Broader Perspectives

Extraction and Separation of Cd and Te from Cadmium Telluride Photovoltaic Manufacturing Scrap

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The extraction and separation of cadmium, tellurium, and copper from CdTe PV module scrap was investigated. Several leaching technologies were assessed and the extraction of CdTe from samples of PV modules was optimized for maximum efficiency and minimum cost. A dilute aqueous solution of hydrogen peroxide and sulfuric acid was sufficient to completely leach out cadmium and tellurium from these samples. The same method successfully removed cadmium and tellurium from actual manufacturing scrap; copper was partially extracted. Subsequently, cation-exchange resins were used to separate cadmium and copper from tellurium. Complete separation (i.e., 99·99%) of Cd from Te was accomplished. The estimated costs of these processes for 10 MW/year processing are about 2 cents per W. Copyright © 2006 John Wiley & Sons, Ltd.

1. INTRODUCTION

Photovoltaic modules at the end of their useful life have to be decommissioned and disposed of, or reused in some way. Environmental regulations impact the complexity and the cost of dealing with end-of life PV modules. For example, the inclusion of spent PV modules in the European directives 'waste from electric & electronics equipment (WEEE)' and 'restrictions on the use of certain hazardous substances (RoHS)', could impact crystalline-Si and CdTe PV modules that contain lead and cadmium compounds, respectively. US federal regulations and those in California may characterize the same ones, as well as spent CIGS PV modules, as 'hazardous waste'.[1] If spent modules and manufacturing scrap are characterized as hazardous, their handling and disposal would cost about 20 times more than that of non-hazardous waste.[2] Recycling the semi-metals from spent PV modules addresses this issue because the hazardous elements in a photovoltaic module typically are less than 0·1% of its mass. For example, the total weight of Cd in today's CdTe PV modules is about 0·05%; thus, its separation would clean a volume 2000 times larger.

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Our research aims to develop methods to completely separate and recover Cd from spent modules, but also focuses on the cost-effective recovery of Te so that it can be reused in PV manufacture.

2. BACKGROUND

Previous investigators tested four methods for treating CdTe PV module wastes: (1) Leaching with solutions of ferric chloride/hydrochloric acid[3]; (2) oxygen-pressure leaching using sulfuric acid[3]; (3) nitric-acid leaching [4–6]; and (4) leaching with sulfuric acid/hydrogen peroxide.[7–9] The first method failed to separate Cd from Fe (tellurium was not leached into solution). Oxygen-pressure leaching separated them to a significant degree, but the residues contained 4–7% of cadmium mixed with tellurium and sulfur. Further, due to the high pressure and temperature needed, this process is capital intensive, and thus, unattractive for low-cost recycling. Nitric-acid leaching recovered 96% of the tellurium, leaving Cd in solution. However, the subsequent recovery of Cd by electrolysis was based on artificially high Cd concentrations (e.g., 10 000 ppm instead of $\sim$1000 ppm obtained from leaching). Also, leaching with highly concentrated nitric acid requires elevated temperatures between 60 and 80°C that inevitably create nitric-acid fumes. Bohland *et al.*[7–9] investigated leaching using a solution of 3·6 N H_2SO_4 acid and 1–2%wt. H_2O_2. Cadmium telluride dissociated, and both metals were transported into the aqueous phase. The spent etchant was neutralized and the elements were precipitated into a sludge phase that was conditioned and then leached with concentrated potassium hydroxide. The filtrate was subjected to electrowinning to recover metallic tellurium from the cathode. The investigators succeeded in recovering 80% of Te at 99·7% purity. However, cadmium was not recovered but remained in the sludge with other metals, polymeric materials, and glass fines. Apparently, none of these methods were successful in completely recovering the metals from low-concentration leachate solutions.

Our method involves two steps: leaching in H_2SO_4/H_2O_2, followed by cation-exchange separation of Cd from Te. The first step is a modification (with measurable cost benefits) of Bohland *et al.*[7–9] sulfuric acid/hydrogen peroxide procedure. Other investigators have not evaluated this second step.

