

## Influence of sulfur-crosslinking in vulcanized rubber chips on mercury(II) removal from contaminated water

Panu Danwanichakul<sup>\*</sup>, Duangkamol Dechojarasri,  
Salina Meesumrit, Suporn Swangwareesakul

*Center of Excellence on Natural Rubber, Department of Chemical Engineering, Faculty of Engineering, Thammasat University,  
99 Moo 18 Paholyothin Road, Klong-Luang, Pathumthani 12120, Thailand*

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### Abstract

The adsorption of Hg(II) by natural rubber chips was investigated. First, the effect of chip size (5 mm × 5 mm and 10 mm × 10 mm) on the adsorption kinetics was studied. The pseudo-second-order modeling was found to explain the kinetics well. The smaller chips had higher adsorption rate so they were used for the rest of the research. Next the effects of sulfur, zinc oxide and carbon black on the adsorption capacity of Hg(II) at equilibrium conditions were investigated. The effect of sulfur was studied through different standard vulcanizing systems. The amount of zinc oxide was varied to be 3, 4 and 5 part per hundred parts of rubber (phr) while the carbon black (N-330) loading was varied to be 0, 30 and 50 phr, respectively. It was found that adsorption capacity increased with the degree of crosslink density, generated by sulfur reacting with rubber molecules. In addition, the adsorption capacities of various amounts of zinc oxide corresponded with their crosslink densities while the addition of carbon black seemed to obstruct Hg(II) adsorption.

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### 1. Introduction

Mercury is a persistent substance usually contaminating both surface and groundwater and cannot be decomposed easily, thereby tending to accumulate in living organisms in the food chains. Mercury is harmful to essential organs of human beings so its removal from water is necessary. There are many methods to treat water contaminated with heavy metals including chemical precipitation, ion exchange, membrane filtration and adsorption. Among these, adsorption is the simplest one which can be accomplished either by physical attraction among adsorbates and adsorbents or by chemical reactions among them. The removals of mercury from water by adsorption have been extensively investigated by using various kinds of adsorbents such as activated carbon [1,2], chitosan [3,4], mesoporous silica [5], natural and synthetic materials [6–8] and low cost waste tire rubber [9–15]. In addition, some literature also reported

that waste tire rubber could immobilize Hg(II) contaminated in soil [16].

Even though satisfactory results of mercury adsorption using waste tire rubber were reported, the reasons for that have come from only speculations. Since the rubber particles are non-porous, the chemical compositions should be the governing factors. Common chemicals having been used in the production of tire rubber are zinc oxide, carbon black and sulfur, one or all of which could be responsible for sorption affinity for mercury. Tharin [9] reported that tire rubber could remove mercury from process stream. It was speculated that a reaction between mercury and crosslink sulfur in tire rubber was the cause of sorption affinity. Griffith [10] also believed that the sorption of mercury comes from the reaction of mercury with disulfide bonds in vulcanized rubber. In addition, Snoeyink and Weber [11] thought that carbon black might play an important role in mercury adsorption considering that both carbon black and activated carbon are carbon. Rowley et al. [13] proposed another mechanism based on ion exchange between zinc ions in vulcanized rubber and mercury ions in water. Although the results confirmed that such mechanism occurred during adsorption, the

<sup>\*</sup> Corresponding author. Tel.: +66 2 5643001x3123; fax: +66 2 5643001x3123.  
E-mail address: [dpanu@engr.tu.ac.th](mailto:dpanu@engr.tu.ac.th) (P. Danwanichakul).

Table 1  
Compositions of masterbatch formulations

Ingredients	C30CV	C30SEV	COEV	C30EV	C50EV	C30Z4EV	C30Z3EV
NR (STR 20)	100	100	100	100	100	100	100
Carbon black	30	30	0	30	50	30	30
6-PPD	3	3	3	3	3	3	3
Stearic acid	1	1	1	1	1	1	1
Zinc oxide	5	5	5	5	5	4	3
CBS	0.5	1.25	3.5	3.5	3.5	3.5	3.5
TMTD	0.1	0.25	0.5	0.5	0.5	0.5	0.5
Sulfur	2.5	1.5	0.4	0.4	0.4	0.4	0.4

speculations involved sulfur and carbon black cannot be ruled out. However, the effect of different loadings of sulfur, carbon black, and even zinc cannot be tested with waste tire rubber because it comes from various sources so the compositions are not correctly quantified and uncontrollable.

Unlike previous research work focusing on using waste tire rubber particles for practical applications, this research is rather of academic interest. Here, we used the rubber chips with known compositions prepared in the laboratory. We began with the study of the effect of rubber chip size on the adsorption kinetics and then investigated the effects of sulfur, carbon black, and zinc oxide, which are the common substances in the rubber products and possibly influence Hg(II) adsorption capacity of the rubber chips.

