Remediation of a soil polluted by mercury with acidic potassium iodide

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Abstract

A new chemical process has been studied to clean up a mercury-polluted soil by using acidic potassium iodide (KI) solution. A highly contaminated soil (max. 47.1 mg Hg/g) was used as a model sample. Evaluation was made on the effects of aqua regia, HCl, NaOH, Na-EDTA and KI solutions to extract mercury from polluted soil in a batch process. A mixture of 100 mM KI + 50 mM HCl (pH = 1.5) was found to be most effective. The acidic KI solution was passed through a column packed with 9.8 g polluted soil at a flow rate of 25 ml/h. After 15 fraction volumes, the mercury content decreased from 113.5 to 26.2 mg. The leachate from the column test containing HgI_4^{2-} was treated with granular activated carbon.

1. Introduction

Since middle 1960s the consumption of mercury has decreased due to the awareness to its toxic nature. A large amount of mercury had been used for manufacturing chlorine and caustic soda by the mercury process which has been switched over since 1973 in Japan to the diaphragm process where no mercury is used. The use and production of mercury-containing agrochemicals were also prohibited since 1974 in Japan. However, various types of environmental pollution by mercury still have been reported since mercury has widespread over the environment. Due to improper handling and disposal of mercury-containing materials considerable amount of mercury was found in sediments [1, 2]. In recent years, soil pollution by heavy metal has become one of the serious environmental problems especially at sites where chemical industry situated [3]. Once soil has been contaminated by heavy metal, it is difficult to

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clean it up. To clean up soil polluted by mercury, electrolytic [4] and extraction processes [5, 6] have been developed. The remedial technology using ligands has been considered most suitable for removing heavy metals from soil [7]. It has been known that industrial-grade sulfuric acid contains about 15 mg/l mercury which derives from copper or zinc sulfide concentrates. Mercury in sulfuric acid has been removed by the addition of potassium iodide (KI) to precipitate HgI_2 [8]. The precipitation of HgI_2 is favored by high concentration of H_2SO_4 and low temperature. On the other hand, no precipitate forms even from 10% H_2SO_4 at room temperature or higher, since mercury forms a soluble complex, HgI_4^{2-}.

The objective of the present study is to develop a new cost-effective extraction method to clean up mercury-polluted soil. For this purpose, a soil seriously polluted by mercury was used as a model sample which was collected from a site where a chemical plant situated before. The effects of different inorganic and organic ligands were evaluated by batch and column processes. Furthermore, the leachate from the column process was treated with granular activated carbon.

2. Materials and methods

2.1. Soil sample and chemicals

A 2 kg of soil (Gleysol) sample contaminated by mercury was collected from an industrial site in Tokyo, Japan, where a chemical plant stood. The pH of the soil suspension (30 g soil + 30 ml water) was 8.3. The sample was air-dried at room temperature and subsequently dried under vacuum for one week. The fraction larger than 4.75 mm was sieved off and rejected for the subsequent experiment because it contained only a trace amount of mercury (i.e. <2 mg/kg). The soil was classified into fractions of different particle size, 4.75, 0.59, 0.25, 0.149 and 0.105 mm. A 15, 2.0, 4.2, 2.0 and 1.0 g of the above fractions, respectively, were taken to determine the content of organic matter. The approximate value of the organic content was determined by heating the soil at 500 °C in an electric furnace [9]. The mercury content was determined by digesting with aqua regia at 60 °C for 8 h [10].

Disodium ethylenediaminetetraacetate (Na-EDTA) and KI of reagent grade (Kanto Chemical Co. Inc., Japan) were used as extraction agents. A commercially available granular activated carbon (Activated Charcoal; Wako Pure Chemical Ind. Ltd., Japan) was used for the treatment of the leachate collected from the column process described below. All other chemicals were of reagent grade.

2.2. Batch process

A series of 25 ml of aqueous solutions were prepared in glass tubes in the pH range of 1.4–13 adjusted with 50 mM HCl or NaOH solution. Another series of 25 ml of solutions were prepared containing 50 mM Na-EDTA or 100 mM KI at different pH adjusted in the same way as above. A suitable amount of soil depending on the

particle size was added to each tube. The suspension was shaken for 24 h at 20 °C. The mixture was centrifuged and the supernatant was withdrawn from each tube. The residue was extracted twice with 25 ml of aqueous solution in the same pH range. A 0.1 g of 0.105 mm soil containing maximum mercury was taken to study the effects of pH, extraction agents and shaking time. The supernatant was subjected to the ICP measurement (ICPS 1000 II; Shimadzu Corp., Japan) for the determination of mercury. Three replicate soil samples were analyzed.