3. LEACHING OF METALS FROM MANUFACTURING SCRAP

3.1. Experiments: materials and methods

In the leaching experiments, we used samples weighting 300 g which were cut from commercial CdTe PV modules, and also fragmented (by a hammer mill) manufacturing scrap from First Solar LLC, Toledo, OH, USA. The composition of the metals in the PV module samples (w/o connectors), was approximately 0·055 Cd wt.%; 0·062% Te wt.%; and 0·010 Cu wt.%. The leaching experiments were carried out at ambient temperature in a tumbling machine. We assessed the efficiency of two oxidative-leaching procedures in extracting cadmium and tellurium from PV glass; hydrogen peroxide leaching in sulfuric acid, and hydrogen peroxide leaching in hydrochloric acid. The strength of the acids ranged from 1·0 to 4·0 M. Kinetic studies of leaching were conducted in constant solid-to-liquid ratios at ambient temperature. The glass–solution mixture was sampled at regular intervals and the samples then were filtered through syringe filters with pore sizes of 0·20–0·70 μm. The filtrate was diluted with 5% HNO_3 and the solutions were analyzed for Te, Cd, and Cu using a Varian Liberty 100 inductively coupled plasma (ICP) emission spectrometer. The uncertainty of the ICP analysis was determined with frequent calibrations to be $\pm$ 2·0% for Cd and Cu and $\pm$ 3% for Te. The detection limit of ICP for Cd is 1·5 μg/L, for Cu is 2·0 μg/L, and for Te is 27 μg/L.

3.2. Results

3.2.1. Selection of leaching acid

Our experiments showed that, at the same strength, a sulfuric-acid solution extracted more cadmium and tellurium than hydrochloric acid. Figure 1(a) shows the leached mass of cadmium as the percentage of the mass of
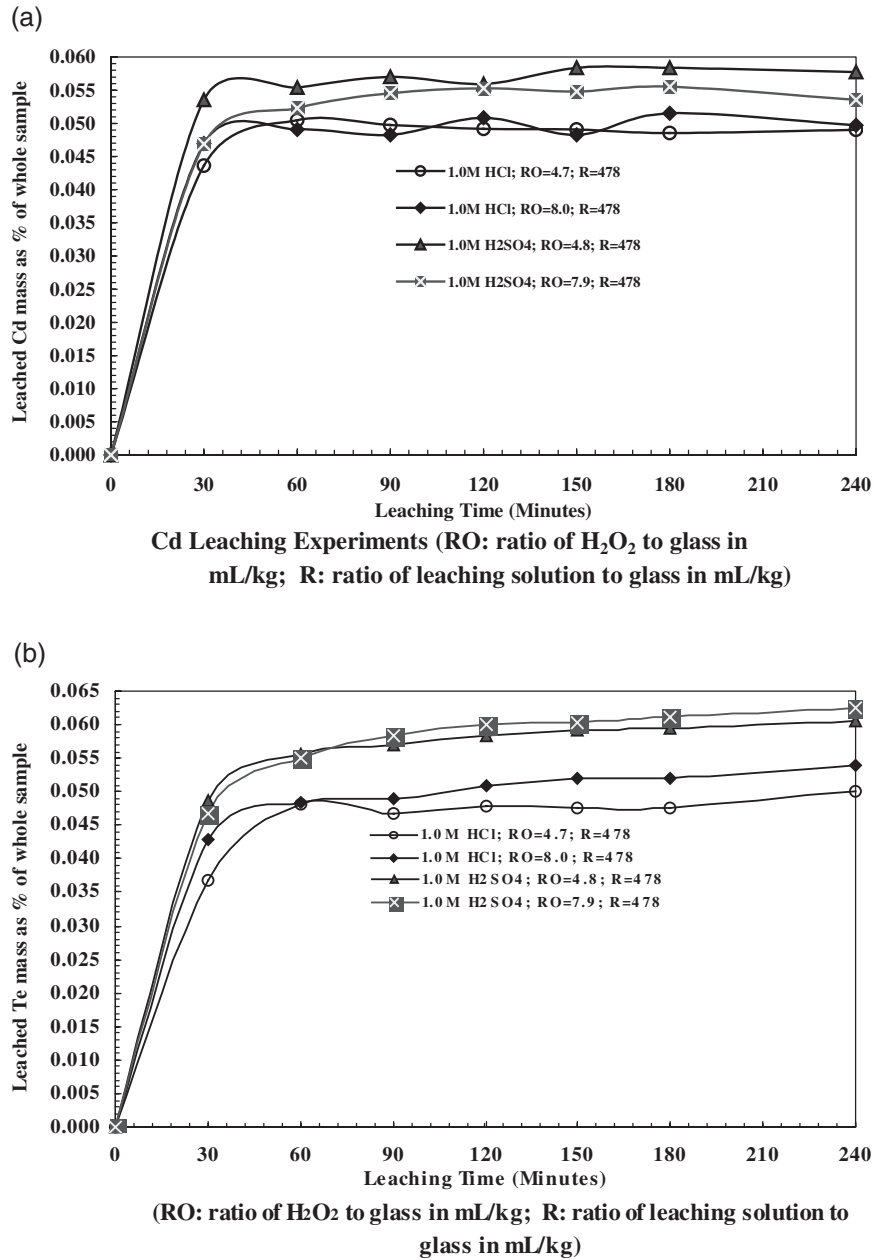
(a)