## 2. Experimental

### 2.1. Raw materials

Natural rubber (STR 20) was received from Teckbeehang Co., Ltd., Thailand. Carbon black (N-330, particle size about 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. Tetramethyl thiuramdisulphide (TMTD) was obtained from JJ-Degussa Chemicals (T) Ltd. Sulfur was purchased from Kurusapa business organization (Suksapan Panit), Thailand. Finally, mercuric chloride (HgCl<sub>2</sub>) was supplied by the Success Chemical Limited Partnership.

### 2.2. Sample formulations

In order to produce vulcanized rubber, sulfur is often used as a curing agent together with accelerators (such as CBS and TMTD) and activators (such as ZnO). Normally, the vulcanizing system is classified into several subsystems based on the ratio of sulfur content to accelerator content. The system is named “Conventional Vulcanization” or so called “CV”, when the compound is prepared with high sulfur content and low accelerator content. On the other hand, when the compound is prepared with low sulfur content and high accelerator content, the vulcanization is called “Efficient Vulcanization” or “EV”. If the ratio of sulfur content to accelerator content is in between those of CV and EV systems, it is called “Semi-Efficient Vulcanization” or SEV.

The rubber chips were prepared in seven different formulae. For each formula, components other than sulfur, accelerators (CBS and TMTD), carbon black and ZnO, which are necessary in vulcanization of natural rubber were used in the same amount as shown in Table 1. The composition of each component is reported in g per 100 g of natural rubber, usually called phr (part per hundred parts of rubber).

### 2.3. Sample preparation and compounding

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

### 2.4. Cure characterization and vulcanization

The compound was then tested with a moving die rheometer (TECH-PRO, rheoTECH MD+) to obtain optimal cure time at a curing temperature of 150 °C. The test method complies with ASTM D5209. After curing in a compression mould for a period of 90% cure time, we obtained a rubber sheet 2 mm thick. For C30CV, the sheet was cut into square pieces of 5 mm × 5 mm and 10 mm × 10 mm to test the effect of chip size, whereas chips of size 5 mm × 5 mm were prepared for other formulae.

### 2.5. Determination of adsorption capacity

Mercuric chloride was used in the preparation of the synthetic aqueous solutions. The initial concentration of Hg(II) was about 5 ppm. For the kinetic study, 1 g of rubber chips was put into 20 ml of a stock HgCl<sub>2</sub> aqueous solution. The solution concentration was measured by using atomic absorption spectrophotometry at many intervals during being shaken on an orbital shaker. To obtain the equilibrium concentration, the mixture was shaken up to 8 h at the speed of 160 rpm and at 30 °C. Equilibrium adsorption was studied by varying mass of rubber chips ranging from 0.2 to 1.0 g. The adsorption capacity

is defined as

$$q_t = \frac{(C_0 - C_t) \times V}{w}, \quad (1)$$

where  $q_t$  is the adsorption capacity at any time (mg Hg(II)/g rubber),  $C_0$  the initial Hg(II) concentration (ppm),  $C_t$  the Hg(II) concentration at any time (ppm),  $V$  the solution volume (ml), and  $w$  is the mass of rubber chips (g rubber). When the system reaches equilibrium, the adsorption capacity is represented by  $q_e$ .

The rubber chips of C30CV formula were chosen to study the effect of pH on adsorption capacity. The pH was adjusted by using HCl and NaOH aqueous solution to obtain the values of 1.81, 7.89 and 12.4. After 8 h, the mercury containing rubber chips were removed. The concentration of Hg(II) left in water was measured and the rubber chips were used later in desorption experiment. They were put in fresh water and left shaken at 160 rpm for 1 h. The concentration of Hg(II) in water was then measured.

## 2.6. Determination of crosslink density

The crosslink density of the rubber vulcanizate was determined on the basis of rapid solvent-swelling measurements by saturating thin pieces of vulcanized rubber chips in toluene for 78 h at 30 °C. The assessment of the crosslink density was done by using the Flory–Rehner equation [17]. The typical Flory–Rehner equation is shown below.

$$-\ln(1 - V_r) - V_r - \chi V_r^2 = V_0 n \left( V_r^{1/3} - \frac{V_r}{2} \right), \quad (2)$$

where  $V_r$  is the volume fraction of rubber in the swollen gel at equilibrium,  $V_0$  the molar volume of swelling agent (105.9 ml/mol for toluene), and  $n$  is the physical degree of crosslink.  $\chi$  is a characteristic parameter of the interaction between the rubber network and the swelling agent, which could be calculated through solubility parameters by Knocke and Hemphill [14].

$$\chi = \frac{0.34 + (\delta_s - \delta_r)^2 V_0}{RT}. \quad (3)$$

Here  $\delta_s$  and  $\delta_r$  are the solubility parameters of the swelling agent and the rubber network, respectively,  $R$  the universal gas constant (1.987 cal/(mol·K)), and  $T$  is the absolute temperature (K). The volume fraction of rubber,  $V_r$ , in the swollen gel at equilibrium can be written as

$$V_r = \frac{m_0 \Phi(1 - \alpha) / \rho_r}{(m_0 \Phi(1 - \alpha) / \rho_r) + ((m_1 - m_2) / \rho_s)}, \quad (4)$$

where  $m_0$ ,  $m_1$  and  $m_2$  are the weights of the rubber samples in air, swollen state, and after drying in a vacuum oven at 90 °C for 32 h, respectively,  $\Phi$  the mass fraction of rubber in the vulcanizate,  $\alpha$  the mass loss of the gum rubber vulcanizate during swelling, and  $\rho_r$  and  $\rho_s$  are the rubber and the solvent densities, respectively.

