Immobilization of mercury(II) in contaminated soil with used tire rubber

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Abstract

The effectiveness of used tire rubber for immobilizing Hg(II) in a contaminated soil was evaluated using batch extraction and field rainwater leaching tests. The contaminated soil was prepared using a clay-loam spiked with mercury oxide or mercury chloride to yield a Hg(II) content of 300 mg/kg. When the contaminated soil was treated with 4% of tire rubber, Hg(II) concentration in an acetic acid leachate was reduced from 3500 ppb down to 34 ppb. Hg(II) concentration in the initial rainwater leachate was reduced from 84 ppb for untreated soil to 1.2 ppb for the rubber-treated soil. After 8 months of rainwater infiltration in the field, Hg(II) concentration decreased to less than 0.2 ppb for the treated soil. The rubber-treatment inhibited the evolution of metallic Hg^0 from the spiked soil samples possibly by retarding the reduction of Hg(II) to Hg^0. Batch extraction and adsorption results indicated that the rubber had high adsorption capacity for Hg(II) when pH values were between 2 and 8. © 1998 Elsevier Science B.V.

Keywords: Mercury; Immobilization; Rubber; Leachability; Stabilization; Adsorption; Contamination; Soil; TCLP; Evolution

1. Introduction

Mercury in contaminated soils is a unique pollutant that requires innovative remediation solutions. Heavy metals, such as Cd, Pb, As, and Cr, have been immobilized with cement- and lime-based stabilization/solidification (S/S) technologies [1–3]. The con-

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ventional S/S treatments cannot effectively reduce the leachability of Hg [1,3]. This is mainly due to relatively high solubility of Hg hydroxide and strong tendency for Hg to form soluble complexes with organic and inorganic ligands.

Various sulfur compounds have been used for the immobilization of Hg in the contaminated soils [1,4]. Sulfur has high affinity for Hg, and Hg sulfide precipitate has very low solubility in water. Chang et al. [5] reported that Hg could be immobilized in a Hg-bearing sludge with a two-step treatment. The process involved a pretreatment by adding sodium sulfide and ferrous sulfate in the sludge and a solidification treatment using cement. However, the leachability of Hg in the treated solid increased with curing time. The release of Hg from a tricalcium silicate (the major component of cement) slurry was also observed at long hydration times [1]. Because the solubility of Hg can be increased in the presence of excess amount of sulfide [1,6], the amount of alkali sulfide added in the contaminated material has to be carefully controlled.

In the present work, ground tire rubber particles were utilized for the immobilization of Hg(II) in a spiked soil. Both batch extraction and field rainwater infiltration tests indicate that Hg(II) can be effectively immobilized by the rubber. The experimental results suggest that a cost-effective immobilization process may be developed using the tire rubber particles.

2. Experimental procedures

2.1. Treatment of contaminated soil

Uncontaminated soil was a clay-loam collected from a garden on the campus of Stevens Institute of Technology. The soil sample was air-dried and passed through No. 12 (i.e. 1.70-mm) sieve to remove large particles. It contained 68% of fines and 32% of sand. The organic matter and mercury contents in soil sample were 4.7% and 1.2 mg/kg, respectively. Mercury oxide (HgO, red) or mercury chloride (HgCl$_2$) were added in the soil sample in dry form to yield a Hg(II) content of 300 mg/kg. The Hg(II) chemicals were used as model contaminants because they are more soluble than metallic Hg^0 and HgS [7]. In contaminated soils, Hg can be present as metallic, ionic, and organic forms [8,9]. After the addition of 20% water and mixing, the contaminated soil samples were aged for a day in capped high density polyethylene containers. One day of aging period was used to simulate a newly contaminated soil. Our experimental results suggested that Hg leachability decreased when the aging time increased.

Hg(II)-immobilization treatment was performed by adding ground tire rubber particles in the aged soil samples. The samples were mixed and kept in the capped containers until they were tested for Hg leachability. The used tire rubber contained approximately 2–4% sulfur and less than 32% of carbon black. Rubber hydrocarbon content in the tire rubber was approximately 40%.

In a separate treatment, S/S materials (i.e. quicklime, fly ash, and cement), water, and tire rubber were added in the spiked soil samples. The soil samples were spiked at higher Hg(II) concentrations to yield a Hg(II) content of 300 mg/100 g of the total solid. The treated samples were cured for 21 to 24 days in the capped containers. At the

same time, two untreated samples were aged in the capped containers as control samples.