Cd Leaching Experiments (RO: ratio of H$_2$O$_2$ to glass in mL/kg; R: ratio of leaching solution to glass in mL/kg)

(b)

(RO: ratio of H$_2$O$_2$ to glass in mL/kg; R: ratio of leaching solution to glass in mL/kg)

Figure 1. (a) Comparison of the efficiency of leaching Cd with H$_2$SO$_4$/H$_2$O$_2$ and HCl/H$_2$O$_2$ solutions. (b) Comparison of the efficiency of leaching Te with H$_2$SO$_4$/H$_2$O$_2$ and HCl/H$_2$O$_2$ solutions

the sample (mainly glass), and Figure 1(b) shows the same for tellurium. Based on these results, sulfuric acid was chosen as the acid-leaching agent and further studies were limited to the H$_2$SO$_4$/H$_2$O$_2$ system. The effect of the following parameters then was investigated: the strength of the acid, the ratio of hydrogen peroxide volume to the weight of the PV module (mainly glass), and the ratio of the volume of the leaching solution to the weight of the PV modules.

(a)

(RO: ratio of H₂O₂ to glass in mL/kg; R: ratio of leaching solution
to glass in mL/kg)

(b)

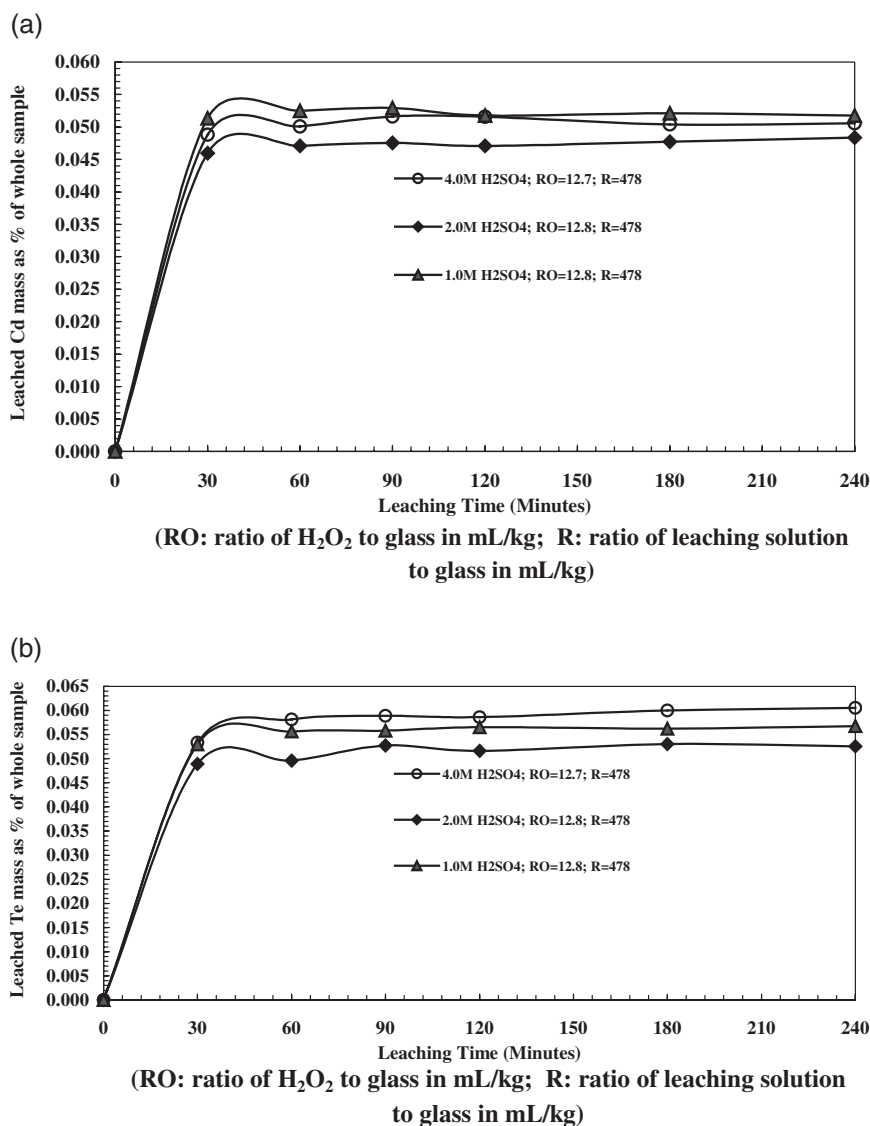(RO: ratio of H₂O₂ to glass in mL/kg; R: ratio of leaching solution
to glass in mL/kg)

