ORIGINAL ARTICLE

# Sorption and desorption of toluene, m-xylene, p-cresol and water by natural rubber chips

**Panu Danwanichakul[1], Savalee Jaroenkarn[2], Pore Jumpathi[2], and Duangkamol Dechojarassri[3]**

## Abstract

**Danwanichakul, P., Jaroenkarn, S., Jumpathi, P. and Dechojarassri, D.**
**Sorption and desorption of toluene, m-xylene, p-cresol and water by natural rubber chips**
**Songklanakarin J. Sci. Technol., 2006, 28(5) : 1071-1082**

**The transport mechanism of several pure liquid organic substances into natural rubber chips composed of different fillers was investigated. It was found that, for the same type of chips, the Fickian diffusion of toluene was the fastest, followed by m-xylene, water and p-cresol. The toluene uptake was highest which was as high as 3.42 times of the chip weight. This was closely followed by m-xylene uptake, which was much higher than p-cresol uptake and water uptake which was only 0.02 times of the chip weight, implying that natural rubber could be used to remove these organic substances contaminated in water. The desorption of substances into air followed the similar trend as sorption. Besides, for any substances, the results showed that unfilled chips had the largest sorption capacity, followed by ones with calcium carbonate and carbon black.**

**Key words :** sorption, desorption, organic substances, natural rubber, hydrophobicity

**[1]Ph.D.(Chemical Engineering), Asst. Prof., [2]B.Eng. student in Chemical Engineering, [3]M.Eng.(Chemical Engineering), Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Rangsit Campus, Klong-Luang, Pathum Thani, 12120 Thailand.**
**Corresponding e-mail: dpanu@engr.tu.ac.th**

**Received, 20 January 2006 Accepted, 13 April 2006**

## บทคัดย่อ

**ภาณุ ด่านวานิชกุล[1] สวลี เจริญการ[1] พอภ์ จำปาทิ[1] ดวงกมล เดโชจรัสศรี[1]**

**การดูดจับและการคายออกของโทลูอีน เอ็ม-ไซลีน พี-ครีซอล และน้ำโดยชิ้นยางธรรมชาติ**

**ว. สงขลานครินทร์ วทท. 2549 28(5) : 1071-1082**

**ทำการศึกษากลไกการถ่ายโอนสารอินทรีย์บริสุทธิ์ในสถานะของเหลวหลายชนิดเข้าไปยังชิ้นยางธรรมชาติที่มีส่วนประกอบของสารตัวเติมต่างชนิดกัน พบว่ากลไกถ่ายโอนของสารเข้าไปยังชิ้นยางเป็นแบบฟิคเกียนโดยโมเลกุลของโทลูอีนแพร่เข้าไปได้เร็วที่สุด ตามด้วยเอ็ม-ไซลีน น้ำ และพี-ครีซอล ตามลำดับ ปริมาณการดูดซับโทลูอีนของชิ้นยางมีค่าสูงสุดถึง 3.42 เท่าของน้ำหนักของชิ้นยางเอง รองลงไปคือปริมาณการดูดซับเอ็ม-ไซลีน ซึ่งมีค่ามากกว่าสารพี-ครีซอลและน้ำ สำหรับน้ำมีปริมาณการดูดซับเพียง 0.02 เท่าของน้ำหนักชิ้นยางเท่านั้น บอกให้ทราบว่าชิ้นยางธรรมชาติสามารถนำไปใช้ประโยชน์ในการดูดจับสารอินทรีย์ที่ปนเปื้อนในน้ำได้ นอกจากนี้ในการทดสอบการคายออกของสารสู่อากาศ พบว่าผลเป็นไปในทำนองเดียวกับการดูดจับสาร และเมื่อเปรียบเทียบการดูดจับสารชนิดเดียวกันพบว่ายางที่ไม่มีสารตัวเติมจะสามารถดูดจับสารได้ปริมาณมากกว่า รองลงมาคือยางที่ผสมด้วยหินปูน และผงเขม่าดำตามลำดับ**

---

[1] **ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ มหาวิทยาลัยธรรมศาสตร์ อำเภอคลองหลวง จังหวัดปทุมธานี 12120**

One of the methods employed to treat contaminated water is the utilization of potential materials such as activated carbon (Daifullah and Girgis, 2003), some polymer adsorbents (Li *et al.*, 2002) and zeolites (Ghiaci *et al.*, 2004) to remove hazardous compounds from water. Used rubber tires have also been investigated as sorption media in water treatment. They have been used as ground rubber and rubber chips.

