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High mercury leachate containing HgS_2^{2-} complex ion: Detoxifying solidification and high efficiency Hg extraction

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ABSTRACT

Clean and efficient treatment of high-mercury leachate produced from remediation of mercury-polluted soil has become a huge challenge for environmental scientists. In this work, cement solidification was firstly adopted to treat the high-concentration mercury leachate, which had high alkalinity. Different mercury concentrations, namely 3.120 mg/L Hg mercury leachate and 9.243 mg/L Hg mercury concentrated leachate, were separately solidified by Portland cement. The results indicated that simply using the cement can properly solidify both the leachates to meet the waste landfill standard, with liquid (mL)/solid (g) ratio (L/S ratio) of 4:10–6:10. In order to make full use of mercury in the leachates, a Hg extraction method was subsequently carried out under different experimental parameters, such as temperature and pH value. It was shown that the Hg extraction ratio could reach as high as 99.84% and almost all the mercury in the leachate could be transformed to HgS precipitate; moreover, the Hg concentration in the treated leachate was reduced from 3.120 to 0.005 mg/L at pH 2.98 and 30°C, which was much less than the limit of the national standard, indicating that the leachate had been completely cleaned and could be discharged freely. Hence, simple cement solidification renders high-mercury leachate nontoxic, and the Hg extraction method can successfully recover the Hg and enable the residual leachate to be discharged safely.

Introduction

Mercury and its compounds have attracted worldwide attention due to their high toxicity; moreover, mercury has also been designated as one of "the priority hazardous substances" by the Agency for Toxic Substances and Disease Registry (USA) (Wang et al., 2012). In particular, active mercury species such as methylmercury show extremely strong toxicity, and can easily destroy the central nervous systems of animals and humans (Holmes et al., 2009).

According to the Chinese survey bulletin of soil pollution in 2014, it was reported that mercury pollution in soil has already become serious and urgently needs to be remediated. Among the soil remediation methods, the chemical washing remediation method has the advantages of high efficiency, rapid effect and strong controllability, and is more and more widely used (Dermont et al., 2008). At present, potassium iodide (KI), ethylenediamine tetra acetic acid (EDTA), $Na_2S_2O_3$ and so on are often used as leaching agents for washing remediation of mercury-contaminated soil, mainly due to the fact that they

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react with mercury to form highly stable complex ions (Wasay et al., 1995; Klasson et al., 1997; Subirés-Muñoz et al., 2011; Beata and Katarzyna, 2012). In order to further improve the extraction ratio of mercury in contaminated soil and increase the removal ratio of active mercury, Na_2S solution has been used to extract high-Hg (168 mg/kg) contaminated soil. According to previous experimental results, about 72% of total Hg and 86% of the mobile Hg was removed after mercury-contaminated soil was leached by 0.7 mol/L Na_2S solution at 25°C for 4 hr with a liquid (mL)/solid (g) ratio (L/S ratio) of 10:1, and leachate whose Hg concentration was as high as 3.120 mg/L with high alkalinity was subsequently produced in this process (Lu et al., 2017).

Since the soil washing remediation method has been widely used, a large amount of leachate containing high mercury concentrations has been also simultaneously produced in the process of soil remediation and needs to be handled properly, to prevent secondary pollution problems (Singanan, 2015). Wasay et al. (1995) reported that a leachate containing 1340 mg/L of HgI_4^{2-} obtained from the column washing process was treated by granular activated carbon, and the mercury removal rate reached up to 99% when the pH was adjusted to around 7. Klasson et al. (1997) found that the filtrate obtained from storm sewer sediment leached by KI/I_2 (0.4 mol/L/0.2 mol/L) solution could be recycled effectively by adding steel wool, which could remove the solubilized mercury. Subirés-Muñoz et al. (2011) used iron powder to recycle the effluent obtained from mercury soil flushed using KI extraction solutions at low temperature (50°C), and the recovered leachate showed a similar leaching effect compared with fresh KI leaching solution. As mentioned above, only the treatment of KI leachate has been carried out, whereas the treatment of the other leachates has been rarely reported. Among them, leachate containing the HgS_2^{2-} complex ion is one of the most stable and intractable effluents, and its cleaning and effective treatment presents a big challenge.

