Bioleaching of spent Ni–Cd batteries by continuous flow system: Effect of hydraulic retention time and process load

Ling Zhao, Dong Yang, Nan-Wen Zhu*

School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

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ABSTRACT

Spent Ni–Cd batteries bring a severe environmental problem that needs to be solved urgently. A novel continuous flow two-step leaching system based on bioleaching was introduced to dissolve heavy metals in batteries. It consists of an acidifying reactor which was used to culture indigenous thiobacilli and a leaching reactor which was used to leach metals from spent batteries. The indigenous acidophilic thiobacilli in sewage sludge was used as the microorganisms and the sludge itself as culture medium. Bioleaching tests at different hydraulic retention time (HRT) and process load in the leaching reactor were performed. The results showed that the longer the HRT (1, 3, 6, 9 and 15 days) was, the more time required to achieve the complete leaching of Ni, Cd and Co. The maximum dissolution of cadmium and cobalt was achieved at higher pH values (3.0–4.5) while the leaching of nickel hydroxide and nickel in metallic form (Ni^0) were obtained separately in different acidity (pH 2.5–3.5). It cost about 25, 30 and more than 40 days to remove all of the three heavy metals with the process load of two, four and eight Ni–Cd batteries under the conditions that the ingoing bio-sulphuric acid was $1\,L\,d^{-1}$ and HRT was 3 days.

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1. Introduction

Nowadays end-of-life batteries especially the spent nickel–cadmium (Ni–Cd) batteries bring more and more environmental problems due to the simultaneous presence of the valuable metals nickel, cobalt and the extremely toxic metal cadmium in high concentration constituting the electrodes. The traditional techniques to recover these batteries are mainly pyrometallurgical and hydrometallurgical processes which have some limitations [1,2]. Pyrometallurgical processes are not easy to control, not flexible and high energy-consumers. Hydrometallurgical techniques, similar to those in the mining industry, have proven to be quite expensive or inefficient [3,4]. Moreover, the two methods are proven to bring secondary pollution [5,6].

A novel process for the recovery of metals from spent Ni–Cd batteries was bioleaching, which was a traditional method in the mining industry [7]. In recent years, bioleaching was also proved to be a possible way to remove heavy metals from metals contaminated materials such as anaerobically digested sewage sludge, contaminated river sediment, and incinerator fly ash [8]. In this method, the indigenous acidophilic thiobacilli in sewage sludge can grow and produce bio-sulphuric acid using elemental sulphur or ferrous sulphate as the energy source with oxygen as the terminal electron acceptor and carbon dioxide as the sole

carbon source. The pH of the sludge decreased to under 1.0 and the oxidation–reduction potential (ORP) increased to 370–400 mV, which resulted in the dissolution of the metallic scraps of the spent batteries. Then the metals containing leachate was further recovered by different methods such as re-precipitation, cementation, solvent extraction or electrowinning, etc. [9].

The bioleaching of the batteries was achieved in a continuous flow two-step leaching system which consisted of an acidifying reactor and a leaching reactor. The acidifying reactor was used to culture indigenous thiobacilli in sewage sludge and the leaching reactor was used to leach metals from spent batteries [10].

The hydraulic retention time (HRT) of the bio-sulphuric acid in the leaching reactor is an important parameter represents the time that the medium being in contact with the battery material. If the HRT was too short, the electrode materials of batteries cannot be dissolved sufficiently. While if it was too long, bigger volume of leaching reactor was needed and the pH decreased slowly. In this work, the leaching efficiency and leaching behavior of the three heavy metals Ni, Cd and Co of battery in different HRT with a given process load and different process load (disposal capacity) in a given HRT were investigated.