The ground natural rubber was used to absorb naphthalene, toluene and mercury from contaminated water by batch tests and it was found that treatment of mercury took longer time than other two substances and that the sorption capacity for naphthalene was higher than that for toluene (Gunasekara *et al.*, 2000). In another work (Kershaw *et al.*, 1997), an aqueous solution of benzene and o-xylene were tested with ground rubber using both batch and column tests and it was shown that o-xylene could be better treated than benzene because o-xylene is more hydrophobic even though molecules of benzene are smaller and should diffuse into the rubber more easily. The sorption capacity of ground rubber for several substances was also reported (Kim *et al.*, 1997). The highest capacity was for m-xylene, followed by ethylbenzene, toluene, trichloroethylene, 1,1,1-trichloroethane, chloroform and methyl chloride, respectively. Instead of using ground rubber, Smith *et al.* (2001) utilized rubber chips to treat water contaminated with phenol and p-cresol and it was found that p-cresol was absorbed better than phenol. The effect of the chip size was also studied and the results showed that smaller chips had higher sorption capacity, reflecting the influence of surface area of the absorbent in the sorption process.

To understand how the rubber can remove organic compounds from contaminated water, it is necessary to understand the interaction between the substances and rubber molecules and also the interaction between rubber molecules and water. Rubber molecules, like any polymer, can swell in large volume of good solvents. The transport mechanism of molecules into the rubber matrix is different from the case of activated carbon since it involves both adsorption to the rubber surface and absorption inside the rubber matrix. It would be interesting to investigate the transport of various substances, both hydrophilic and hydrophobic compounds, into and out of the rubber so that we can adjust the structure for improving the sorption capacity. The rubber used in all works mentioned above was from waste rubber so the composition of chemicals in rubber might not be accurately known. In this preliminary work, we are interested in the effect of different fillers in the rubber chips on sorption and desorption capacity and then compared with unfilled rubber. The rubber compound was made into a sheet and then cut into pieces of the same size. We thoroughly studied the transport mechanism of pure liquid substances into and out of the chips.

## Materials and Methods

### 1. Preparation of rubber chips

Natural rubber (STR 20) was provided by Teckbeehang Co., Ltd, Thailand. Carbon black (N-330, particle size of 33 nm), stearic acid and zinc oxide (ZnO) were supplied by Loxley Public Co., Ltd. N-(1, 3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) and N-cyclohexyl-2-benzothiazyl sulfenamid (CBS) were obtained from Sunny World (1989) Co., Ltd. Sulphur was purchased from Kurusapa Business Organization (Suksapan Panit), Thailand. Tetramethyl Thiuramdisulphide (TMTD) was received from J. J.-Degussa Chemicals (T) Ltd.

The rubber chips were prepared in three different formulae based on fillers, which were one with carbon black (C30), one with calcium carbonate (Ca30) and one without any filler (R100). Other components which are necessary in vulcanization of the rubber were used in the same amount for each formula as shown in Table 1. The composition of each component is reported in grams per 100 grams of natural rubber (STR20).

All components were mixed together step by step in an internal mixer (Brabender, Lab station) at the mixing speed of 40 RPM and at initial temperature of 50ºC. First, the rubber was crushed in the mixer for 3 min. and then a filler was added and continued mixing for 3 min. Subsequently, stearic acid and ZnO was added and mixed for 2 min. This was followed by adding 6-PPD and mixing for another 2 min. Finally, CBS, TMTD and sulphur as the curing agent were added and mixed together for 2 min. The compound was taken out and kneaded with a two-roll mill.

The compound was then tested with a moving die rheometer (TECH-PRO, rheoTECH MD+) to obtain optimal cure time at curing temperature of 150ºC. After curing in a compression mould for a period of 90% cure time, we obtained a rubber sheet with 2 mm thick. It was cut into square pieces of 1x1 cm$^2$. All three types of chips with different formula were tested in the following experiments.

### 2. Sorption of Pure Liquid Substances

The pure liquid substances used in this experiment were toluene, m-xylene, p-cresol and water. 15 ml of liquid was filled in a glass bottle with a glass stopper. A rubber chip was weighed before being taken inside the bottle and left to swell. The chip was taken out at different period of time for being weighed. Each time before weigh-

**Table 1. Compositions of rubber chips in 3 different formula.**

| Ingredients | Rubber (R100) | Carbon Black (C30) | $CaCO_3$ (Ca30) |
|---|---|---|---|
| STR 20 | 100 | 100 | 100 |
| **Filler** | **0** | **30** | **30** |
| 6-PPD | 3 | 3 | 3 |
| Stearic acid | 1 | 1 | 1 |
| Zinc oxide | 5 | 5 | 5 |
| CBS | 3.5 | 3.5 | 3.5 |
| TMTD | 0.5 | 0.5 | 0.5 |
| Sulphur | 0.4 | 0.4 | 0.4 |

ing the chip, the adhering liquid on the chip surface was removed by using a piece of filter paper. The experiment proceeded until maximum swelling was reached when the weight of the chip did not change any more. The experiments were done in triplets and the results are from the averages.