2.2. Leaching tests

The cured and aged samples were tested for the leachability of Hg(II) using the toxicity characteristic leaching procedure (TCLP) [10]. The TCLP test was conducted in a 0.1 M acetic acid solution (pH = 2.88) at a solution to solid ratio of 20:1. The acetic acid solution was used for extraction because the pH values of the samples were greater than 5. The extraction suspension was tumbled for 18 h, and then filtered through a borosilicate microfiber filter with a pore size of 0.7 μm to separate the liquid from the solid. The solution samples were digested for total Hg analysis according to U.S. EPA Method 7470A [11]. The total Hg concentration in the leachate was analyzed using a cold-vapor atomic absorption spectrophotometer (Varian AA-1475 with VGA-76). The detection limit of the method was 0.2 ppb Hg.

In another extraction test, after the addition of 0.1 M acetic acid solution to the solid samples, the suspension pH was adjusted between 3 and 13 using a sodium hydroxide solution or nitric acid solution. After 18 h of mixing, the final pH values of the suspensions were measured and the suspensions were filtered for the analysis of Hg in the solution.

Two soil samples were prepared for field rainwater infiltration test. HgO (red) was added to the samples to yield a Hg content of 300 mg/kg. After the addition of 20% water the samples were mixed. The used tire rubber particles were added to one of the samples to reach a rubber content of 4 g/100 g of dry soil. Both treated and untreated samples were aged in capped containers. After 2 days of aging, half of the uniform sample (i.e. 300 g of wet sample) was taken from each container for the infiltration test. The other halves of the samples were aged in the capped containers and used for TCLP test and total Hg analysis later.

The field rainwater infiltration test was conducted by transferring the rubber-treated and untreated loose soil samples in high density polyethylene columns. The columns had a 7.6 cm inside diameter with a height of 8.9 cm. A borosilicate microfiber filter was placed on a screen at the bottom of the column. The soil height in the columns was approximately 4 cm. Half of the column was buried under ground to keep the temperature of the soil samples similar as that of the natural soil. The columns were subject to rainwater leaching in the field for approximately 8 months. The leachate coming out of the bottom of the columns was collected routinely for Hg(II) and pH analyses.

2.3. Mercury adsorption

Adsorption kinetics, optimal adsorption pH, and adsorption capacity of the rubber particles for Hg(II) were determined with a set of batch experiments. The adsorption experiments were conducted by mixing the rubber particles with a Hg(II) nitrate solution. Then, the solution was separated from the rubber particles by filtration for the measurements of the equilibrium pH and Hg(II) concentration. The amount of the Hg(II)

adsorbed was calculated based on the initial Hg concentration and equilibrium Hg concentration in the filtrate.

3. Results and discussion

3.1. Hg(II) adsorption by used tire rubber particles

The adsorption results in Fig. 1 indicate that Hg(II) adsorption by the tire rubber is a slow process. The adsorption approached equilibrium in approximately 50 h. The adsorption of heavy metals on the surface of metal hydroxides usually reach equilibrium within 2 h [12]. The slow adsorption in Fig. 1 may be attributed to the diffusion of Hg(II) into the rubber matrix. The adsorption results suggest that when the rubber particles are mixed with contaminated soil, it will take a few days for the adsorbent to effectively immobilize Hg(II).

Contaminated soils may have very low or high pH, which can significantly affect the immobilization of Hg(II). The results in Fig. 2 indicate that Hg(II) adsorption by the rubber was higher in low pH range. Hg(II) adsorption increased when pH decreased from 10 to 7. The reduced Hg adsorption at higher pH values may have been caused by the formation of mercury complexes with hydroxyl ions. Mercury can form stable complexes, such as $HgOH^+$ and $Hg(OH)_2^0$, with hydroxyl ions [13]. When pH increases, more mercury–hydroxyl complexes are formed. According to the adsorption results in Fig. 2, the rubber treatment of Hg-contaminated soil should be performed in acidic to neutral pH range. If the contaminated soil contains other heavy metals, the leachability of the metals in the rubber-treated soil at relatively low pH values should also be investigated.