At present, several methods including adsorption, ion-exchange, precipitation, membrane filtration and so on have been applied to treat wastewaters containing mercury (Melamed and Da, 2006; Jamali, 2012). Cyr et al. (2002) used F-400 granular activated carbon as the absorbent to treat pharmaceutical wastewater which contained 3.8 mg/L Hg, mainly in the form of thimerosal and Hg(II), and the mercury removal ratio could reach 99.8%. The US Environmental Protection Agency (EPA) treated the wastewater from an Air Pollution Control (APC) system with hydroxide precipitation and ferric chloride as the precipitant, and the mercury concentration was reduced from 219 to 0.48 μg/L (US EPA, 2007). Hollerman et al. (1999) utilized SIR-200, which is an ion exchange resin containing thiol functional groups, to dispose of wastewater from near the headwaters of the Upper East Fork Poplar Creek, and the mercury concentration was reduced from 1093 ng/L to less than 51 ng/L. Urgun-Demirtas et al. (2012) selected microfiltration and ultrafiltration membranes as tools to treat refinery wastewater under an operating pressure of ≥2.8 bar, and the Hg concentration was reduced from 5 to 6 ng/L to less than 1.3 ng/L, which met the water quality criterion for mercury.

As can be seen from the above-mentioned results, wastewater containing Hg^{2+} and organic mercury such as thimerosal or with low mercury content could be effectively handled, but otherwise the above methods could fail. The leachate used in this work contained high Hg content (more than 3 mg/L) which mainly existed in the form of HgS_2^{2-} and had high alkalinity, therefore a cleaner and safer treatment method was needed.

Cement solidification/stabilization technology has been widely used to treat inorganic solid wastes due to its remarkable immobilization properties, especially for solid wastes containing heavy metals such as Cd, Cr, Cu, Ni, Pb, Zn and so on (Shi and Roger, 2004; Paria and Yuet, 2006), but it could not be directly applied to remediating mercury-contaminated soil, as reported by Shi and Roger (2004). Mcwhinney et al. (1990) and Ortego et al. (1989) found that mercury ions solidified by Portland cement had the tendency to hydrolyze to form HgO, and mercury in the cement-solidified sludge still presented a strong volatilization potential. Hence Zhang et al. (2009) used CS_2-modified activated carbon to adsorb the mercury in polluted soil, and then solidified the soil using Portland cement, and Zhang and Bishop (2002) used an -SH functionalized zeolite to treat mercury-contaminated soil followed by immobilization with Portland cement; both the solidification methods achieved better results after the pretreatment. Therefore, it is worth determining whether solidifying high-concentration mercury leachate with high alkalinity using Portland cement can obtain a cement-cured product with good block-forming properties, high strength and non-toxicity. Owing to the high mercury concentration of the leachate, mercury recovery is of vital significance in reducing environmental pollution. Hence, Hg extraction was also carried out in this study.

In this work, two processes, cement solidification and mercury extraction were selected to treat the leachate. Firstly, leachates with different Hg concentrations were solidified by Portland cement and the leaching toxicity of the solidified cement was assessed. Then in order to reduce the environmental burden by recovery of mercury, the efficiency of Hg extraction from the leachate as a function of parameters such as temperature and pH was also investigated.

1. Experimental

1.1. Materials

The leachate as raw material was produced from our previous work, and the mercury concentration in the leachate was 3.120 mg/L (Lu et al., 2017). The concentrated leachate, which contained 9.243 mg/L Hg, was obtained by distilling the leachate. The reagents used in the experiment were analytically pure and the water used was deionized water.

1.2. Cement solidification process

In order to effectively immobilize the mercury in the leachate, the cement solidification method was adopted. Portland cement PC32.5 produced by Anhui Conch Cement Company Limited was used as the solidification agent, and its composition range and performance index of this type of cement both met national standard GB175-1999. In order to investigate the solidification effects for different concentrations of mercury leachate, two groups of samples, namely, leachate (3.120 mg/L Hg) and concentrated leachate (9.243 mg/L Hg) were prepared and different liquid (mL)/solid (g) ratios (L/S ratios, leachate/cement) (2:10, 4:10, 6:10, 8:10) were applied, then the safety of

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