Figure 2. (a) Effects of acid strength on the efficiency of leaching Cd. (b) Effects of acid strength on the efficiency of leaching Te

3.2.2. Effects of the acid's strength

The PV modules were leached at ambient temperature with concentrations of sulfuric acid varying from 1·0 to 4·0 M, keeping a liquid/solid ratio of ∼478 ml/kg-glass. With the hydrogen peroxide ratio, Ro, fixed at ∼12·8 ml/kg-glass, a 1 M sulfuric acid solution was equally effective as a 4 M sulfuric-acid solution in removing cadmium (Figure 2a), and was almost as effective as the 4 M solution for extracting tellurium (Figure 2b). Using the lower concentration solutions results in lower costs for both the acid and the neutralizing agents.

3.2.3. Effects of the amount of hydrogen peroxide

Hydrogen peroxide, used in the leaching process to oxidize tellurium, played an important role in the leaching of CdTe. In accordance with our quest for minimizing the cost of chemicals, we determined the minimum amount of hydrogen peroxide in dilute (1·0 M) solutions of sulfuric acid, required to obtain a complete extraction of cadmium and tellurium. This occurred in a 4·8 ml solution per kg of waste sample. Keeping the H₂O₂

(a)

**(RO: ratio of H$_2$O$_2$ to glass in mL/kg; R: ratio of leaching solution
to glass in mL/kg)**

(b)