The adsorption isotherm in Fig. 3 was obtained by mixing the rubber in a Hg(II) solution for 2 days. The solution pH value was controlled at 6.7 using sodium hydroxide
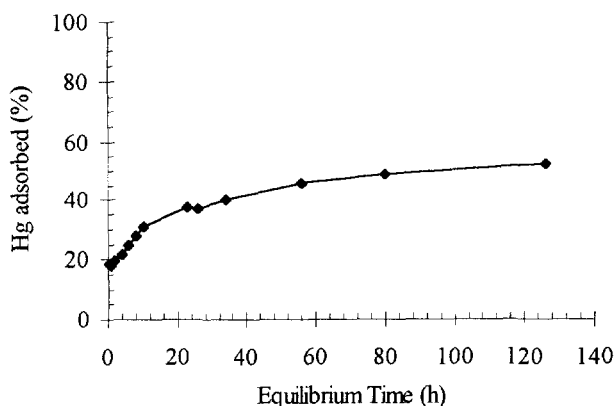

Fig. 1. Adsorption of Hg(II) by used tire rubber particles as a function of time. Initial Hg(II) concentration: 50 ppm; rubber content: 1 g/l; equilibrium pH: 6.5.
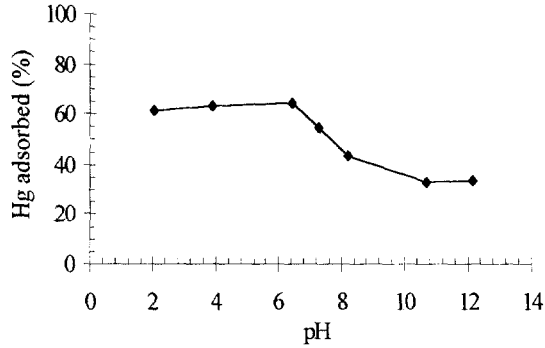
Fig. 2. Adsorption of Hg(II) by used tire rubber particles as a function of pH. Initial Hg(II) concentration: 10 ppm; rubber content: 1 g/l; adsorption time: 20 h.

or nitric acid solution. A steep increase in the amount of Hg(II) adsorbed in low equilibrium Hg(II) concentration range suggests that the rubber had high affinity for Hg(II). It may be used to reduce soluble Hg(II) to very low concentration. The plateau in the adsorption isotherm indicates the adsorption capacity of the tire rubber. The solid line in Fig. 3 was calculated using the Langmuir isotherm as described by the following equation:

$$\Gamma = \Gamma_{max} \frac{K_{ads}[Hg]}{1 + K_{ads}[Hg]}$$

where Γ is the amount of Hg(II) adsorbed by the rubber in mg/g, Γ_{max} is the adsorption capacity in mg/g, K_{ads} is the adsorption equilibrium constant, and $[Hg]$ is the equilibrium Hg concentration in the solution in mg/l. A good agreement between the experimental data and the model calculations indicates that Hg(II) uptake by the rubber followed the Langmuir type of adsorption. The Γ_{max} and K_{ads} were determined to be 14.6 mg Hg/g and 4.7 l/mg, respectively.
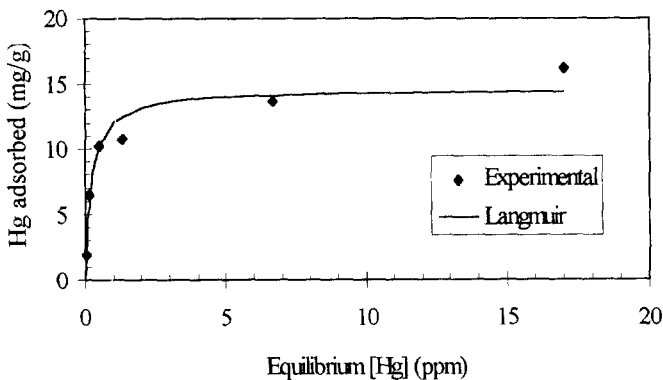

Fig. 3. Hg(II) adsorption isotherm by used tire rubber particles. Rubber content: 10 g/l; equilibrium pH: 6.7; adsorption time: 48 h.

The high adsorption capacity of the tire rubber particles may be attributed to the sulfur groups in the rubber. A variety of sulfur groups, such as polysulfides ($-CH_2-S_x-S_y-CH_2-$) and thiocarbonyls (N–C–S–), are present in the tire rubber. Hg(II) may have been adsorbed to the sulfur sites through the formation of surface complexes, $\equiv$S–Hg. $\equiv$S represents the sulfur sites associated with the rubber.