2. Experimental procedure

2.1. Continuous flow two-step leaching system

To achieve the continuous production of acid and leaching of batteries, a continuous flow two-step leaching system consisting

* Corresponding author. Tel.: +86 21 34203732; fax: +86 21 34203732.
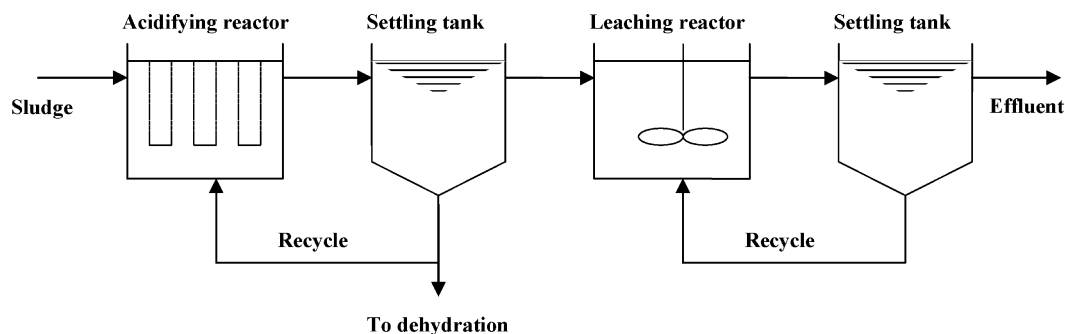*E-mail address:* nwzhu@sina.com (N.-W. Zhu).

Fig. 1. Diagram of the continuous flow two-step leaching system.

of an acidifying reactor and a leaching reactor with two settling tanks following them respectively was adopted (Fig. 1). The acidifying reactor was used to produce bio-sulphuric acid through the oxidation of elemental sulphur by indigenous thiobacilli in sewage sludge. The fresh sludge was continuously fed into the acidifying reactor, which operated at a fixed level with overflow going to the settling tank. In the first settling tank, part of the thickened sludge was recycled to the acidifying reactor to maintain the concentration of the active acidophilic thiobacilli. The supernatant from the settling tank was conducted into the leaching reactor which contained anodic and cathodic materials obtained from Ni–Cd batteries. The effluent containing high concentration of heavy metals was collected for further recovering of Ni, Cd and Co.

2.2. Sewage sludge and acclimation

The sewage sludge used was obtained from the primary sludge clarifier and secondary activated sludge unit from the Minhang wastewater treatment plant in Shanghai, China. A mixture of primary (50%, v/v) and secondary (50%, v/v) sludge was used in the experiments. The results of the mixed sludge analysis are presented in Table 1. The sludge was kept aerated before utilization.

The bacteria in the acidifying reactor were the indigenous acidophilic thiobacilli in sewage sludge and the culture was the sludge itself. So the start-up of the process required the acclimation of acidophilic microflora. A sample of 400 mL sludge was transferred into a 1000-mL Erlenmeyer flask with 1% (w/v) of powdered elemental sulphur added and incubated at 30 °C, 200 rpm. It took 12 days that the pH value of sludge dropped under 2.0, which was the initial acclimation. Then 80 mL of this acidified sludge was mixed with another 320 mL of the sludge sample, 1% (w/v) sulphur as the energy, and incubated under the same conditions. The procedure was repeated 3–5 times. The rate of pH reduction to 2.0 was maximized and the indigenous sulphur-oxidizing bacteria were assumed to be adapted [11].

2.3. Operation of the systems at different hydraulic retention time

Before the operation of the system, 5% (v/v) of the acclimated bacteria was inoculated to fresh sewage sludge with 1% (w/v) of elemental sulphur added in. Then the sludge was transferred into the acidifying reactor, in which air was supplied with an air diffuser to ensure enough CO_2 and high level dissolved oxygen concentration

(DO > 2.0 mg L^{-1}). The aeration rate was 0.18–0.2 vvm (volume of air: volume of sludge in reactor: min) and the volume percent of CO_2 in air is 0.036%, which is appropriate for the growth of thiobacilli [12]. Keep the agitation 100 rpm until the pH of the mixture reduced to lower than 2.0, the system run.

The fresh sludge was continuously fed to the acidifying reactor by about 1 L d^{-1}. The valid volume of the acidifying reactor was 4 L. In the first settling tank, part of the thickened sludge (about 20%) was recycled to the acidifying reactor. The supernatant transferred into the leaching reactor was controlled at 0.6 L d^{-1} by a pump.

Five systems operated synchronously with the same parameters except the volumes of the leaching reactor, which were 0.6, 1.8, 3.6, 5.4 and 9 L respectively. The corresponding hydraulic retention times of the leaching reactor were 1, 3, 6, 9, 15 days. The ambient temperature was 27–30 °C. The agitation in the leaching reactor was 100 rpm to keep the complete mix.