### 3. Desorption of Pure Liquid Substances

Right after the sorption experiment, we took the chip out of the bottle and allowed the substance to evaporate from the chips into the atmosphere at the room temperature (around 30ºC). The chip was weighed several times until the weight was constant.

## Results and Discussion

The swelling of the chip at any time is reported in terms of percentage of the mole uptake, $Q_{t,\,ab}$, which can be calculated from

$$Q_{t,ab} = \frac{\text{Moles of a substance in the chip}}{\text{Initial mass of the chip } (g)} \times 100 \ (g) \tag{1}$$

In desorption, the shrinking of the chip at any time is described differently as

$$Q_{t,\,de} = \frac{\text{Moles of a substance in the chip}}{\text{Final mass of the chip after desorption in completed } (g)} \times 100 \, (g) \tag{2}$$

The results are shown in Figures 1 and 2. For toluene and m-xylene, the initial rate of sorption was almost the same and it reached 95% of equilibrium within 4 hrs whereas the initial rate of desorption of toluene was greater than m-xylene. The desorption of toluene reached 95% of the maximum in about 4 hrs, much shorter than 13 hrs for m-xylene. As expected for the hydrophilic substances, p-cresol and water, both the initial rate of sorption and desorption were smaller than hydrophobic substances. It could take 120 and 8 hrs for sorption (95% of equilibrium) of p-cresol and water, respectively and could take 20 and 4 hrs for desorption (95% of maximum).

### 1. Transport Mechanism of Sorption of the pure substance

Sorption mechanism can be studied using the relation (Kumar *et al.*, 1997),

$$\log\left(\frac{Q_t}{Q_\infty}\right) = \log k + n \log t, \tag{3}$$

where $Q$ is the equilibrium mole uptake, $k$ and $n$ are parameters. The parameter $k$ describes interaction between rubber and the substance whereas $n$ represents the mechanisms of molecules of substance diffusing in the rubber matrix. The values of $n$ and $k$ are shown in Table 2, with $R^2$ greater than 0.95.

For any pair of substance-rubber, the value of $n$ is close to 0.50, implying that the transport is Fickian diffusion. The diffusion into most rubbery polymers tends to behave according to Fick's law of diffusion while glassy polymers exhibit "anomalous" or "non-Fickian" behavior because polymers in rubbery state respond quickly to changes while the properties of glassy polymers are time-dependent (Crank, 1995). The equilibrium uptake shows that natural rubber, as a hydrophobic material, absorbs toluene a little better than m-xylene, both of which are also hydrophobic while the uptake was much less for p-cresol and water, which are hydrophilic compounds.

A rubber chip can absorb toluene as much as 3.42 times of its weight while absorption of water was only 0.02 times of its weight. For any substance, unfilled chips had higher uptake than ones with calcium carbonate, which was higher than one filled with carbon black. This can also be seen through the comparison of $k$ values. The structure of filled rubber, especially with carbon black, possesses less mobility, thereby, obstructing volume expansion during sorption. Unlike carbon black, calcium carbonate is not usually used for reinforcement but it is added for reducing production cost. The effect of fillers is similar to that of other factors inhibiting volume expansion in rubber, such as high extent of crosslinked network,

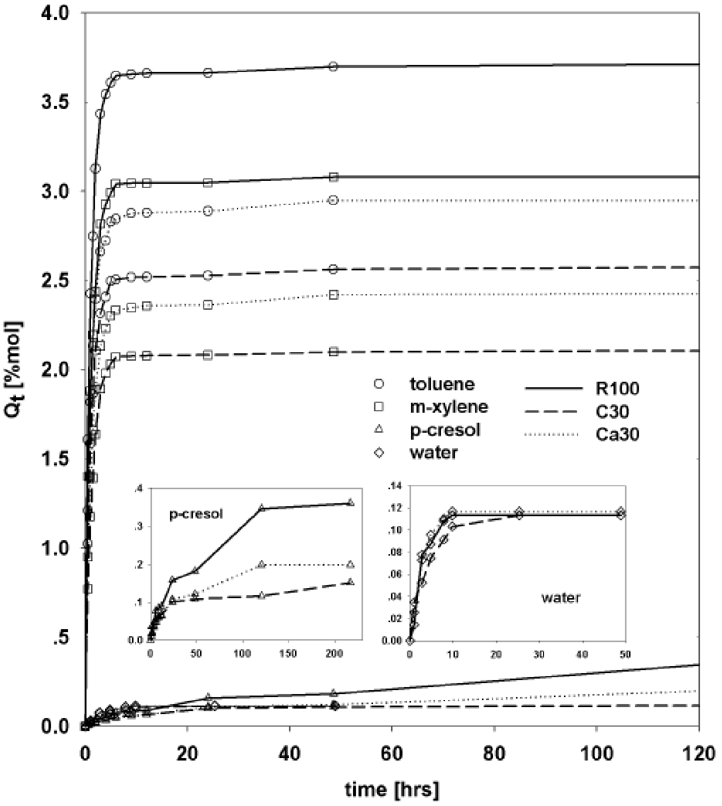

**Figure 1.** **% mole uptake versus sorption time for toluene, m-xylene, p-cresol and water absorbed in three types of rubber chips, R100, C30 and Ca30. The symbols differentiate the types of chips and the lines differentiate the types of organic compounds.**