## 2.7. Determination of morphology

The rubber chips of C30EV formula were chosen to investigate the morphology after swelling in toluene for 78 h. The samples were cut and the cross sectional surface was coated with gold before being observed with the scanning electron microscope (SEM) model JEOL 5410.

## 3. Results and discussion

### 3.1. Adsorption kinetics of chips with different sizes

In this section, C30CV rubber was chosen for studying the adsorption kinetics by comparing chips of size 5 mm × 5 mm with those of 10 mm × 10 mm, provided that both systems of different size chips were subjected to the same revolution (160 rpm). The kinetics was analyzed using pseudo-first-order Lagergren and pseudo-second-order kinetic models. These models were written in expressions similar to those of reaction kinetics. In adsorption, a driving force comes from the difference of concentrations in bulk phase and at the adsorbent surface. This driving force resulted in mass diffusion of Hg(II) to the rubber chips.

The equation for the pseudo-first-order is described as

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \quad (5)$$

where  $q_t$  and  $q_e$  are the adsorption capacity (mg Hg(II)/g rubber) at any time  $t$  and at equilibrium, respectively.  $k_1$  is the Lagergren rate constant of the pseudo-first-order adsorption ( $\text{min}^{-1}$ ). Integrating Eq. (5) and using conditions,  $q_t(0) = 0$ , and  $q_t(t) = q_t$ , the equation becomes

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (6)$$

Therefore,  $k_1$  and  $q_e$  can be obtained from the slope and the intercept of the plot of  $\ln(q_e - q_t)$  versus  $t$ , respectively.

The equation representing the pseudo-second-order is expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \quad (7)$$

where  $k_2$  is the rate constant of the pseudo-second-order adsorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ). For the conditions,  $q_t(0) = 0$ , and  $q_t(t) = q_t$ , the integration of Eq. (7) yields

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

The plot of  $(t/q_t)$  versus  $t$  is a straight line.  $q_e$  and  $k_2$  can be obtained from slope and intercept of the plot, respectively.

Based on Eqs. (6) and (8), the results are plotted as shown in Fig. 1. The values of  $k_1$ ,  $k_2$  and  $R^2$  of both models were obtained as given in Table 2. It is seen that the values of  $R^2$  in the case of pseudo-second-order are higher, implying that second-order kinetic model is more reliable to describe these experimental data. That the rate constant for smaller chips is slightly greater implies that adsorption using smaller chips is slightly more rapid