Two spent nickel–cadmium batteries with the same brand (KR6 SIZE AA 600 mAh from Shanghai Pinxin industry) were treated in every system. These batteries were physically separated in their different parts: anode, cathode, steel, separators, and current collectors. On an average, the weight of Ni–Cd battery parts corresponds to anode 35.4%, cathode 26.2%, and steel, separators, and current collectors 38.4% of the total [13]. The total weight of each sample was 10.77 g × 2 including the anode, cathode and electrolyte as well as a small quantity of additive material.

2.4. Operation of the systems with different process load

Three systems operated synchronously with the same parameters except the amount of the treated materials which were two, four and eight batteries. The supernatant transferred into the leaching reactor was controlled at 1 L d^{-1}. The valid volume of the leaching reactor was 3 L. The other conditions were the same with the above.

2.5. Analysis method

During the leaching process, the heavy metals (Ni, Cd and Co) of the effluent solution were measured at 3–5-day interval by plasma emission spectrometry (ICP-AES, Iris Advantage 1000). The pH in the two main reactors was determined each day using a pH meter (Mettler Toledo 320-S). Phase composition of the disaggregated electrode materials was identified by X-ray power diffraction, the

Table 1
Characteristics of the tested sludge

pH	Solid content (g L^{-1})	Volatile solid content (g L^{-1})	Metals (mg L^{-1})							
			Cd	Ni	Co	Fe	Cu	Cr	Zn	Pb
6.41	28.28	15.4	0.14	0.78	0.01	184.8	2.88	1.10	21.5	0.21

patterns being obtained with a Rigaku Geiserflex D/MAX-RC diffractometer (Cu Kα radiation), equipped with a curved crystal graphite monochromator and the following conditions, 50 kV, 80 mA and a scan speed $8°$ $(2\theta)\,min^{-1}$. The surface morphology of the anode and cathode of spent Ni–Cd batteries was analyzed by scanning electron microscopy (SEM, JSM-7401F).

3. Results and discussion

3.1. Chemical composition and morphological characterization of electrode materials before and after attack by bio-sulphuric acid

The SEM photographs of the cathodic and anodic configuration of spent Ni–Cd battery before and after treatment are shown in Fig. 2(a–c). Because the anode material presents powdery so the SEM photographs and XRD after treatment cannot be obtained. In Fig. 2(a) spherical crystalloid particles are nickel hydroxide, the main components of the dark cathodic material [14]. While the light-grey anodic material shows nubby crystal structure, as in Fig. 2(c). Both show a relative homogeneous size and shape with a small quantity of adulterant. In Fig. 2(b), it appears that the homogeneous structure was destroyed by the bio-sulphuric acid. Perhaps the 'destroy' in crystal structure made the oxidation and dissolution of metallic phases much easier [15].

Fig. 3(a and c) shows the presence of diffraction lines corresponding to metallic nickel (Ni^0), nickel hydroxide and γ-NiOOH in the cathode, and metallic cadmium (Cd^0), cadmium hydroxide in the anode. The $Ni(OH)_2$ and $Cd(OH)_2$ identified correspond to the active electrode phases of the battery in discharged conditions. γ-NiOOH and Cd^0 were the phases present in charged conditions. The electrolyte KOH was also detected. No evidence of cobalt was found by XRD. Probably because it was co-precipitated as solid solution, being part of the $Ni(OH)_2$ structure or the cobalt concentration is too small to be detected by XRD [16]. Fig. 3(b) shows that after 20 days leaching, only metallic Ni presented in the solid residue of the cathode.