**Table 2. The values of equilibrium % mole uptake and parameters, *n* and *k*, for each pair of substance-rubber chip.**

| substance-rubber | Q [%mol] | *n* | *k* [1/s$^n$] | $R^2$ |
|---|---|---|---|---|
| toluene-R100 | 3.711 | 0.475 | 0.013 | 0.9826 |
| toluene-C30 | 2.573 | 0.521 | 0.008 | 0.9867 |
| toluene-Ca30 | 2.949 | 0.494 | 0.010 | 0.9891 |
| m-xylene-R100 | 3.081 | 0.400 | 0.023 | 0.9987 |
| m-xylene-C30 | 2.106 | 0.505 | 0.009 | 0.9908 |
| m-xylene-Ca30 | 2.426 | 0.496 | 0.010 | 0.995 |
| p-cresol-R100 | 0.360 | 0.498 | 0.001 | 0.9717 |
| p-cresol-C30 | 0.151 | 0.528 | 0.002 | 0.9734 |
| p-cresol-Ca30 | 0.198 | 0.486 | 0.002 | 0.9274 |
| $H_2O$-R100 | 0.113 | 0.322 | 0.035 | 0.9568 |
| $H_2O$-C30 | 0.113 | 0.482 | 0.006 | 0.9918 |
| $H_2O$-Ca30 | 0.117 | 0.404 | 0.015 | 0.9769 |

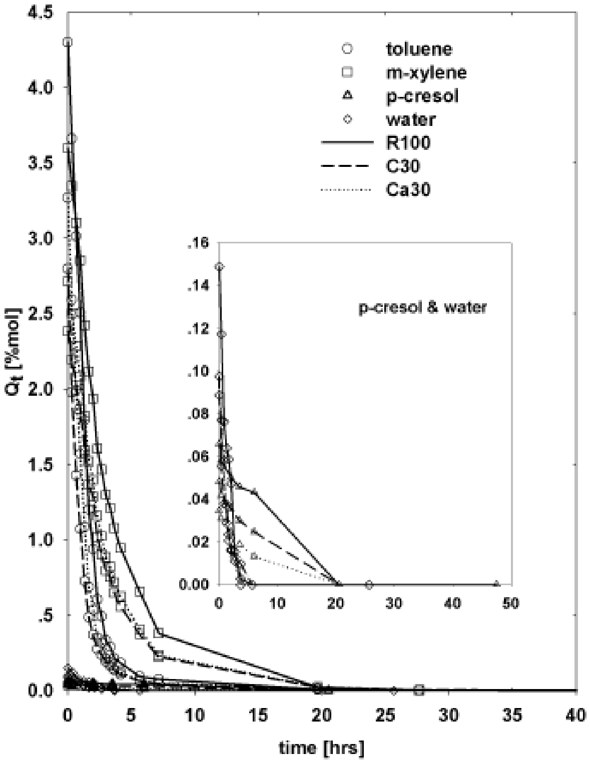

**Figure 2. % mole uptake versus desorption time for toluene, m-xylene, p-cresol and water absorbed in three types of rubber chips, R100, C30 and Ca30. The symbols differentiate the types of chips and the lines differentiate the types of organic compounds.**

which is formed by chemical reactions between a crosslinking agent and rubber molecules (Kumar *et al.*, 1997), and the composition of blending materials in polymer blends. For example, to increase mechanical properties of natural rubber, polystyrene was blended to form interpenetrating polymer network (Mathew *et al.*, 2002) and nitrile rubber was blended to form a polymer membrane (Mathai *et al.*, 2002)

Because the transport mechanism into the rubber is Fickian diffusion, the diffusion coefficient, Dab of organic compound molecules into the rubber could be estimated by using the equation for mole uptake during a short-time period (Kumar *et al.*, 1997),

$$\frac{Q_t}{Q_\infty} = 4\left[\frac{D_{ab}t}{\pi h^2}\right]^{1/2}, \tag{4}$$

or equivalently,

$$D_{ab} = \pi\left[\frac{h\Theta}{4Q_\infty}\right]^2. \tag{5}$$

Here, $h$ is the initial thickness of the chip, and $\Theta$ is the slope of the linear portion of the curve of $Q_t$ versus $t^{1/2}$, where t is sorption time.