2.3. Column process

A schematic diagram of the column process is given in Fig. 1. The column used was 1 cm in internal diameter by 10 cm in height with a sintered glass filter at the bottom. The column was packed with 9.8 g of soil composed of different fractions of particle size. The column was attached with 1 l of reservoir containing a mixture of 100 mM KI + 50 mM HCl as a carrier solution. The flow rate of the carrier solution was controlled at 25 ml/h. The fraction volume was collected periodically and analyzed for mercury.

2.4. Treatment of leachate

The leachate was collected from the above column process which contained 1340 mg/l HgI$_4^{2-}$. A 1.0 or 5.0 ml of the leachate was taken separately in a series of tubes. After the pH was adjusted in the range of 2–10, the volume was made up to 25 ml with water. A 1 g of granular activated carbon was added to each tube. The resulting suspension was shaken for 5 h at 20 °C and then filtered through a 0.45 μm nitrocellulose membrane filter. The filtrate was analyzed for pH and mercury.
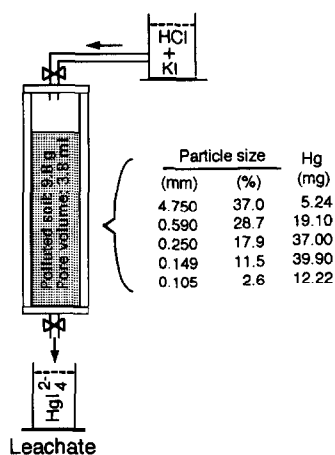

Particle size		Hg
(mm)	(%)	(mg)
4.750	37.0	5.24
0.590	28.7	19.10
0.250	17.9	37.00
0.149	11.5	39.90
0.105	2.6	12.22

Fig. 1. Schematic diagram for cleaning mercury-polluted soil by column process.

3. Results and discussion

3.1. Batch process

The soil sample was characterized in terms of particle size, contents of mercury and organic matter. The mercury content was determined by digesting soil with aqua regia. The content of organic matter was measured as ignition loss. It has been known that ignition loss gives an approximate amount of organic matter in sediments [11]. The results of the soil characterization are given in Fig. 2 showing increase in contents of mercury and organic matter with decrease in particle size. Therefore, mercury was mainly concentrated in fine particles where the concentration of organic matter was also high. The finest soil particle (0.105 mm) showed as high as 47.1 mg/g mercury content. The analysis of the aqua regia extract showed that the finer soil particles contained higher concentrations of Al, Fe and Ca.

The soil sample was treated with different media in a batch process, i.e. aqua regia, HCl, NaOH, Na-EDTA and KI solutions. Fig. 3 shows the effects of HCl, NaOH, 50 mM Na-EDTA and 100 mM KI solutions to extract mercury at different pH values from the finest soil (0.105 mm in particle size) from which 47.1 mg/g of mercury can be extracted by aqua regia. The results of the HCl and NaOH extraction show that treatment of soil with water of pH 5–12 has no effect to remove mercury from the soil. But by decreasing pH to <2 or by increasing pH to about 13 a small amount of mercury dissolved from the soil. This phenomenon is closely related to the speciation of inorganic mercury which can be calculated using the stability constants [12]. The mercury speciation is shown in Fig. 4. At pH <2, Hg^{2+} ion is the predominant species which accounts for the solubilization of mercury from the soil at low pH. Mercury is
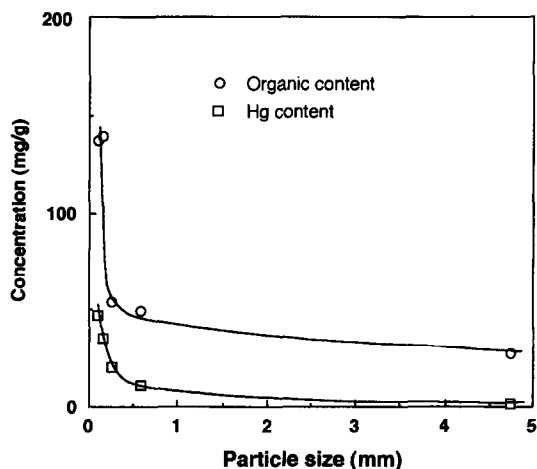