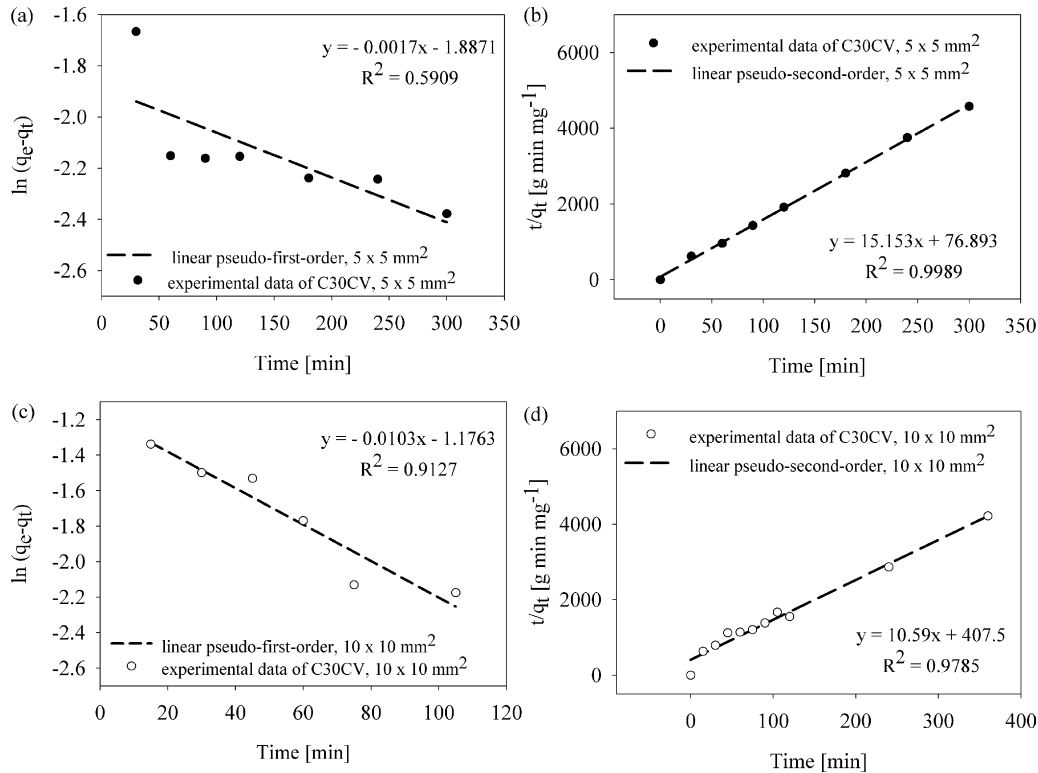


Fig. 1. Sorption kinetic model of Hg(II): (a) pseudo-first-order of chip size 5 mm × 5 mm, (b) pseudo-second-order of chip size 5 mm × 5 mm, (c) pseudo-first-order of chip size 10 mm × 10 mm and (d) pseudo-second-order of chip size 10 mm × 10 mm.

Table 2  
The values of  $k_1$ ,  $k_2$  and  $R^2$  of pseudo-first-order and pseudo-second-order

Rubber chip size	Pseudo-first-order		Pseudo-second-order	
	$k_1$ (min <sup>-1</sup> )	$R^2$	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$R^2$
5 mm × 5 mm	0.0017	0.5909	0.0707	0.9984
10 mm × 10 mm	0.0103	0.9127	0.0601	0.9937

due to their larger surface area per unit volume which is significant in an adsorption process. Fig. 2 shows good agreement between the plots of experimental data and the results from the second-order model. The plots are shown in terms of amounts

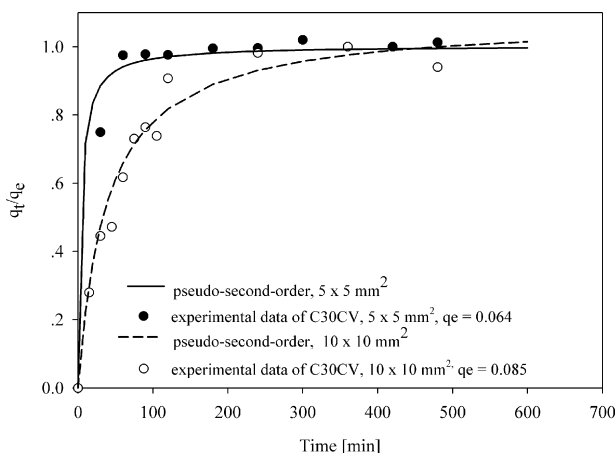


Fig. 2. The good consistency between experimental data and second-order model is shown for both chip sizes.

of Hg(II) adsorbed in the rubber chips at any time per amounts at equilibrium,  $q_t/q_e$ . As can be observed in Fig. 2, the curve of smaller chips shows higher initial slope reflecting higher rate of adsorption. Thus, smaller chips would be used for the rest of the experiments. The adsorption capacity increased with time and reached a maximum within 8 h, beyond which the adsorption capacity remained constant. This was considered to be at equilibrium so in later experiments we set the shaking time at 160 rpm to be 8 h for the adsorption to reach equilibrium. The equilibrium time depends greatly on shaking speed so this could be different from other literatures [12].

### 3.2. Adsorption equilibrium

Various amounts of rubber chips ranging from 0.2 to 1.0 g were used while the Hg(II) concentration was fixed about 5 ppm. The equilibrium concentration of the solution was measured and the adsorption capacity was calculated according to Eq. (1). Considering all formulae, it was found that when using 0.2 g rubber, the adsorption capacity was 0.30–0.40 mg Hg(II)/g rubber and when using 1 g rubber, the adsorption capacity was 0.07–0.09 mg Hg(II)/g rubber. As the adsorbent dosage is increased, there is less commensurate increase in adsorption resulting from the lower adsorptive capacity utilization of the adsorbent. The ability to remove Hg(II) may be expressed in terms of sorption percentage, defined as

$$\% \text{ sorption} = \frac{C_0 - C_{eq}}{C_0} \times 100. \quad (9)$$

Table 3  
The Freundlich parameters at different pH

pH	$K_F$ ((mg Hg(II)/g rubber)(ppm <sup>n</sup> ))	$n$
1.81	0.0416	1.30
7.89	0.0989	0.21
12.4	16.17	0.17

Compared among all formula, it was observed that % sorption in all experiments ranged from 78 to 98%, showing that adsorption of Hg(II) depended on the amounts of different compositions in the rubber chips. In order to study the effect of different components, the empirical Freundlich isotherm, often used for studying the equilibrium adsorption, was applied to the results. It is expressed as

$$q_e = K_F C_e^{1/n}, \quad (10)$$

or in the linear form as

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (11)$$

Here,  $K_F$  and  $n$  are Freundlich parameters. Upon plotting  $\ln q_e$  and  $\ln C_e$ , a straight line should be obtained. Its slope and intercept yield the values of  $n$  and  $K_F$ , respectively. The parameter  $K_F$  describes the adsorption capacity under a standard condition ( $C_e$  equals unity) so a higher value of  $K_F$  implies higher adsorption capacity while another parameter,  $n$  indicates how dramatically the binding strength changes as the adsorption density changes.