3.2. Metals dissolution at different hydraulic retention time

The dissolution mechanisms of the electrodes in the leaching reactor could be described in terms of both an indirect attack via bio-sulphuric acid and a direct bacterial attack on metal materials due to a certain amount of microorganisms existed in the supernatant [17]. In direct solubilization, sulphur-oxidizing bacteria attack the metallic materials directly through enzymatic actions, which is a possible mechanism that enhances the oxidation of metallic metals that are difficult to be solubilized. In indirect leaching, bio-sulphuric acid produced by sulphur-oxidizing bacteria solubilizes the dissoluble metals [18]. Generally, the acid
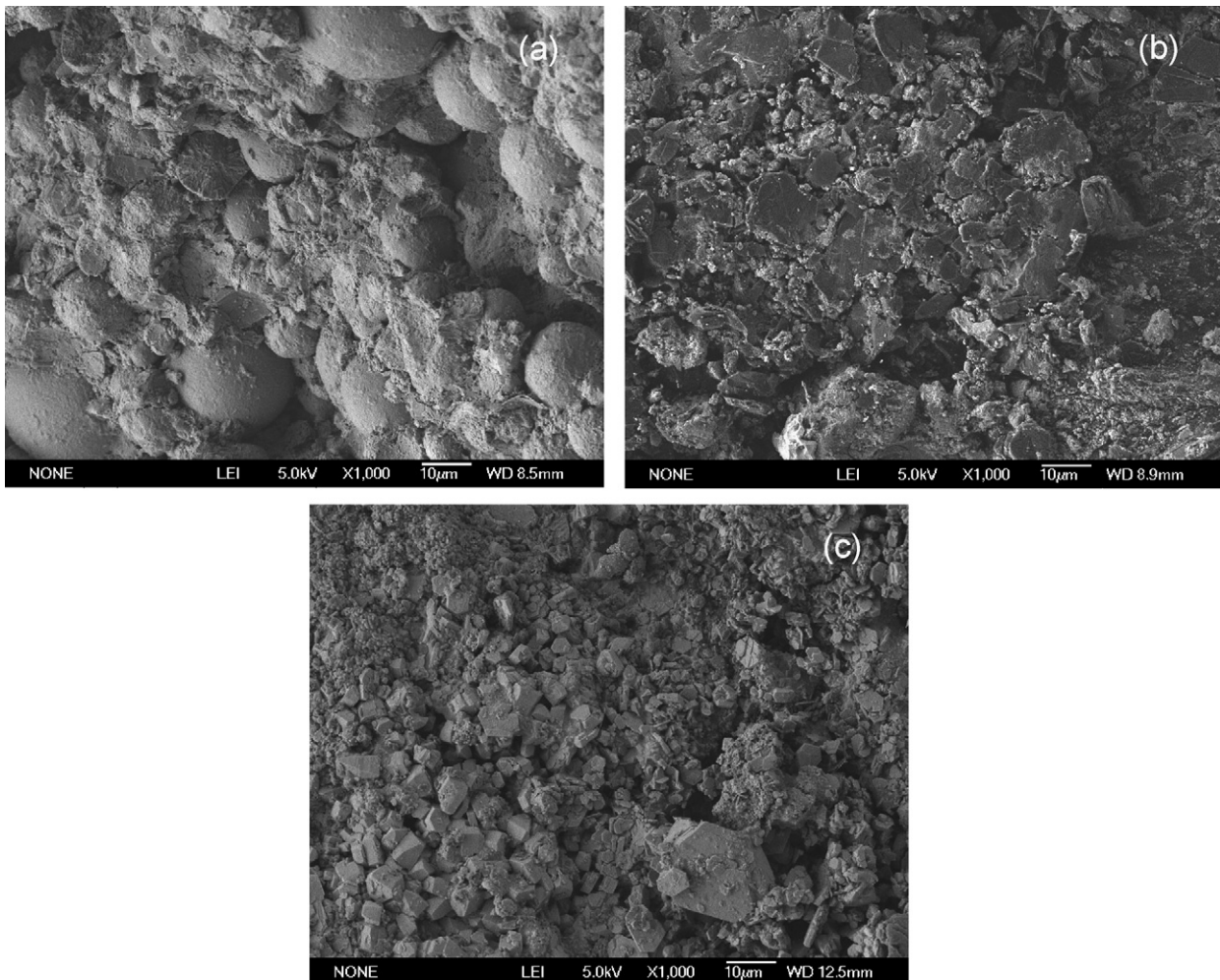