**(RO: ratio of H$_2$O$_2$ to glass in mL/kg; R: ratio of leaching solution
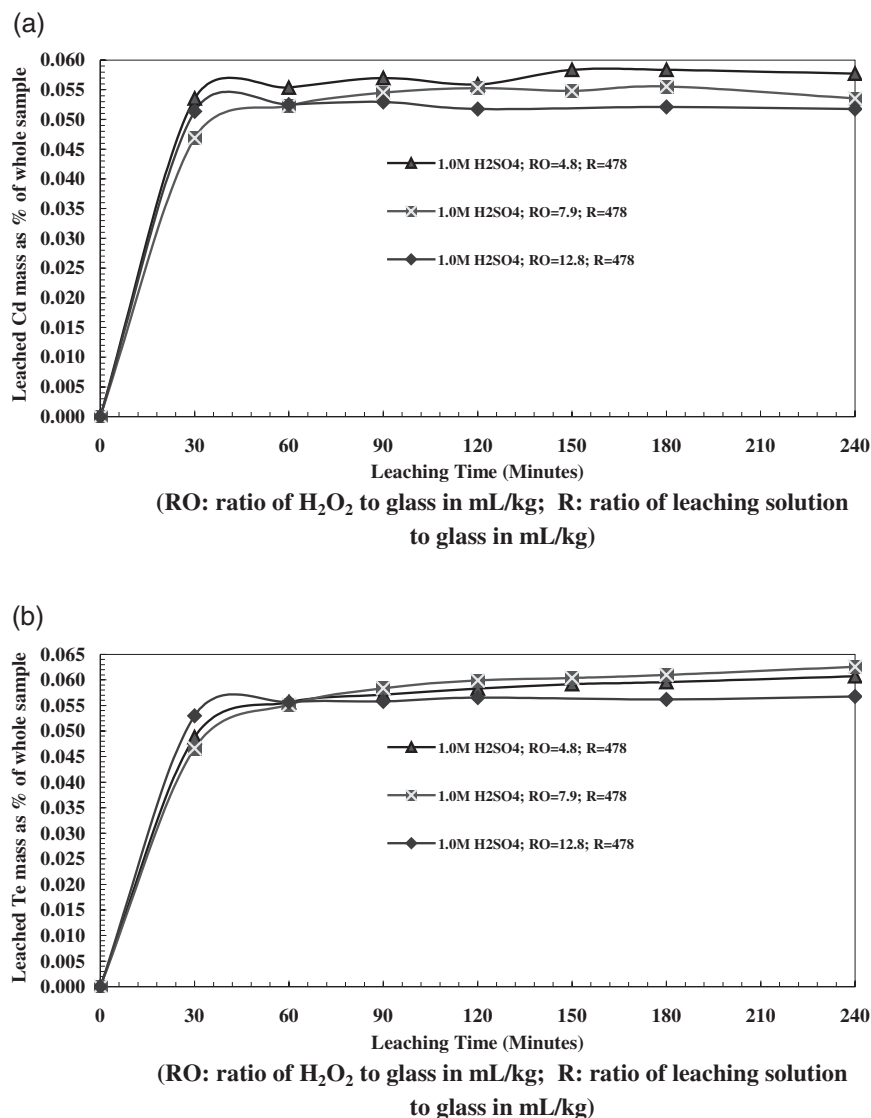to glass in mL/kg)**

Figure 3. (a) Effects of different concentrations of hydrogen peroxide on the efficiency of leaching Cd. (b) Effects of
different concentrations of hydrogen peroxide on the efficiency of dissolving Te

amount at a minimum improved the efficiency of cadmium extraction, especially at leaching times longer than
120 min. The leaching efficiency of solutions with different concentrations of hydrogen peroxide are shown in
Figure 3(a and b) as a function of time.

4. SEPARATION OF METALS BY ION EXCHANGE

In the first phase of the separation testing, we used analog solutions containing only cadmium, tellurium, and
copper at the concentrations obtained from the leaching experiments. Through a series of batch and column
experiments, we selected two types of ion-exchange resins based on their selectivity, pH range, and cost.
The details of the controlled experiments, and the chemical equilibria and chemical kinetics of the separation
processes are described in detail elsewhere.[10] The column studies culminated to 99·998% retention of cadmium
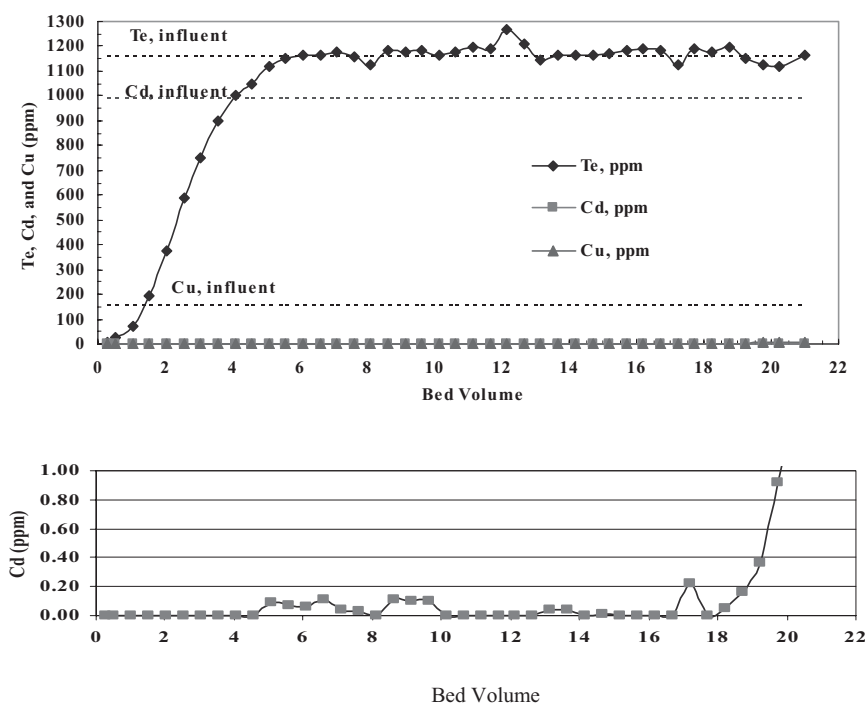
Figure 4. Removal of Cd from Cd- and Te-containing solution using Resin A. Two columns in series (resin volume: 100 mL each). Influent concentrations: Te: 1150 ppm; Cd: 989 ppm. Solution flow rate: 750 ml/h. upper plot: all elements; lower plot: Cd detail)