Table 3 displays the values of diffusion coefficients for each pair of substance-rubber along with the corresponding values of $R^2$. It shows that the linear relation ($Q_t \propto t^{1/2}$) is good for all pairs except for p-cresol-R100 and $H_2O$-R100 whose $R^2$ are less than 0.95. Other quantities also included in the table are sorption coefficient, $S$, and permeation coefficient, $P$. They are defined as the following.

$$S = \frac{M_\infty}{M_0}, \tag{6}$$

**Table 3. The values of diffusion, sorption and permeation coefficients of various substances into different rubber chips.**

| Substance-Rubber | $D_{ab}$ [cm$^2$/s] | $R^2$ - | $S$ - | $P$ [cm$^2$/s] |
|---|---|---|---|---|
| toluene-R100 | 7.94E-07 | 0.995 | 3.420 | 2.71E-06 |
| toluene-C30 | 7.53E-07 | 0.997 | 2.371 | 1.79E-06 |
| toluene-Ca30 | 7.44E-07 | 0.997 | 2.718 | 2.02E-06 |
| m-xylene-R100 | 6.96E-07 | 0.992 | 3.271 | 2.28E-06 |
| m-xylene-C30 | 6.60E-07 | 0.998 | 2.236 | 1.48E-06 |
| m-xylene-Ca30 | 6.76E-07 | 0.999 | 2.576 | 1.74E-06 |
| p-cresol-R100 | 9.70E-09 | 0.938 | 0.389 | 3.78E-09 |
| p-cresol-C30 | 3.11E-08 | 0.996 | 0.163 | 5.07E-09 |
| p-cresol-Ca30 | 1.80E-08 | 0.953 | 0.214 | 3.86E-09 |
| $H_2O$-R100 | 3.00E-07 | 0.924 | 0.020 | 6.12E-09 |
| $H_2O$-C30 | 1.54E-07 | 0.996 | 0.020 | 3.13E-09 |
| $H_2O$-Ca30 | 2.82E-07 | 0.968 | 0.021 | 5.94E-09 |

where $M$ is the mass of organic substance at equilibrium sorption and $M_0$ is the initial mass of a chip, and

$$P = D \times S \tag{7}$$

The diffusion coefficient of toluene molecules is the greatest, followed by m-xylene, water and p-cresol, reflecting that molecules of hydrophobic substances can penetrate into a rubber chip more easily than the hydrophilic molecules. In addition, smaller size of toluene results in higher value of diffusion coefficient than that of m-xylene and a similar comparison can also be seen for the pair of water and p-cresol. Sorption involves the initial penetration and dispersion of substance molecules into the rubber matrix, so the sorption coefficient is dependent on the strength of rubber-solvent interaction. Permeability of compound molecules into a rubber chip depends on both diffusion and sorption. Therefore, permeation coefficient is defined as the product of diffusion coefficient and sorption coefficient.

It is found that the sorption coefficient shows the same trend as the equilibrium uptake by considering either the substance or the rubber formulae as the parameter. It is the maximum for the pair of toluene and R100. This indicates that the best accommodation of substance molecules is in the highly flexible chains of unfilled rubber. The trend of permeation coefficient was the same as diffusion coefficient, implying that diffusion has a greater effect on permeation of organic compound molecules than sorption. Regarding the rubber formulae, we can see that for all substances except p-cresol, all coefficients for unfilled rubber were greater than for rubber filled with calcium carbonate and carbon black, respectively. For p-cresol, it may be attributed to small errors in the experiment since p-cresol liquid is more viscous than others leading to additional mass sticking to the surface while weighing the swelling chips.

To complete the study of transport mechanism, we compared the experimental results with theoretical ones obtained from the solution of the differential equation explaining unsteady state mass transport through a thin membrane (Crank, 1995). The mole uptake could be derived from the integration of concentration profile throughout the chip volume. The equation is

$$\frac{Q_t}{Q_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[ \frac{-D_{ab}(2n+1)^2 \pi^2 t}{h^2} \right]. \tag{8}$$

The $D_{ab}$ values used in Eq. (8) are estimated before and given in Table 3. The comparisons between the experimental and theoretical results are shown in Figure 3. The theoretical results from Eq. (8) are shown as several lines which are in good accordance with the experimental results shown as symbols. The inset pictures are included for clarity for the results of p-cresol and water of which % mole uptakes are much lower than those of toluene and m-xylene. The consistency between theory and experiment is clearly seen for every substance, except p-cresol. This may imply again that weighing chips swelling in viscous liquid p-cresol contained some errors.