Fig. 2. Contents of mercury and organic matter as a function of particle size. Extraction of mercury, aqua regia; soil 15, 2.0, 4.2, 2.0 and 0.1 g for 4.75, 0.59, 0.25, 0.149 and 0.105 mm, respectively; shaking time, 5 h; temperature, 20 °C; ignition of organic matter, 500 °C.
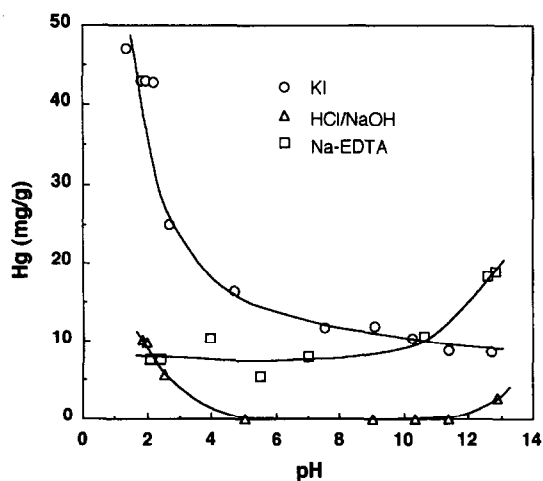
Fig. 3. Extraction of mercury with different media as a function of pH. Soil, 0.1 g (0.105 mm); shaking time, 5 h; KI solution, 100 mM; Na-EDTA solution, 50 mM; HCl or NaOH solution, 50 mM; temperature, 20 °C.
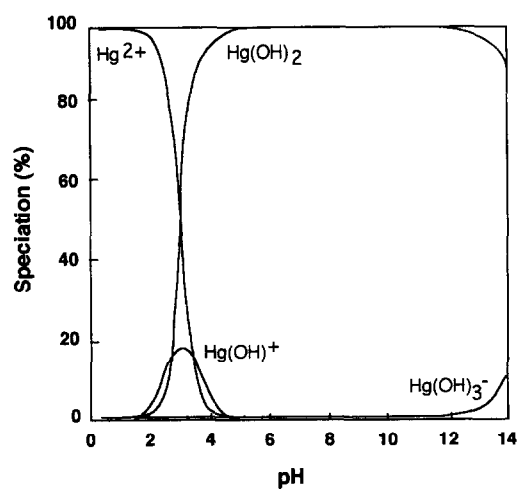

Fig. 4. Chemical speciation of mercury as a function of pH.

immobilized as solid $Hg(OH)_2$ in the pH range of 5–12 which cannot be removed by washing with water. Formation of ionic species $Hg(OH)_3^-$ accounts for dissolution of mercury at extremely high pH.

EDTA salts have been used as cleaning agent for soils polluted by heavy metal [13–15]. The effect of Na-EDTA to clean up mercury-polluted soil was not practical as shown in Fig. 3. Only about 20 m/g of mercury was removed at pH 12.8. The mercury removal was lower in the pH range of 2–11.

The effect of KI solution was very high especially at low pH. The amount of mercury solubilized by KI increased with decreasing pH. More than 40 mg/g of mercury was removed at pH < 2. Iodide ion plays an important role in extracting mercury from the soil at pH < 2 because it forms a soluble complex with mercury, HgI_4^{2-} as shown below:

$$\text{soil-Hg(OH)}_x + 4\,I^- \xrightarrow{\text{pH}<2} HgI_4^{2-} \text{ (aq.)} + xOH^- + \text{soil.} \tag{1}$$
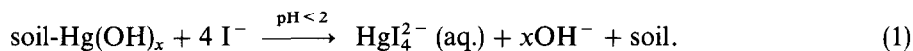
The higher mercury removal by KI than by HCl is due to the fact that the stability constant of HgI_4^{2-}, 29.8, is much higher than that of $HgCl_4^{2-}$, 16.2 [12].

