption of 1-naphthol with tomato cuticular fractions was much higher than that of atrazine according to sorption amount instead of  $K_{f,OC}$  due to the  $K_{f,OC}$  values could not compare each other directly (Shechter *et al.*, 2006). This may result from different molecular structure of 1-naphthol and atrazine (Fig.3), such as less molecular dimension and higher polar functional group (–OH) of 1-naphthol than that of atrazine, which were facilitated strongly specific interaction of 1-naphthol, with cuticular materials.

The  $K_{oc}$  values of all the samples were in the range of values reported for soil/geologic samples (Salloum *et al.*, 2001). Consistent with the similar result of elemental analysis and atomic ratios,  $K_{oc}$  values of TC1 (655 ml/g OC) and TC2 (667 ml/g OC) were almost similar, as  $K_{oc}$  value of TC4 (833 ml/g OC) was close to TC5 (799 ml/g OC). Sorption capability of cutin biopolymer (TC4) was 2.4 times higher than the nonsaponifiable fraction (TC3). For TC3 (main composition is polysaccharide), the lowest carbon content and highest polarity ((N+O)/C,

Table 2 Regression parameters of isotherms of 1-naphthol with tomato cuticular fraction and corresponding sorption coefficients

Sorbent <sup>a</sup>	Freundlich $R^2$	$N$	$K_f^b$	$K_{f,OC}^c$	$K_d$ (ml/g)	$K_{oc}$ (ml/g)	Linear $R^2$	$K_{oc}/K_{ow}$
TC1	0.991	0.90	817	1288	416	655	0.983	1.31
TC2	0.991	0.88	961	1517	422	667	0.965	1.33
TC3	0.990	0.82	403	908	153	344	0.990	0.69
TC4	0.995	0.88	1219	1756	578	833	0.984	1.66
TC5	0.996	0.85	1344	1915	561	799	0.988	1.59

<sup>a</sup> The definition of the sorbents see Table 1; <sup>b</sup>  $K_f$  is the sorption capacity coefficient ((mg/kg)/(mg/L) <sup>$N$</sup> ); <sup>c</sup>  $K_{f,OC}$  is the carbon-normalized capacity coefficients ((mg/kg)/(mg/L) <sup>$N$</sup> ).

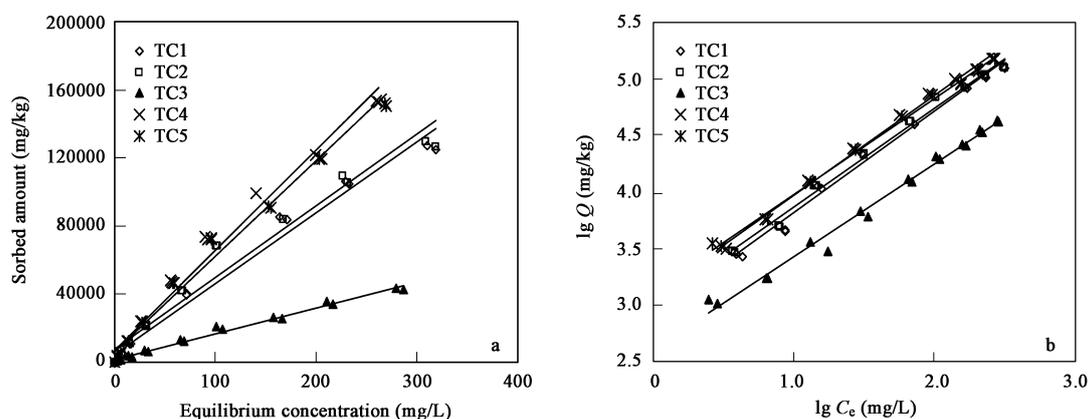


Fig. 2 Sorption isotherms of 1-naphthol to tomato cuticular fractions. (a) linear regression; (b) Freundlich regression.

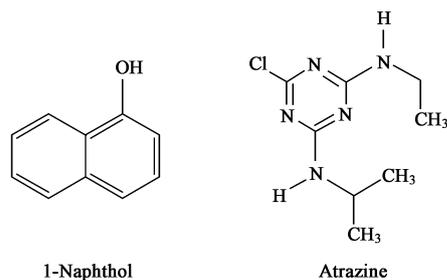


Fig. 3 Molecular structures of 1-naphthol and atrazine.

0.84) resulted in the low sorption capability and nonlinear sorption isotherm (lowest  $N$ , 0.82).