## 2. Transport Mechanism of Desorption of the pure substance

The analysis of desorption mechanism is similar to sorption experiment. We consider desorption as the diffusion process of substance molecules from the rubber volume into air. Therefore, in this section, $Q_{t,\text{air}}$ refers to mole "loss" into air, defined as

$$Q_{t,\text{air}} = \frac{\text{Moles of a substance evaporated}}{\text{Final mass of the chip } (g) \text{ after desorption is completed}} \times 100\ (g) \qquad (9)$$

At zero desorption time, $Q_t$, air is equal to zero and it increases as the substances evaporate into air until the mass of the chip is constant at which point $Q_{,\text{air}}$ is obtained. The values of parameters from linear plots of (Eq. 3), log ($Q_{t,\text{air}}/Q_{,\text{air}}$) versus log $t$, are shown in Table 4, with $R^2$ greater than 0.95.

It is observed that for toluene and m-xylene, $Q_{,\text{air}}$ was greater than $Q$ in all types of chips. It is possible that rubber mass and some components in the rubber including fillers dissolved in pure liquid organic compounds, leading to reduced mass of rubber chips after desorption compared with the original chips. However, for p-cresol and water, some values of $Q_{,\text{air}}$ were less than $Q$ . This could be ascribed to that desorption had not truly been completed - there was some mass of substances still remaining inside the rubber volume and probably being adsorbed within carbon black

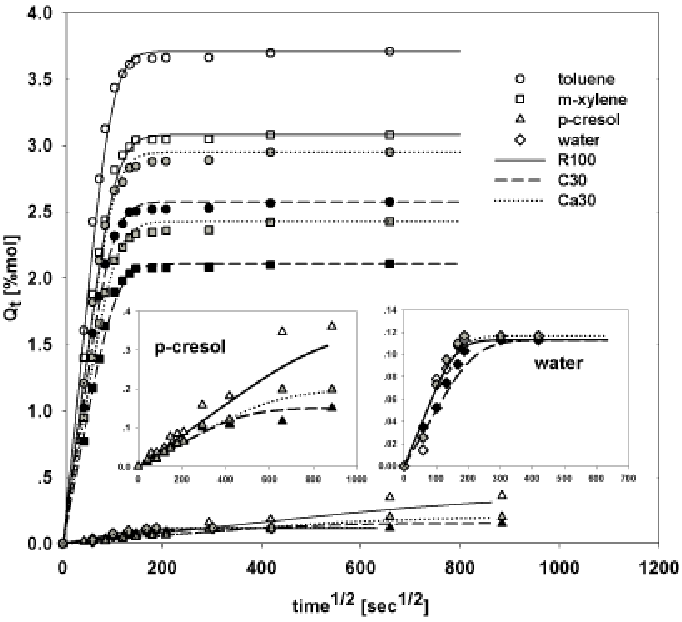

**Figure 3. The relation of % mole uptake with time$^{1/2}$ for all substances absorbed in all types of chips. Symbols represent experimental data and all lines represent theoretical results. The shade used with symbols is only for differentiation between sets of results.**

**Table 4. The values of % mole desorbed to air and parameters, *n* and *k*, for each pair of substance-rubber chip.**

| **substance-rubber** | $Q_{,air}$ [%mol] | $n$ | $k$ [1/s$^n$] | $R^2$ |
|---|---|---|---|---|
| toluene-R100 | 4.300 | 0.975 | 0.00015 | 0.998 |
| toluene-C30 | 2.798 | 0.667 | 0.00262 | 0.996 |
| toluene-Ca30 | 3.268 | 0.828 | 0.00059 | 0.998 |
| m-xylene-R100 | 3.599 | 1.084 | 0.00003 | 0.995 |
| m-xylene-C30 | 2.385 | 1.022 | 0.00005 | 0.995 |
| m-xylene-Ca30 | 2.716 | 1.037 | 0.00005 | 0.998 |
| p-cresol-R100 | 0.066 | 0.388 | 0.00745 | 0.994 |
| p-cresol-C30 | 0.048 | 0.465 | 0.00460 | 0.992 |
| p-cresol-Ca30 | 0.035 | 0.622 | 0.00124 | 0.997 |
| $H_2O$-R100 | 0.149 | 0.348 | 0.03017 | 0.980 |
| $H_2O$-C30 | 0.097 | 0.379 | 0.02744 | 0.961 |
| $H_2O$-Ca30 | 0.089 | 0.342 | 0.03834 | 0.983 |

particles. Carbon black was tested to adsorb organic compound and was found that its sorption capacity was 20-60% of the tire rubber (Kim *et al.*, 1997). Therefore, carbon black could contribute 5-15% of total adsorption capacity.