in the column and an essentially cadmium-free effluent stream (Figure 4). Tellurium broke through the column quickly, and the column took approximately 800 ml (4 bed volumes) before becoming completed exhausted with tellurium. On the other hand, the cadmium was adsorbed for substantially longer, not achieving breakthrough until 19 bed volumes.

The cadmium concentrations in the first 3400 ml (16 BV) of the effluent solution fractions were often below the detection limit of ICP (i.e., <1·5 μg/L). Throughout the range of 0–3800 ml, the highest measured Cd concentration was 0·5 mg/kg (ppm), and the average concentration was 0·04 mg/kg (ppm); in the range 0–3300 ml, the average concentration was 0·02 mg/kg, corresponding to a 99·998% removal of Cd. Overall, the solution fractions collected before breakthrough were basically free of cadmium, indicating that the subsequent recovery of pure tellurium is feasible.

Figures 5 and 6 show the separation efficiencies attained with solutions obtained from leaching actual manufacturing waste. The later contained significant amounts of Na, Ca, Cu, Al, and trace amounts of Sn and Cr. The separation efficiencies in these solutions were, as previously, 99·99% or higher, but the capacities of the columns (i.e., bed volumes) were about 50% lower than in the separation of the analog solutions.

The cost of leaching and ion-exchange separations was estimated to be about 2 cents per W ($105/tonne waste) for a 10 MW/yr recycling facility processing about 700 PV modules a day (8·3 tonne/day) and recovering 8·2 tonne glass, 5·3 kg of Te and 4·5 kg of Cd per day. This cost estimate includes materials and capital costs but it does not include labor.