Fig. 2. Typical scanning electron microscopy for the initial cathode material of spent Ni–Cd battery (a), cathode solid residue after 20 days bioleaching (b) and the initial anode material (c) (1000×).
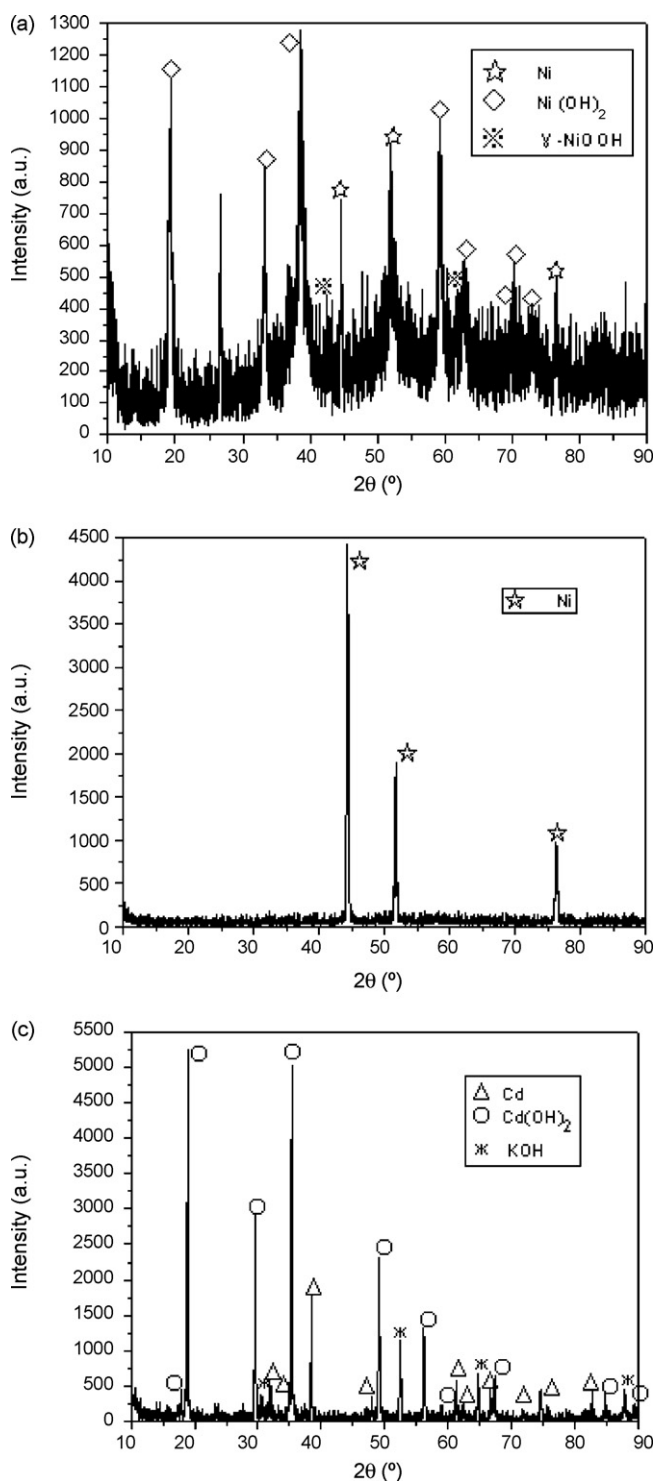
Fig. 3. XRD patterns of the initial cathode material of spent Ni–Cd battery (a), cathode solid residue after 20 days bioleaching (b) and the initial anode material (c).

Fig. 4. Change of nickel (a), cadmium (b) and cobalt (c) concentration in the overflow during bioleaching process at different HRT.

dissolution and neutralization reactions are very fast, but the oxidation–reduction reaction is slow. If there was only acid dissolution or neutralization reaction in the dissolution process, it would not need too much time to get the maximum dissolution ratio [19].