3.2. Leachability of Hg(II) in the treated soils

Hg(II) concentrations in the TCLP leachates are presented in Fig. 4 for soil samples treated with different amounts of rubber. The leachate pH was approximately 3.7 for both the treated and untreated soil samples. When untreated soil (i.e. no rubber addition) was aged for 3 weeks, the total Hg concentration in the leachate was 3.5 ppm. After 8 months of aging in capped containers, the Hg concentration reduced to 0.74 ppm for the untreated soil. If all of the Hg in the soil sample was released, leachate Hg concentration should be 6 ppm. The decrease in the amount of leachable Hg indicates that some of the Hg was strongly associated with the soil. Mercury may have diffused into the intraparticle pores or penetrated into the soil mineral lattice during the 8 months of aging [14].

The leachability of Hg(II) was reduced significantly when the amount of rubber in the soil samples increased from 0 to 7 g/100 g soil (Fig. 4). At a rubber content of 4 g/100 g, Hg(II) concentration was reduced to 0.034 ppm for the sample aged for 3 weeks. Longer aging time further reduced the leachability of Hg(II) in the treated soil sample. The results suggest that the adsorbed Hg species were very stable. Chang et al. [5] reported that the leachability of Hg in sodium sulfide and cement treated solid increased with curing time. The increase in the leachability of Hg may be attributed to the oxidation of sulfide by the air.
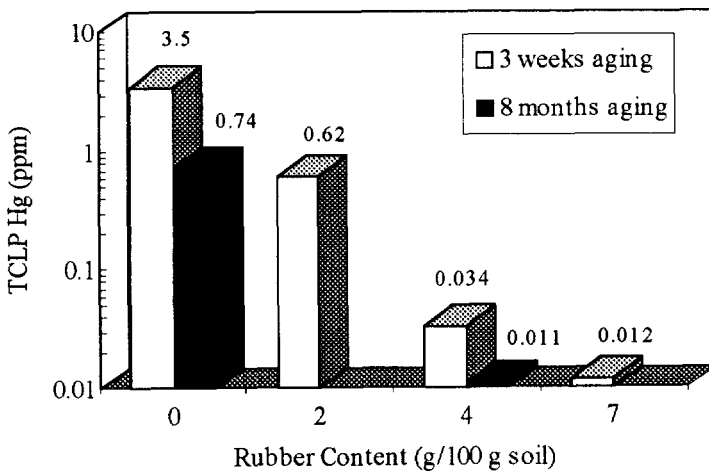

Fig. 4. Total Hg concentration in TCLP leachate for the samples aged in capped containers. Contaminant: HgO (red).

Based on the Hg(II) content of 300 mg/kg soil and the rubber content of 4 g/100 g soil, the Hg(II) to rubber ratio in the treated soil was 7.5 mg/g. This ratio is approximately half of the adsorption capacity of the rubber (Fig. 3). When rubber content in the treated sample was 2 g/100 g, Hg(II) was not immobilized well (Fig. 4). Therefore, the amount of rubber added in the soil should be more than half of the amount calculated based on the adsorption capacity of the rubber particles. The U.S. Environmental Protection Agency TCLP protocol has been used to classify wastes under the Resource Conservation and Recovery Act (RCRA). A material with a TCLP concentration above 0.2 ppm Hg is classified as hazardous. The results in Fig. 4 demonstrate that the leachability of Hg(II) from the contaminated soil was reduced below the TCLP limit when the amount of rubber particles added in the soil was 4 g/100 g or more. At the rubber content of 4 g/100 g soil (i.e. 40 kg/ton), the cost of the rubber particles is approximately US$25/ton of the treated soil.

The leachability of Hg(II) from the treated and untreated soil samples at different pH values is compared in Fig. 5. The conditions used for the leaching test were the same as those for the TCLP test except that the pH was adjusted to different values. For the untreated soil sample, a minimum Hg(II) leachability was observed at pH approximately 6. Hg(II) release from the treated soil samples decreased continuously when pH decreased from 12.5 to 3. The treated samples spiked with HgO and $HgCl_2$ had similar leachability. The results in Fig. 5 suggest that the leachability of Hg(II) in the treated soil samples was controlled by the rubber particles, especially at low pH. At alkaline pH, the treated soil samples showed relatively high Hg(II) leachability because the rubber had lower affinity for Hg(II) at higher pH (Fig. 2).