Subsequently, cadmium was eluted from the ion-exchange columns and was recovered by electrowinning, whereas tellurium was recovered by precipitation using sodium carbonate and sodium sulfide. Further work on the purification of these products is in progress.
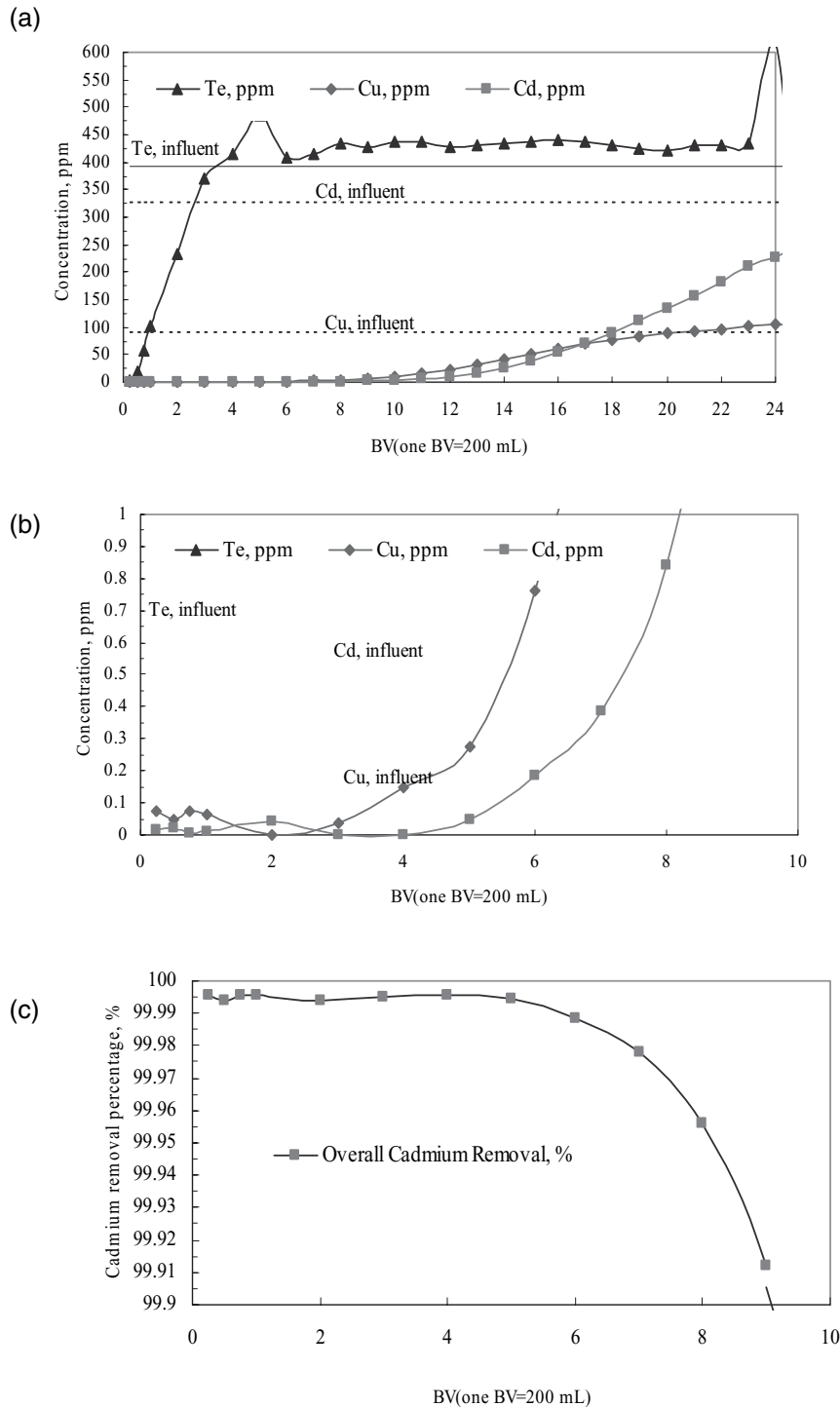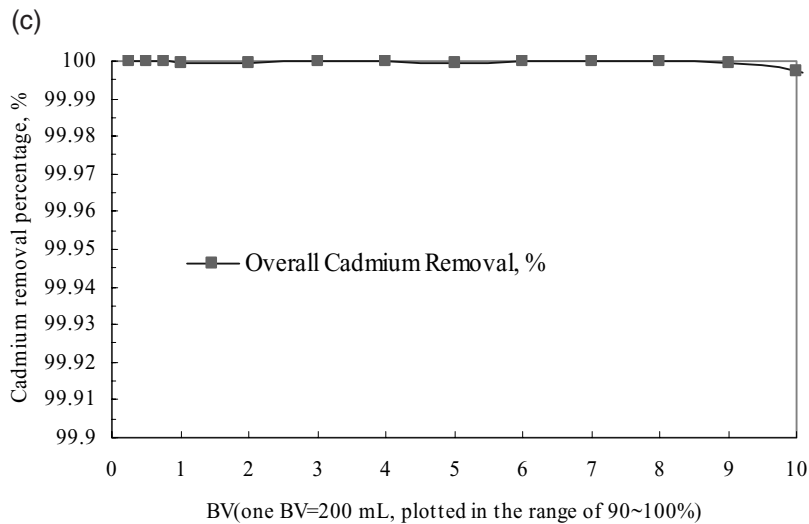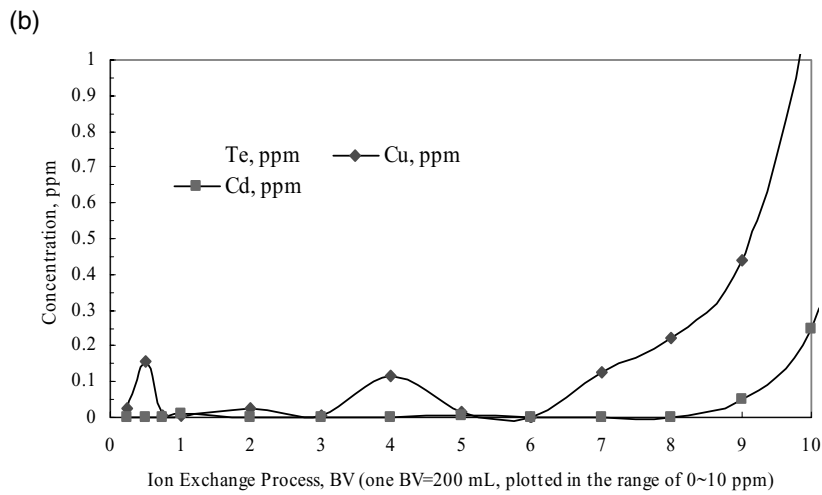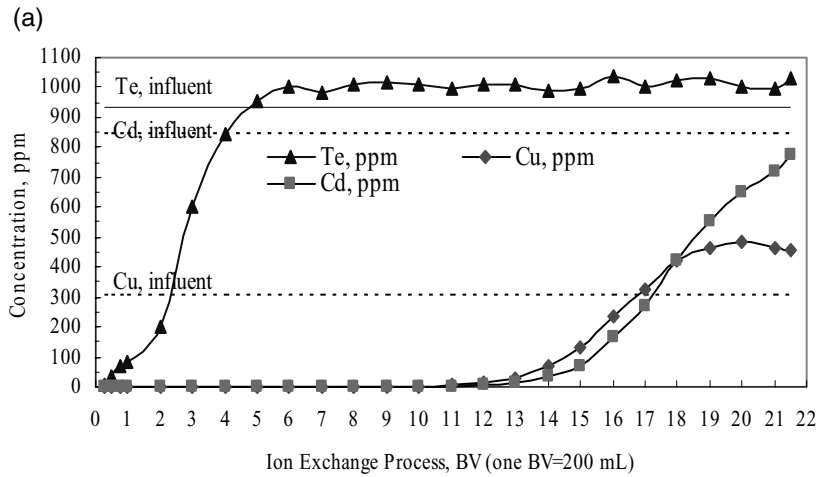
(a)