The results of the leaching experiments at different HRT are presented in Fig. 4(a–c). When the HRT was 1 day, the complete
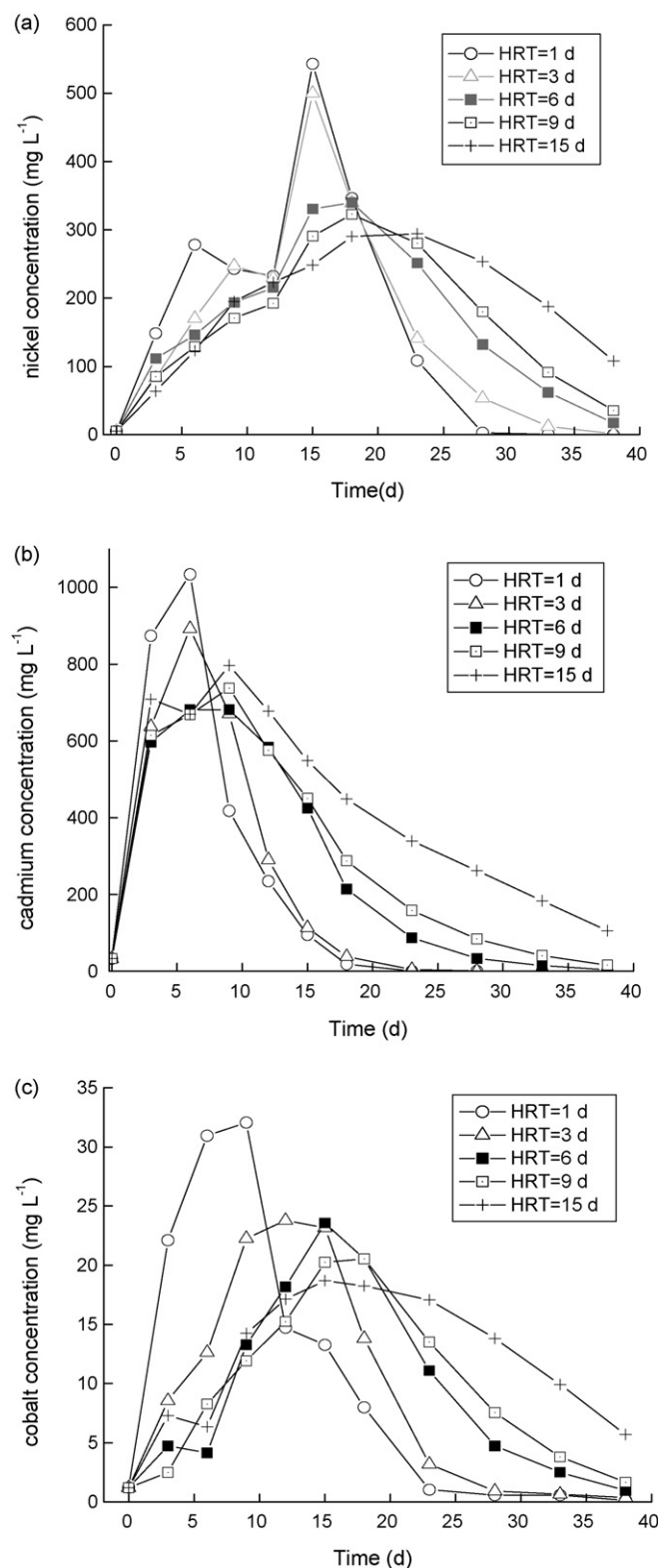
leaching (the concentration of the heavy metals in the overflow from the leaching reactor approached that in its inflow) of Ni, Cd and Co cost about 25, 18 and 30 days. When the HRT was 15 days, it took more than 40 days to finish the leaching. The longer the HRT (1, 3, 6, 9, and 15 days) was, the more time it needed to finish the
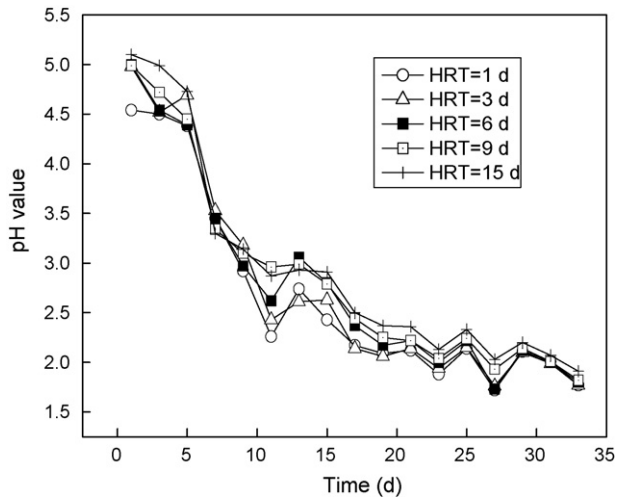
Fig. 5. Change of pH value in the leaching reactor with time at different HRT.

leaching. It was found that under the condition of the HRT was 1 or 3 days, the maximum concentration of Ni, Cd and Co observed occurred on the about 15th, 5th and 8th day respectively. With the prolonging of the HRT, the maximum dissolution time was delayed. The results of main metals dissolution were summarized in Table 2.