The TCLP leachability of Hg(II) from the soil samples treated with CaO, fly ash, cement, and rubber are presented in Fig. 6. The leachability of Hg(II) from all of the treated samples was reduced compared to the Hg(II) leachability from the untreated soil in Fig. 4. The sample treated with a combination of CaO and fly ash had lower Hg(II)
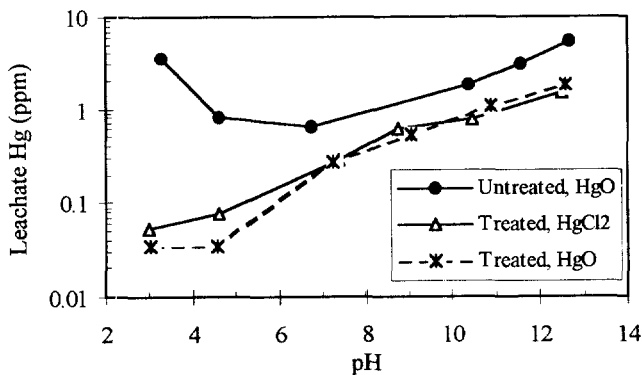

Fig. 5. Extraction of Hg from the treated and untreated soils at different pH values. Extraction solution: 0.1 M acetic acid; extraction time: 18 h; contaminants: HgO or $HgCl_2$; rubber content in the treated soils: 4 g/100 g; aging time: 42 days for untreated soil, 34 days for the treated samples.
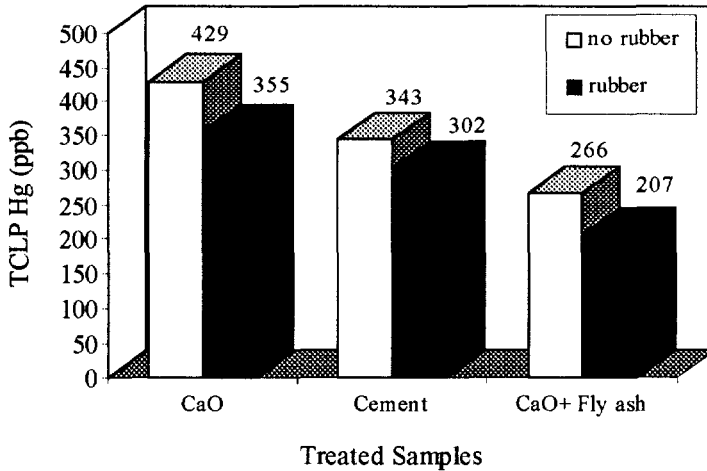
Fig. 6. Total Hg concentration in TCLP leachate for soil samples treated with different stabilization materials. Contaminant: HgO (red); additive contents in 100 g soil: 10 g CaO, 30 g cement, or 10 g CaO + 25 g fly ash; rubber content: 4 g/100 g soil + S/S additives; curing time: 24 days.

leachability than the samples treated with CaO or cement. In addition, the rubber treatment further reduced Hg(II) leachability. However, none of the treated samples in Fig. 6 had lower Hg concentration than the TCLP limit for hazardous materials.

The high Hg(II) leachability in Fig. 6 was due to elevated leachate pH. The leachate pH for the samples in Fig. 6 was between 11.0 and 11.4 because of the presence of CaO or cement. According to Fig. 5, rubber treatment is not effective under alkaline condition. The experimental results suggest that rubber-treatment should not be combined with the addition of CaO, cement, and fly ash for the immobilization of Hg(II).

The TCLP is a batch extraction test with dilute acetic acid solution. When the treated soil is subject to long-term weathering and rainwater infiltration in the field, the leaching behavior of Hg(II) will be different from that in the TCLP test. The field leaching data obtained between August 1995 and April 1996 are plotted in Fig. 7. For the untreated soil, Hg(II) concentration in the initial leachate was 84 ppb. Relatively high Hg(II) concentration was observed for the untreated soil sample during the first 3 months of leaching. The increase in Hg(II) concentration in the month of October was coincident with the heavy rains which saturated the soil samples.