(b)

(c)

Figure 5. (a) Composition of column effluent stream (Te, Cd, and Cu). (b) Concentrations of Cd and Cu in same; (c) corresponding cadmium separation. Input is leachate from actual manufacturing waste (initial concentrations: Te: 392 ppm, Cd: 324 ppm, Cu: 92 ppm Cr: ∼1 ppm, Na: 157 ppm, Al: 23 ppm, Sn: 10 ppm, Ca: 182 ppm, pH: 0·42)

Figure 6. (a) Composition of column effluent stream (Te, Cd, and Cu). (b) Concentrations of Cd and Cu in same; (c) corresponding cadmium separation. Input is leachate from actual manufacturing waste (initial concentrations: Te: 933 ppm, Cd: 843 ppm, Cu: 302 ppm, Na: 348 ppm, Al: 53 ppm, Ca: 103 ppm, pH: 0·444–0·5)

5. CONCLUSION

Different leaching solutions were evaluated and leaching under standard ambient conditions with dilute sulfuric acid/hydrogen peroxide solution was found to be equal to, or better than more costly (i.e., concentrated) solutions and more expensive (i.e., high T and P) systems. The optimized acid strength was 1.0 M of H_2SO_4 with a liquid-to-solid ratio of 476 ml/kg, and ratio of H_2O_2 to glass of 4.8.

The feasibility of removing and separating cadmium from tellurium in acidic media was studied using ion-exchange resins. A separation of 99·99% of cadmium was accomplished from actual manufacturing waste at an estimated capital and materials cost of about 2 cents per W for a 10 MW/year recycling facility.

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