First, the effect of pH was investigated as shown in Table 3, upon increasing pH, adsorption affinity of the rubber chip increases. This finding is similar to what was reported in the adsorption of Hg(II) by 2-mercaptobenzimidazole-clay [18]. This has to be explained by Hg(II) speciation diagram [14]. Hg(OH)<sub>2</sub> was thought to be most effectively adsorbed in the vulcanized rubber [14]. In neutral and basic solutions, the dominant species is Hg(OH)<sub>2</sub> which coincides with higher adsorption capacity of Hg(II). In acidic solution with the presence of Cl ions, the dominant Hg(II) species is HgCl<sub>2</sub>, together with smaller amounts of HgCl<sup>+</sup>, Hg<sup>2+</sup>, Hg(OH)<sup>+</sup>, and Hg(OH)<sub>2</sub>, respectively. Moreover, the pH<sub>pzc</sub> of the rubber chip was found to be 6.8 and below this pH the surface of the chip is positive. Therefore, in acidic condition, the electrostatic repulsion will obstruct the adsorption of cationic Hg(II) species on the chips. In what follows, the experiments were done without adjusting pH. The initial pH of the solutions was about 4.5 close to what was reported in the literature [15]. According to Knocke and Hemphill [14], at this pH, the Hg(II) species equally found in the solution are HgCl<sub>2</sub>, HgOHCl and Hg(OH)<sub>2</sub>. Less found in the solution are HgCl<sup>+</sup>, Hg<sup>2+</sup> and HgOH<sup>+</sup>, respectively.

### 3.2.1. Effect of sulfur

The effect of sulfur on adsorption of Hg(II) by vulcanized rubber chips was investigated at equilibrium condition. It was expected that the reaction between sulfur in the rubber and Hg(II) would happen during the adsorption process. This was partly confirmed by doing the desorption experiments

Table 4  
The three vulcanizing systems and corresponding Freundlich parameters are shown

Formula	Sulfur contents (phr)	$K_F$ ((mg Hg(II)/g rubber) (ppm <sup>n</sup> ))	$n$
C30EV	0.4	3.90	4.38
C30SEV	1.5	40.07	0.46
C30CV	2.5	18.31	0.58

of C30CV chips after adsorbing Hg(II). It was found that desorption percentages are on average 0.4% which is rather small. Therefore, it was likely that the adsorption is mainly chemisorption, not physical adsorption. Likewise, it was reported that when waste tire rubber was mixed with Hg(II)-contaminated soil, the leachate from this mixture contained very low concentration of Hg(II) [16].

As stated before, in this study the sulfur content was varied through different standard vulcanizing systems, CV, SEV and EV. The corresponding formulae are C30CV, C30SEV and C30EV, respectively. The results of the three vulcanizing systems are compared in Table 4, together with the amounts of sulfur used. As seen in the table, a conclusion cannot be made immediately about the effect of sulfur content on Hg(II) adsorption capacity. It is possible that the reaction of sulfur atoms in vulcanization was not complete. Some of the sulfur atoms might react with carbon atoms on the rubber molecules and these chemical bonds construct a network inside rubber volume, whereas the remaining sulfur atoms did not react but was simply mixed with the bulk rubber. If sulfur truly affects the Hg(II) adsorption capacity, and if both reacted sulfur atoms and unreacted sulfur atoms play an equivalent role, the adsorption capacity, reflected by  $K_F$ , in Table 4 should increase with sulfur content but this is not seen. Therefore, it is necessary to check whether reacted sulfur atoms or unreacted sulfur atoms play the key role in Hg(II) adsorption. To do so, unreacted sulfur atoms (aka. free sulfur atoms,  $S_{\text{unreacted}}$ ) were to be removed from the rubber chips by readily immersing the chips in toluene, whereas reacted sulfur atoms ( $S_{\text{reacted}}$ ) forming crosslinking network could withstand the dissolution by toluene. The amount of free sulfur atoms was quantified by calculating the weight loss of the rubber sample after being swollen in toluene and dried in the oven. It was assumed that weight loss was totally the amount of unreacted sulfur atoms because the quantities of other ingredients in toluene were so little that they were negligible.