The rubber treatment effectively reduced the release of Hg(II) from the soil. Hg(II) concentration in the initial leachate was 1.2 ppb. After 3 months of leaching, Hg(II) concentration deceased to less than 0.2 ppb. The leachate pH was between 6.5 and 7.3 for both treated and untreated soil samples. The Hg concentrations presented in Fig. 7 were for inorganic Hg. An analysis of the total Hg in the last leachate sample for the untreated soil indicated that most the Hg in the leachate was in inorganic form. Small amount of organic Hg, such as methyl Hg, can be formed in soils especially under flooded conditions. Roulet et al. [15] reported that the methyl Hg levels in flooded soils were less than 1% of the total Hg.
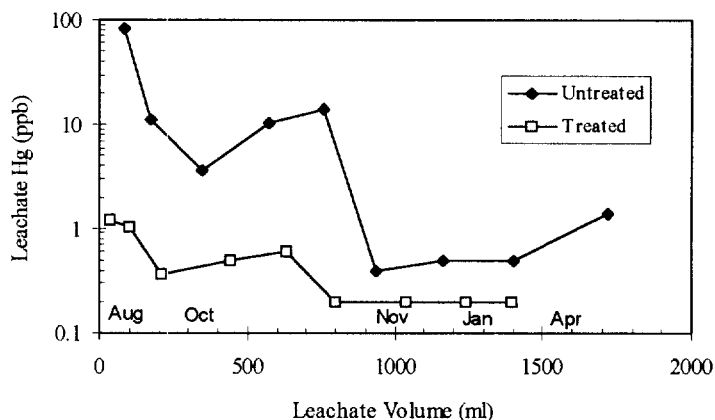
Fig. 7. Rainwater infiltration leaching of Hg(II) from rubber-treated and untreated soil samples in the field between August 1995 and April 1996. Rubber content in the treated soil sample: 4 g/100 g dry soil.

3.3. Evolution loss of Hg in the soil samples

After the samples had been leached in the field or aged in capped containers for 8 months, they were air-dried and analyzed for total residual Hg content in the solid samples according to U.S. EPA Method 7471 [16]. The Hg contents are summarized in Table 1. The residual Hg in the leached-untreated sample was 118 mg/kg of the soil. Based on the total initial Hg content of 300 mg/kg, 182 mg/kg of the Hg was lost during 8 months of the field leaching. The amount of Hg leached from the untreated soil sample was calculated according to the leachate Hg concentrations and the corresponding leachate volumes. Only 0.057 mg Hg/kg of the soil was leached by the rainwater infiltration (Table 1). The residual Hg contents in the leached-treated sample and in the untreated and treated samples that had been aged in the capped containers for 8 months were all similar as the initial Hg content (i.e. 300 mg/kg).

The significant amount of the unbalanced Hg in the leached-untreated soil sample may have been caused by evolution in metallic Hg^0 form. High gaseous Hg^0 level was detected in the head space of the capped container in which the remaining half of the untreated soil sample had been aged for 8 months. However, negligible amount of the Hg was lost in the aged-untreated sample because the sample container was capped and

Table 1
Mass balance of Hg in soil samples after 8 months of leaching or aging

	Field leached soil samples		Samples in capped containers	
	Untreated	Rubber-treated	Untreated	Rubber-treated
Total residual Hg (mg/kg)	118 ± 12	295 ± 30	293 ± 29	317 ± 32
Hg lost to leachate (mg/kg)	0.057	0.002	NA	NA
Unbalanced Hg (mg/kg)[a]	182 ± 12	5 ± 30	7 ± 29	-17 ± 32

[a] Unbalanced Hg = total initial Hg − (total residual Hg + Hg lost to leachate).

stored in the dark. Volatile Hg^0 can be formed in soil, sediment and water from $Hg(II)$ via biological or abiotic processes [17,18] and via chemical and photochemical reductions of $Hg(II)$ in the presence of humic substances [19,20]. The insignificant loss of Hg in the leached-treated sample may indicate that the reduction of $Hg(II)$ to volatile Hg^0 was inhibited when the $Hg(II)$ was strongly associated with the rubber particles.

The leached-untreated sample was evaluated for TCLP leachability. Mercury concentration in the TCLP leachate was only 0.045 ppm. For the untreated sample that had aged for 8 months in capped container, the leachate Hg concentration was 0.74 ppm (Fig. 4). The lower Hg leachability in the leached-untreated sample was due to the evolution loss of the Hg. Therefore, total Hg content in the treated soils should be measured when evaluating the effectiveness of a Hg-immobilization technology. Mercury content in the air should be monitored at the treatment site during a remediation operation.

4. Conclusions

The used tire rubber particles have high adsorption capacity for $Hg(II)$ in acidic and neutral pH range. Both TCLP and field leaching results demonstrate that the rubber particles can be used to effectively immobilize $Hg(II)$ in contaminated soil. Due to the high adsorption capacity of the rubber for $Hg(II)$, only a small amount of rubber is needed for the immobilization of $Hg(II)$ in the contaminated soil. The immobilization treatment can be performed by simply mixing the rubber particles with Hg-contaminated soils. In the future, long-term leaching behavior of the rubber-treated soil should be investigated.

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