It is very intriguing to see that unlike in sorption, in desorption the values of parameter *n* for substance-rubber pairs were much different from one another. For hydrophilic substances, p-cresol and water, we may adopt the Fickian diffusion as their model transport but for m-xylene, according to Alfrey, Gurnee and Lloyd (1966), its transport mechanism is "pseudo-Fickian" diffusion where *n* is about 1.0 and for toluene, the mechanism is "non-Fickian" diffusion where *n* lies between 0.5 and 1.0. Three mechanisms discussed here are differentiated according to relative magnitudes of rates of diffusion and polymer relaxation. The rate of diffusion was much less than that of relaxation in Fickian type but it was much higher in pseudo-Fickian type and both rates were comparable in non-Fickian diffusion. We may interpret from our results that since p-cresol and water were little taken up by the rubber volume so they did not change the structure of the rubber much after desorption. Both toluene and m-xylene may have caused much change in the structures of rubber during sorption so the structures did not return to the original after desorption.

The diffusion coefficient for desorption into air of each substance-rubber pair is also obtained from Eqs. (4) and (5) by replacing $D_{ab}$ with $D_{de}$. The results are shown in Table 5, together with the diffusion coefficient for sorption, re-tabulated for instant comparison. The values of diffusion coefficient of all substances in filled chips were less than that in unfilled chips. Moreover, the values of both coefficients for sorption and desorption were in the same order of magnitude. For toluene, p-cresol and water, as we know that the mechanism is Fickian (or pseudo-Fickian), the diffusion coefficient is correctly assumed constant while for m-xylene, the coefficient should not be a constant as can be seen that the linear fitting was not as good as others. Therefore, the reported values of $D_{de}$ for m-xylene were not totally correct. For other substances, $D_{de}$ was greater than $D_{ab}$, which probably resulted from the lower viscosity of air phase than that of the liquid phase. The calculated diffusion coefficients were then used in Eq. (8) by replacing $D_{ab}$ with $D_{de}$ to obtain the mole loss to air as shown in Figure 4. The theoretical results were in agreement with experimental ones even though the proximity was less than for the sorption case.

**Table 5. The comparison of diffusion coefficients for sorption and desorption.**

| Substance-Rubber | $D_{ab}$ [cm$^2$/s] | $R^2_{ab}$ - | $D_{de}$ [cm$^2$/s] | $R^2_{de}$ - |
|---|---|---|---|---|
| toluene-R100 | 7.94E-07 | 0.995 | 7.93E-07 | 0.942 |
| toluene-C30 | 7.53E-07 | 0.997 | 8.56E-07 | 0.990 |
| toluene-Ca30 | 7.44E-07 | 0.997 | 8.60E-07 | 0.973 |
| m-xylene-R100 | 6.96E-07 | 0.992 | 3.88E-07 | 0.951 |
| m-xylene-C30 | 6.60E-07 | 0.998 | 4.13E-07 | 0.951 |
| m-xylene-Ca30 | 6.76E-07 | 0.999 | 4.18E-07 | 0.955 |
| p-cresol-R100 | 9.70E-09 | 0.938 | 7.26E-08 | 0.978 |
| p-cresol-C30 | 3.11E-08 | 0.996 | 1.35E-07 | 0.996 |
| p-cresol-Ca30 | 1.80E-08 | 0.953 | 6.57E-08 | 0.987 |
| $H_2O$-R100 | 3.00E-07 | 0.924 | 5.12E-07 | 0.963 |
| $H_2O$-C30 | 1.54E-07 | 0.996 | 6.71E-07 | 0.981 |
| $H_2O$-Ca30 | 2.82E-07 | 0.968 | 8.11E-07 | 0.913 |

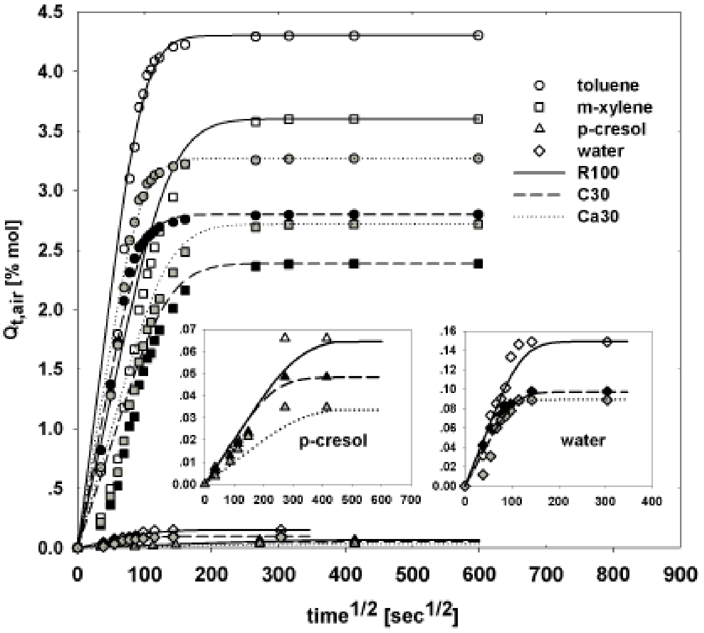

**Figure 4. The relation of % mole loss with time$^{1/2}$ for all substances desorbed from all types of chips. Symbols represent experimental data and lines represent theoretical results. The shade used with symbols is only for differentiation between sets of results.**