The results of the batch extraction of mercury from the soil of different particle size by different media are summarized in Table 1. The extraction of mercury by acidic 100 mM KI solution was more effective than by aqua regia except in the case of 0.105 mm particle. Therefore washing with acidic KI solution can be a promising method to clean up mercury-polluted soil which causes much less detrimental effects on soil than aqua regia. The triplicate extraction with aqua regia and acidic KI solution shows that these methods are highly reproducible. More detailed study was carried out on the acidic KI method and the discussion is given below.

3.2. Kinetic study

A kinetic study was made on the extraction of mercury by acidic 100 mM KI solution at different intervals of shaking time according to the procedure of the batch process. The result is shown in Fig. 5. It was found that the decontamination of the soil was almost complete in 5 h of shaking time at 20 °C. The kinetic data were further analyzed by using the following Lagergren's equation [16]:

$$\log(q_e - q) = \log q_e - (K_{ds}/2.303)t, \tag{2}$$

where q_e and q (both in mg/g) are the amount of mercury desorbed at equilibrium and at time t (h), respectively. A linear regression analysis gave the following equation:

$$\log(q_e - q) = 0.0047 - 0.232/2.303t \tag{3}$$

with correlation coefficient $r = 0.983$. Therefore the desorption of mercury by acidic KI solution follows a first order reaction with a rate constant $K_{ds} = 0.232\,\text{h}^{-1}$.

3.3. Column process

A column study was made for a continuous remediation of mercury-polluted soil. Acidic KI solution was passed through a column packed with 9.8 g of soil containing different particle fractions and the fraction volumes were collected periodically in a 25 ml volumetric flask. The pore volume of the soil was 3.8 ml. The results of the column process are shown in Fig. 6. The mercury concentration in the soil was reduced from 113.5 to 26.2 mg after 15 fraction volumes which indicates that 76% of

Table 1
Remediation of soil polluted by mercury with different extraction media

| Particle size (mm)	Mercury concentration (mg/g)				HCl pH 1.5	NaOH pH 12.8	EDTA pH 12.8	KI, pH 1.5[a]			
	Aqua regia[a]										
	1	2	3	Average				1	2	3	Average
4.75	0.53	0.70	0.60	0.61	0.09	0.15	0.26	1.40	1.42	1.43	1.42
0.59	10.30	10.70	10.50	10.50	0.95	1.15	1.50	10.80	10.35	10.85	10.67
0.25	16.20	16.30	16.25	16.25	4.35	4.30	5.85	20.48	19.96	20.24	20.23
0.149	30.00	30.60	30.30	30.30	5.60	9.80	15.50	34.40	34.95	34.68	34.68
0.105	47.20	47.00	47.10	47.10	10.05	12.00	18.90	47.20	46.80	47.00	47.00

[a] Tripricate extraction.
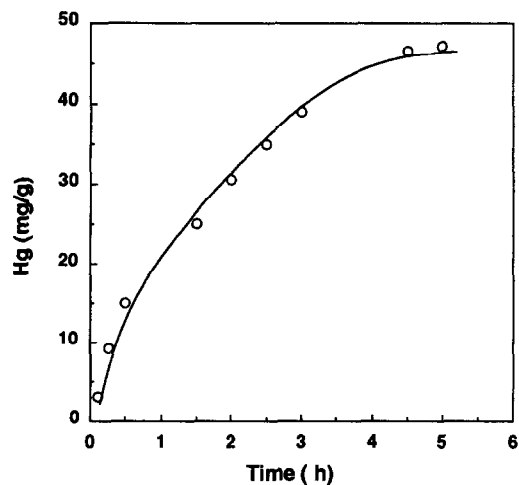
Fig. 5. Kinetic study of the extraction of mercury from the soil with acidic KI solution. pH, 1.5; soil, 1.0 g (0.105 mm); temperature, 20 °C.
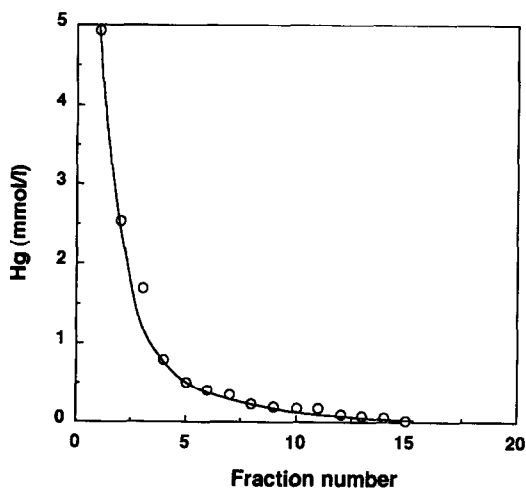