The unreacted sulfur content,  $S_{\text{unreacted}}$ , was calculated from

$$S_{\text{unreacted}} = \left[ \frac{\text{total phr of the compound}}{100 \text{ phr of gum rubber}} \right] \times (\% \text{weight loss}) \quad (12)$$

and the reacted sulfur content,  $S_{\text{reacted}}$ , could be calculated from

$$S_{\text{reacted(phr)}} = S_{\text{total(phr)}} - S_{\text{unreacted(phr)}}, \quad (13)$$

where  $S_{\text{total}}$  is the total phr of the sulfur and %weight loss is the percentage of the sample weight lost after free sulfur was dissolved in toluene. The reacted- and unreacted-sulfur contents are compared in Table 5. The amount of free sulfur for each



Table 5  
The total, reacted, and unreacted sulfur contents are provided, along with the values of  $K_F$  and  $n$  of three vulcanizing systems after being immersed in toluene

Formula	Total sulfur	Reacted sulfur	Unreacted sulfur	$K_F$ ((mg Hg(II)/g rubber)(ppm <sup>n</sup> ))	$n$
C30EV	0.4	0.32	0.08	13.34	0.72
C30SEV	1.5	1.44	0.06	65.73	0.39
C30CV	2.5	2.46	0.04	31.19	0.48

vulcanizing system was much less than the amount of reacted sulfur. In the EV system, the reacted sulfur content was the least while the unreacted sulfur content is the most, reflecting high efficiency of constructing the crosslinking network using only minimal amount of sulfur. The contrary was seen in the CV system.

Unfortunately, reacted sulfur and unreacted sulfur contents as well as the adsorption capacity reflected by  $K_F$  do not show the same trend. However, because the amount of free sulfur was very little, the effect of sulfur, if any, should come from the reacted sulfur. This was confirmed by performing another experiment, in which chips without free sulfur atoms (removing free sulfur atoms by immersing in toluene until saturation and then dried at room temperature) were used to adsorb Hg(II) in water. The similar analysis was done for this experiment and the parameter,  $K_F$ , was obtained and also shown in Table 5.

From Tables 4 and 5, a comparison between values of parameter  $K_F$ , of three vulcanizing systems both before and after being immersed in toluene can be made. The trends of  $K_F$  for chips after immersion and before immersion were the same, confirming that the adsorption capacity should depend on the reacted sulfur, which was still left in the chips after immersion in toluene. Obviously, after being immersed in toluene, the rubber chips could adsorb pronounced amount of Hg(II) in the water. As noticed from SEM micrographs in Fig. 3, after being swollen in toluene and left dried the surface of the chip appears more porous so more amount of Hg(II) can be accommodated on the chip.

The final point to be clarified is how the reacted sulfur adsorbed Hg(II). The amount of reacted sulfur atoms does not correlate with adsorption capacity of the chips possibly because not all reacted sulfur atoms contribute to this adsorp-

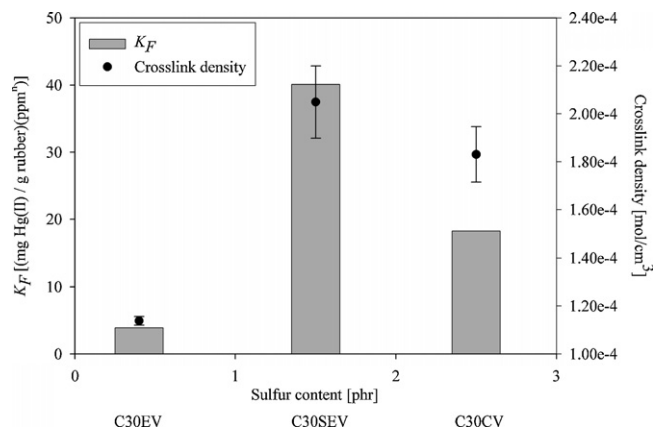


Fig. 4. The Freundlich parameter,  $K_F$ , and crosslink density of three vulcanizing systems show the same trend.

tion. This idea provoked checking the degree of crosslink density of three vulcanizing systems by the method described previously in Section 2.6. The assessment of the crosslink density was done by using the Flory–Rehner equation also provided in Section 2.6. The relation of  $K_F$  and crosslink density of three vulcanizing systems is then shown in Fig. 4. The adsorption parameters  $K_F$  for both cases, before and after immersing in toluene, are in descending order as follows: SEV, CV and EV systems, respectively. Apparently, the results show the same trend as for the crosslink densities, implying that Hg(II) can be absorbed by the crosslink network of the rubber chips.