The principal components of tomato fruit cuticles are waxes, cutin, and pectin or polysaccharide, which exhibited different sorption capacity. Cuticular waxes play a pivotal role in limiting transpirational water loss across the plant surface. The epicuticular waxes of tomato fruits consisted exclusively of long-chain aliphatics, while the intracuticular compartment contained large quantities of pentacyclic triterpenoids as well. And the main portion of the transpiration barrier is located in the intracuticular wax layer, largely determined by the aliphatic constituents, whereas epicuticular aliphatics play a minor role (Vogg and Fisher, 2004). Similar to previous observations (Chefetz, 2003; Chen *et al.*, 2005; Shechter *et al.*, 2006), waxy materials were not active in sorbing hydrophobic organic compounds. Removal of the waxes (6.5 wt%) from the bulk tomato cuticle resulted in a slight increase (2%) in the sorption ability of the sample. Removal of the cuticular waxes resulted in a 15% increase in the atrazine  $K_{oc}$  value (Chefetz, 2003). These observations suggest poor sorption contribution of the surface waxes of the cuticle to overall sorption, probably because of their crystalline nature. Due to low wax content, the isolated waxy material in tomato cuticle was not enough quantity to investigate its sorption property. Therefore, assuming two separate partition compartments (physical mixture) (Chefetz, 2003), the waxy material would contribute to the sorption potential of TC1 according to its relative level in the sample (Table 1),  $K_{d,TC1} = 93.5\% \times K_{d,TC2} + 6.5\% \times K_{d,wax}$ . This calculation resulted in a sorption coefficient of  $K_{d,wax}$  (324 ml/g), and  $K_{oc,wax}$  (497 ml/g OC) which is similar to  $K_{ow}$  of 1-naphthol.

Cutin is the major fraction of the tomato cuticle, corresponding up to 70% of its dry weight. Cutin plays an important role in cuticle as a structural component and as a defense barrier toward pathogens and the uncontrolled loss of water, as well as in transporting substances across the plant tissues (Kallio and Nieminen, 2006). Cutin exhibits a strongly paraffinic nature, and appears to be rubber-like. The paraffinic carbon made up 76% of the total carbon in the tomato cutin sample as calculated from the  $^{13}\text{C}$  NMR spectra (Shechter *et al.*, 2006). Several studies have emphasized the importance of the cutin biopolymer as a sorbent. In the present study, a linear positive relationship between  $K_d$  values and the cutin contents was observed (linear  $R^2=0.989$ , Fig.4). It seems that the content of cutin

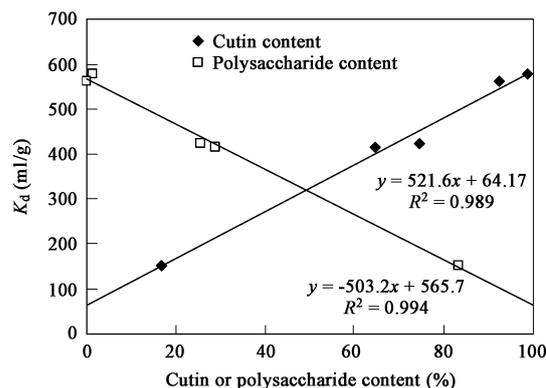


Fig. 4 Relationships of sorption coefficients ( $K_d$ ) of 1-naphthol by tomato cuticular fractions with cutin contents or polysaccharide contents.

monomer controlled the sorption capability of the plant cuticle.

Removal of polysaccharides resulted in a significant increase in  $K_{oc}$  value, i.e.,  $K_{oc,TC5}/K_{oc,TC1}=1.21$ ,  $K_{oc,TC4}/K_{oc,TC2} = 1.25$ . A linear negative trend between the amount of the polysaccharides and  $K_d$  values was occurred (linear  $R^2=0.994$ , Fig.4). Hence, it indicated that polysaccharide component played a negative role in sorption HOCs. Removal of the waxy materials (6.5% by weight) and polysaccharide (24% by weight) from the bulk tomato cuticle caused a significant increase in the sorption ability of the cuticular biopolymer, indicated that the two components of the cuticle (waxes and polysaccharide) are attached to the cutin biopolymer and therefore prevent solute uptake (Shechter *et al.*, 2006). Based on the linear regression equation in Fig.4, the sorption coefficient ( $K_d$ ) of polysaccharide material to 1-naphthol was calculated at given polysaccharide content = 100% and cutin monomer content = 0%. The average value of calculated  $K_d$  is 63 ml/g, thus the  $K_{oc}$  of polysaccharide is 144 ml/g OC ( $K_{oc} = K_d/f_{oc}$ ). The  $K_{oc}$  for polysaccharide is much lower than  $K_{ow}$  of 1-naphthol, attributing to the high polarity of polysaccharide components (Table 1).

According to the composition content of wax, polysaccharide, and cutin in tomato bulk cuticle (Fig.5a) and their sorption coefficients ( $K_d$ ), the calculated  $K_d$  of bulk cuticle was 437.9 ml/g ( $K_{d,bulk\ cuticle} = 6.5\% \times K_{d,wax} + 24\% \times K_{d,sugar} + 69.5\% \times K_{d,cutin}$ ), which was consistent with the experimental value (415.6 ml/g). The relative contributions of different components to the bulk cuticle were presented in Fig.5b. It is further showed that the cutin material dominated the sorption of the bulk cuticle (91.7%).