## Conclusions

In this work, the sorption of four pure organic compounds, which are toluene, m-xylene, p-cresol and water, were investigated by using natural rubber chips of which compositions were different, including one without any filler, one with carbon black (N-330), and one with calcium carbonate. We found that rubber chips could absorb toluene with highest capacity, followed by m-xylene, p-cresol and water, respectively, because non-polar molecules of toluene and m-xylene are more compatible with rubber molecules than polar molecules of p-cresol and water. Moreover, the transport mechanism of these substances into the rubber volume was Fickian diffusion. The obtained diffusion coefficient of toluene was greater than m-xylene because its molecules are smaller and for the same reason, the coefficient of water is greater than p-cresol. When the fillers in rubber were considered, the unfilled chips had highest sorption ability, followed by chips with calcium carbonate and those with carbon black because fillers obstructed the mobility of rubber molecules while accommodating molecules of organic substances in the rubber network. The desorption of these substances to air was also studied. It was found that the mass loss from the chips of toluene was greater than that of m-xylene while the mass loss of water is greater than that of p-cresol, attributable to p-cresol being more strongly absorbed in the rubber network and less volatile than water.

From the sorption behavior of substance, it is confirmed that the rubber chips have potential in the treatment of water contaminated with hydrophobic substances since they absorbed water very little whereas they absorbed hydrophobic substances in large quantity. However, they could absorb hydrophilic substances up to some degrees. In the desorption experiment, the substances could desorb from the chips into the air even though the final structures of the chips may change so they may be reused as sorption media with less efficiency. Fillers have been found to affect the sorption and desorption ability of natural rubber.

## Acknowledgments

This work is financially supported by the Thailand Research Fund in Small Project on Rubber. The authors are also grateful to the departments of chemical and industrial engineering, Thammasat University, for laboratory equipment.

## References

Alfrey, A., Gurnee, E.F., and Lloyd, W.G. 1966. Diffusion in glassy polymer. J. Polym. Sci. C12: 249-261

Crank, J. 1995. The mathematics of diffusion. Oxford University Press, New York.

Daifullah, A.A.M., and Girgis, B.S. 2003. Impact of surface characteristics of activated carbon on adsorption of BTEX. Colloid Surface A. 214: 181-193

Ghiaci, M., Abbaspur, A., Kia, R., and Seyedeyn-Azad, F. 2004. Equilibrium isotherm studies for the sorption of benzene, toluene, and phenol onto organo-zeolites and as-synthesized MCM-41. Sep. and Purif. Technol. 40: 217-229

Gunasekara, A.S., Donovan, J.A., and Xing, B. 2000. Ground discarded tires remove naphthalene, toluene, and mercury from water. Chemosphere 41: 1155-1160

Kershaw, D.S., Kulik, B.C., and Pamukcu, S. 1997. Ground rubber: sorption media for ground water containing benzene and o-xylene. J. Geotech. Geoenviron. 124: 324-334

Kim, J.Y., Park, J.K., and Edil, T.B. 1997. Sorption of organic compounds in the aqueous phase onto tire rubber. J. Environ. Eng. 123: 828-835

Kumar, S. A., Thomas, S., and Kumaran, M. G. 1997. Transport of aromatic hydrocarbons through poly(ethylene-co-vinyl acetate) membranes. Polymer. 38: 4629-4640

Lee, J.W., Jung, H-J, Kwak, D-H, and Chung, P-G. 2005. Adsorption of dichloromethane from water onto a hydrophobic polymer resin XAD-1600. Water Research 39: 617-629

Li, X., Zhang, Q. Zhang, G., Chen, J., Fei, Z., and Liu, F. 2002. Adsorption of phenolic compounds from aqueous solutions by a water-compatible hypercrosslinked polymeric adsorbent. Chemosphere. 47: 981-989

Mathai, A.E., Singh, R.P., and Thomas, S. 2002. Transport of substituted benzenes through nitrile rubber/natural rubber blend membranes. J. Membrane. Sci. 202: 35-54

Mathew, A.P., Packirisamy, S., Stephen, R., and Thomas, S. 2002. Transport of aromatic solvents through natural rubber/polystyrene (NR/PS) interpenetrating polymer network membranes. J. Membrane Sci. 201: 213-227

Smith, C.C., Anderson, W.F., and Freewood, R.J. 2001. Evaluation of shredded tyre chips as sorption media for passive treatment walls. Eng. Geol. 60: 253-261