According to Pearson theory during acid–base reaction, soft acid prefers to coordinate with soft base and hard acids to hard

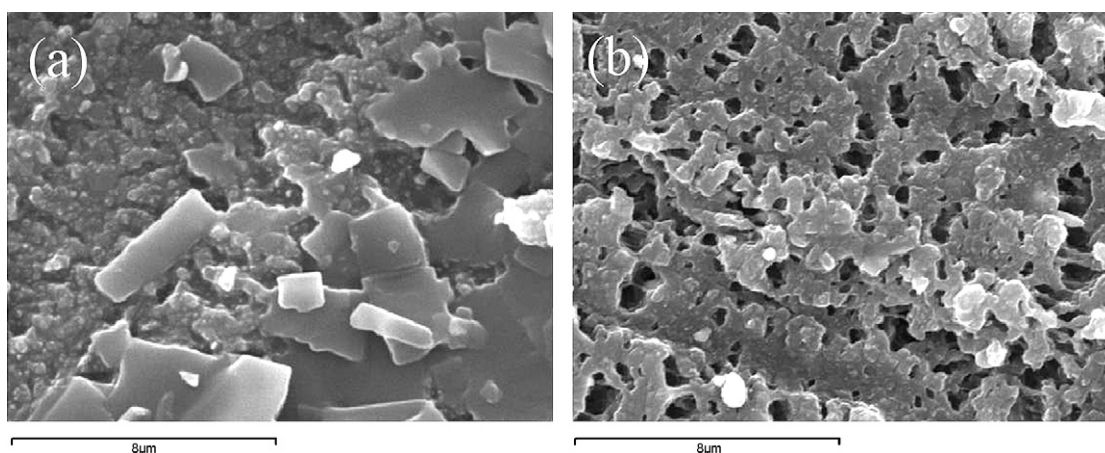
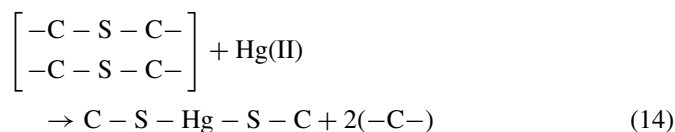


Fig. 3. SEM micrographs for C30EV chip surfaces (15 mV, 7500 $\times$ ): (a) before being immersed in toluene and (b) after being immersed in toluene.

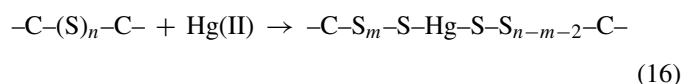
bases [19]. Neutral molecules are softer acids than metal cations. The interaction of Hg(II) species such as HgCl<sub>2</sub>, Hg(OH)<sub>2</sub> and HgOHCl considered as soft acids with sulfur groups in rubber chips as a soft base is highly favorable [18]. The possible reactions could be as the following:



for monosulfidic crosslink,



for disulfidic crosslink, and



for polysulfidic crosslink. It was reported that the ratio of polysulfidic crosslink/(monosulfidic + disulfidic crosslinks) in CV systems are greater than that in EV [20]. Hg(II) species would react with the sulfur atoms in the crosslink of any kind. It was reported that in an acidic aqueous medium, the chemical degradation of crosslinked rubber is facilitated; there was the evidence showing the breaking of C–S and C–S bonds and forming the oxygenated species [21]. It should be noted that the bond energies of C–S and S–S are 714 and 425.3 kJ/mol, respectively [22]. Therefore, it is likely that S–S bonds in disulfidic and polysulfidic crosslink could be broken more easily than C–S bonds in monosulfidic crosslink. Besides, the bond energies of Hg–O and Hg–Cl are 220.9 and 100 kJ/mol, respectively [22]. The breaking of Hg–Cl may, thus, be more easily than Hg–O.

It is likely that the possibility of Hg(II) to react with sulfur atoms in crosslink network depends on the number of crosslink. It should also be pointed out that the crosslink density changes with time because reversion may occur when the oxidation occurs in the chips. The adsorption capacity of the chips is, therefore, changeable. This was corroborated by another study (the results are not provided here), which testifies the adsorption capacity of the chips at different times. The results of adsorption capacity correlated well with the crosslink densities. This work, thus, is not conclusive in the respect of comparison among vulcanizing systems, but rather it confirms that Hg(II) adsorption capacity depends on the degree of crosslinking in the chips.

It is known that a similar reaction between Hg(II) and an amino acid called cysteine, which contains a thiol (–SH) group [23]. The thiol groups on polypeptide chain often react together to form disulfidic bridges (–S–S–). These bridges are important in controlling the three-dimensional structures of proteins, thereby, influencing the correct biological function. Once Hg(II) reacts with these disulfidic bridges, the proteins containing inserted Hg(II) are formed and three-dimensional structures can be changed in a way that toxicity frequently happens. The fact that Hg(II) is easily reacted with thiol groups leads to some studies on development of a good adsorbent for Hg(II). For example, a polymer resin with thiol groups showed high affinity to Hg(II) in adsorption experiments [8]. A derivative of chitosan with thiol

Table 6  
The effect of zinc oxide and carbon black loadings on Freundlich parameters

Formula	phr	K <sub>F</sub> ((mg Hg(II)/g rubber)(ppm <sup>n</sup> ))	n
Zinc oxide			
C30Z3EV	3	1.42	0.84
C30Z4EV	4	311.4	0.30
C30EV	5	1.333	1.53
Carbon black			
COEV	0	1996.8	0.22
C30EV	30	1.333	1.53
C50EV	50	0.1529	28.09

groups was also reported to have an increased sorption capacity for Hg(II) [3].