The changes of pH with time in the leaching reactor are presented in Fig. 5. The relationship of pH and metals leaching can be analyzed by contrast Figs. 4 and 5. Due to the effect of alkaline electrolyte in the scraps of the spent Ni–Cd batteries, the initial pH in leaching reactor was 4.5–5.0 and it decreased with the continuous production and supply of bio-sulphuric acid. In the first 10 days the drop of pH was relatively faster and then it became slow. It was presented in Fig. 5 that the pH in the leaching reactors at different HRT was of little difference. Obviously cadmium and cobalt can be leached mostly at pH of 3.0–4.5 while the completely dissolution of nickel can be achieved at pH about 2.5.

3.3. Metals dissolution at different process load

Fig. 6(a–c) presents the change of nickel, cadmium and cobalt concentration in the overflow during bioleaching process at different process load. It can be seen that metals Ni, Cd and Co can be completely dissolved in all loadings if enough time is given. Under the conditions of this experiment, it cost about 25, 30 and more than 40 days to remove all of the three heavy metals with the process load of two, four and eight batteries respectively. The maximum dissolution time of heavy metals delayed with the increasing load capacity. But the time used was not proportionate with the increasing of the capacity. Finally, 25, 30 and 40 L heavy metal solution were obtained (Table 2).

As for the heavy metal nickel, the maximum dissolution time was 15, 20 and 25 days respectively with the three process loads. The relevant pH at that time was about 2.5, 3.0 and 4.2 (Fig. 7) and the nickel concentration was about 500, 2200 and 3300 mg L^{-1} (Fig. 6(a)). So more concentrated metals solution can be obtained with higher load even though the pH was relatively high during the leaching process. Concerning cadmium and cobalt species in the metallic and hydroxide form, the maximum dissolution achieved at the pH 4.0–4.5 for cadmium and 2.5–3.0 for cobalt in every process load.

Fig. 7 is the change of pH value in the leaching reactor with time at different process load. The initial pH value was 5.37, 8.46 and 9.28 respectively with the process load of two, four and eight spent Ni–Cd batteries due to the influence of alkaline electrolyte (KOH).
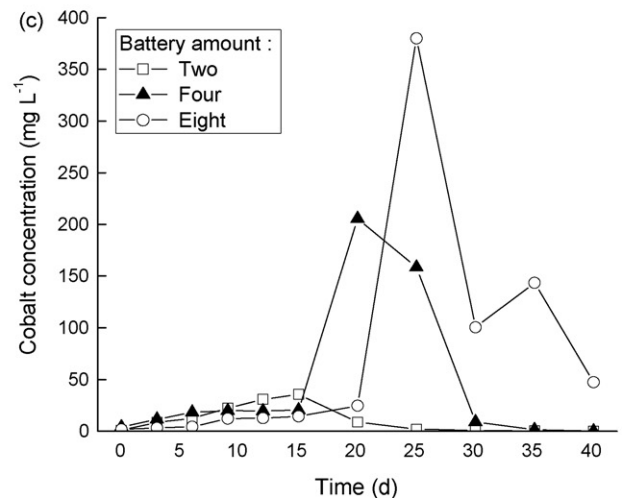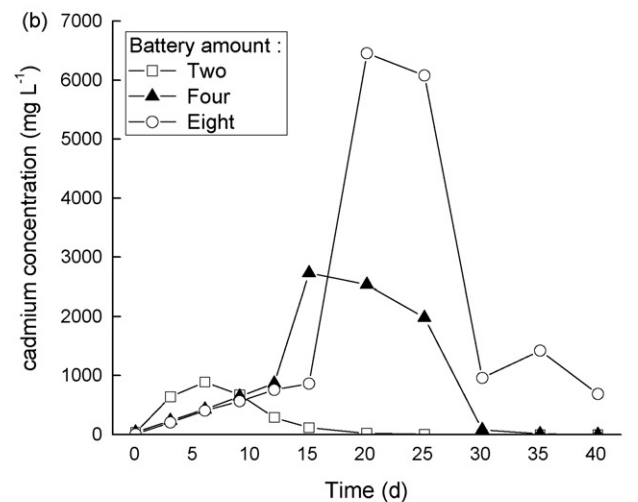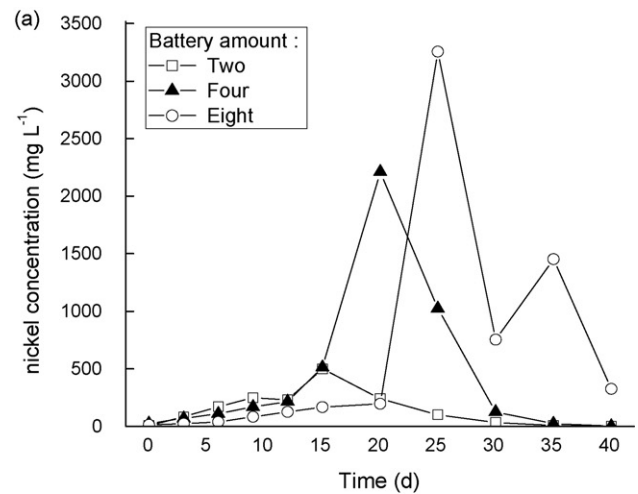