Fig. 6. Concentration of mercury in the leachate as a function of fraction number in the column process. Carrier solution, 100 mM KI + 50 mM HCl; soil, 9.8 g; flow rate, 25 ml/h.

mercury was removed. It was estimated that about 30 fractions were required to meet the standard of soil (0.5 mg/kg soil).

3.4. Treatment of leachate

The combined leachate from the above column process contained 1340 mg Hg/l of HgI_4^{2-}. The leachate diluted by $\frac{1}{25}$ or $\frac{1}{5}$ was treated with granular activated carbon in
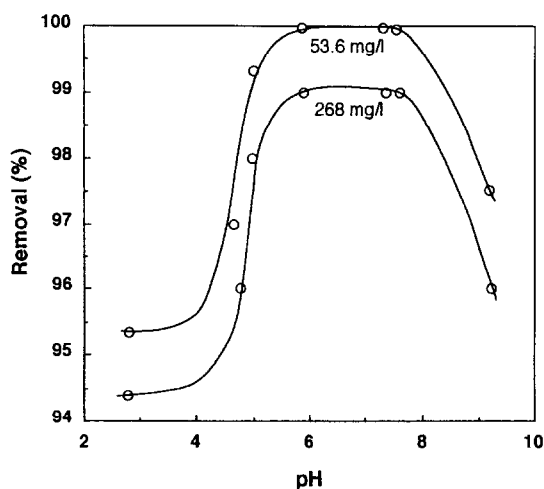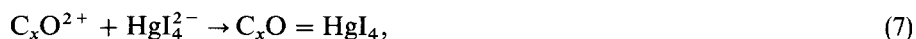
Fig. 7. Removal of mercury from leachate by granular activated carbon as a function of pH. Initial mercury concentration, 53.6 and 268 mg/l; activated carbon, 1.0 g; temperature, 20 °C.

the pH range of 2–10. The results are shown in Fig. 7. The mercury removal was found to be highest in the pH range of 6–7.5. At initial mercury concentrations of 53.6 and 268 mg/l the mercury removal was as high as 99.9% and 99.0%, respectively. The percentage removal slightly decreased at pH <5 and >8. It has been known that removal of mercury is enhanced when mercury is present in a complexed form [17, 18]. The functional oxidized groups present on the surface of carbon particles play a major role with a change in pH of the system in removing mercury complex from wastewater [19]. The mechanism involved at the activated carbon-water interface is given below:

$$C_xO + H_2O \rightarrow C_x^{2+} + 2OH^-, \tag{4}$$

$$C_xO_2 + H_2O \rightarrow C_xO^{2+} + 2OH^-. \tag{5}$$

In neutral to acidic pH range:

$$C_x^{2+} + HgI_4^{2-} \rightarrow C_x = HgI_4, \tag{6}$$

$$C_xO^{2+} + HgI_4^{2-} \rightarrow C_xO = HgI_4, \tag{7}$$

when the pH of the system turns from neutral to alkaline range, due to common ion effect (OH^- and HgI_4^{2-}) the percentage removal of mercury complex decreases. After mercury has been concentrated on the activated carbon from a large volume of soil, the used carbon can be disposed off by the conventional method such as landfill.

4. Conclusions

The acidic KI method was successfully applied for the remediation of mercury-polluted soil. A mixture of 100 mM KI + 50 mM HCl was effective to remove mercury as HgI_4^{2-} from the soil with higher efficiency than aqua regia. The mercury concentration in the soil was reduced to the permissible level of 0.5 mg/kg. Treatment with Na-EDTA attained much less mercury dissolution. The rate of mercury desorption followed a first order reaction with a rate constant $K_{ds} = 0.232\,h^{-1}$. After 15 fractions, 76% of mercury was removed in the column process. The leachate from the column process containing HgI_4^{2-} was treated with activated carbon and more than 99.9% of mercury was removed in the pH range of 5.9–7.5.

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