### 3.2.2. Effect of zinc oxide

The effect of zinc oxide in the chips was studied by changing the amount of zinc oxide to be 3, 4 and 5 phr. Zinc oxide reacts with stearic acid and forms a complex which acts as an activator during the vulcanization. The results are given in Table 6 and the plot of K<sub>F</sub> with varying amounts of zinc oxide is shown in Fig. 5. It was found that the increasing amount of zinc oxide did not increase Hg(II) adsorption capacity of the chips. The adsorption capacity, however, showed the same trend as the degree of crosslinking. Therefore, it may be safe to conclude that zinc oxide is partially affect the Hg(II) adsorption by mechanism of ion exchange [13] and it indirectly affects the adsorption capacity by assisting in the vulcanization process to form the crosslinking of sulfur molecules to the rubber chains.

### 3.2.3. Effect of carbon black

The results for unfilled chips compared with those of chips filled with different carbon black loadings, 30 and 50 phr, are shown in Table 6 and Fig. 6. It was seen that when increasing the amount of carbon black, Hg(II) adsorption capacity decreased. As in the studies of sulfur and zinc oxide effects, the degree of crosslinking was also evaluated and it turned out that when increasing carbon black loading the apparent degree of crosslinking increases. For the case of unfilled rubber (COEV),

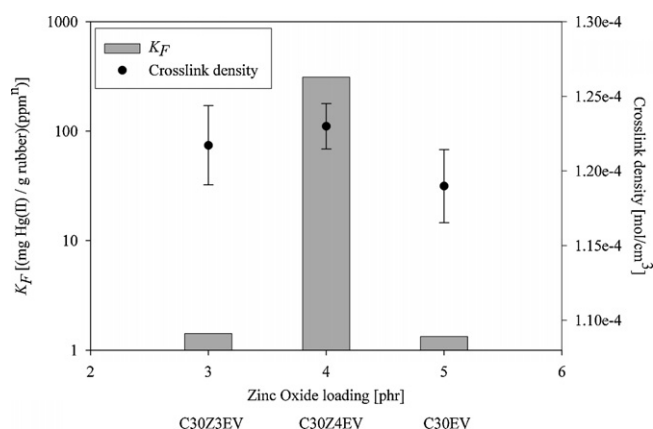


Fig. 5. The Freundlich parameter, K<sub>F</sub>, and crosslink density of various amounts of zinc oxide used during vulcanization are compared.

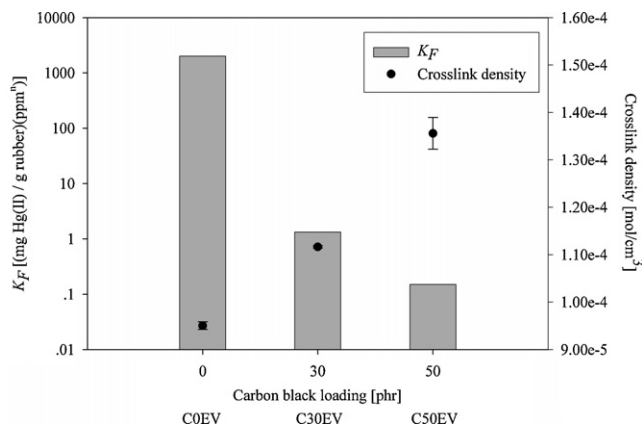


Fig. 6. The parameter in Freundlich relation,  $K_F$ , and degree of crosslinking are plotted against different carbon black loadings.

the degree of crosslinking is attributable to the reacted sulfur in the chips. When adding carbon black as filler, the additional physical interaction among carbon black particles and the rubber molecules causes the structure to be less flexible, and this made diffusion of Hg(II) into the rubber structure more difficult, leading to a lower amount of Hg(II) adsorbed. If the effect of sulfur was dominant in this study, the adsorption capacity for every case should be at least equal to the case of unfilled rubber but it was not such a case. As long as Hg(II) cannot diffuse into the rubber matrix, the sulfur atoms does not affect the adsorption.

#### 4. Conclusions

Vulcanized rubber chips were used as a model adsorbent for proving the effect of sulfur, zinc and carbon black on Hg(II) adsorption in water. The chips with smaller size yielded higher rate of adsorption. The mechanism of Hg(II) adsorption linked closely with sulfur which was used as a vulcanizing agent in rubber production. Since Hg(II) adsorption capacity correlated with the crosslinking density in the chips, it was possible that Hg(II) could react with this reacted sulfur in the crosslinking network. The adsorption is, thus, related to this specific reaction and may be considered as chemisorption.

The effect of zinc oxide was also studied and it was found that zinc oxide did not directly affect the adsorption but it did indirectly by acting as an activator in vulcanization process. Lastly, the amount of carbon black loading seemed to discourage the adsorption process because the interaction of carbon black particles with rubber molecules reduced the mobility of rubber structures, thereby obstructing the diffusion of Hg(II) into the rubber.

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