Sorption abilities ( $K_{oc}$ ) of tomato cuticular fractions were dependent on their compositions. The positive relationship of  $K_{oc}$  values with cutin contents and negative relationship of  $K_{oc}$  values with polysaccharide contents were also observed (Fig.6). The relationship between  $K_{oc}$  values and polarities ((N+O)/C) was plotted in Fig.7. Sorption abilities of cuticular fractions increased with the decrease of sorption medium polarities, in consistent with previous results (Salloum *et al.*, 2002; Chen, *et al.*, 2005). The  $K_{oc}$  values of 1-naphthol for wax material and polysaccharide was much less than the predicted values

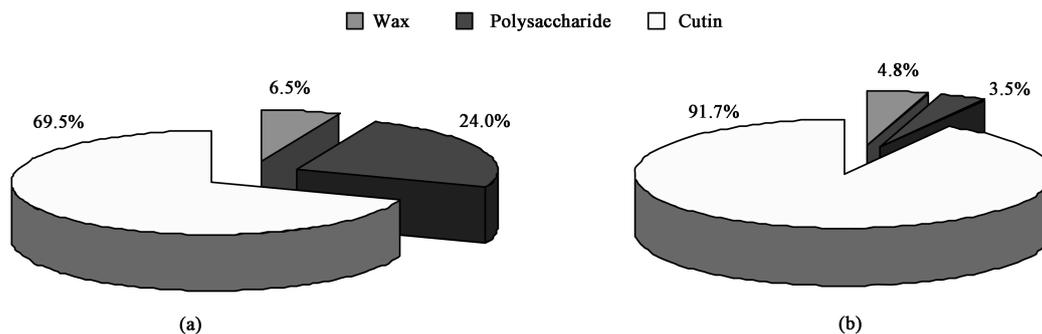


Fig. 5 Composition of tomato bulk cuticle material (a) and their relative contributions to total sorption capacity of TC1 (b).  $K_{d,bulk\ cuticle} = 6.5\% \times K_{d,wax} + 24\% \times K_{d,sugar} + 69.5\% \times K_{d,cutin}$ .

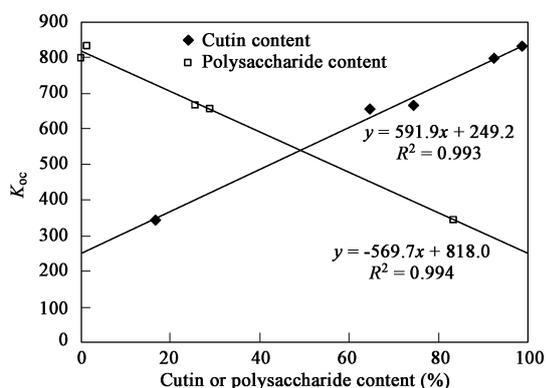


Fig. 6 Relationships between sorption coefficients ( $K_{oc}$ ) of 1-naphthol by tomato cuticular fractions with cutin contents or polysaccharide contents.

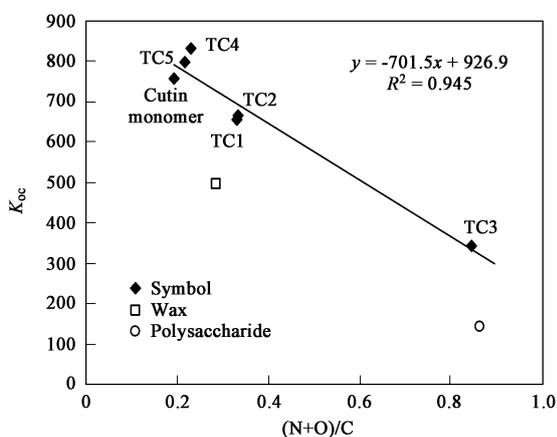


Fig. 7 Relationships between sorption coefficients ( $K_{oc}$ ) of 1-naphthol by tomato cuticular materials with their polarity indexes  $((N+O)/C)$ .

from the relationship between  $K_{oc}$  and  $(N+O)/C$  (Fig.7), which was attributed to poor accessibility of waxes to organic solute due to the crystalline nature (Chen and Xing, 2005) and weak sorption medium of polysaccharide because of high polarity.

In summary, this study demonstrates that the cutin monomer played pivotal role in sorption, while the waxes and pectin fractions “suppressed sorption of cutin”. The cutin biopolymer is the principal composition of the tomato cuticle and it is the main sorbent in the bulk cuticle. Linear positive relationship between  $K_{oc}$  values and cutin

monomer contents and negative relationship between  $K_{oc}$  values and polarity indexes  $((N+O)/C)$  were observed. However, the physical nature of the cuticle (attached by pectin and waxes) limits the accessibility of its sorption sites, protecting the plant from kinds of toxic environment pollutant. These results contributed to better understand sorption characteristics of plant cuticular materials.

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