Fig. 6. Change of nickel (a), cadmium (b) and cobalt (c) concentration in the overflow during bioleaching process at different process load.

So the initial heavy metals concentration of the effluent was lower with the higher process load [20]. With the continuous supply of fresh bio-sulphuric acid, the pH decreased.

From the above results, pH was an essential factor that influences the metals dissolution. Most of the metals dissolution needed

Table 2
Summary of the results of total metals dissolution with different HRT and process load

HRT (d) of the leaching reactor	Metals concentration of collected leachate (mg L^{-1})			Contribution of sludge (mg L^{-1})[a]			Total collected leachate (L)
	Ni	Cd	Co	Ni	Cd	Co	
1	157.58	225.90	17.61	0.66	0.11	0.007	24
3	117.10	164.03	12.73	0.87	0.12	0.008	33
6	94.81	139.91	10.30	0.74	0.082	0.010	40
9	90.64	138.33	11.12	0.74	0.082	0.010	40
15	78.79	121.82	10.57	0.74	0.082	0.010	40
Process load (amount of battery)							
Two	153.79	215.78	19.22	0.98	0.097	0.007	25
Four	253.92	376.03	30.95	0.98	0.097	0.007	30
Eight	374.12	547.45	45.81	0.98	0.097	0.007	40

[a] Data determined from the average concentration of the acid supernatant flowing into the leaching reactor.

relative short time in the initial 5–10 days. It can be inferred that at the initial bioleaching the predominant mechanism responsible for the solubilization of metals from the spent Ni–Cd batteries was non-contact mechanism (acid dissolution) [21]. And the longer HRT was advantageous for the dissolution of some materials difficult to dissolve such as metallic phases. Perhaps the direct mechanism of oxidation by thiobacilli existed due to existence of large amount of live thiobacilli in the leaching reactor, which was confirmed by inoculation to the medium plated on Petri dishes.

3.4. Comparison of the dissolution of Ni, Cd and Co

The leaching behavior of the metals Ni, Cd and Co was different. In Fig. 4(a), when the HRT was relatively short (1 and 3 days), the leaching of metallic Ni showed two stages. During the first 5–10 days the maximum dissolution of Ni (about 300 mg L^{-1}) was obtained, then it decreased in the following days. But in the 15th day it suddenly increased to the maximum (550 mg L^{-1}). After that, it decreased again until the leaching was finished. But at the longer HRT, the phenomenon was not obvious. The leaching of nickel hydroxide and nickel in metallic form (Ni^0) were obtained separately since the leaching of these species occurs sequentially at different acidity levels (Fig. 3(a and b)) [22].

The phenomenon of cadmium concentration change was different to that of nickel and similar to the minor metal cobalt (Fig. 4(b and c) and Fig. 6(b and c)). According to Fig. 4(b) most of cadmium was leached in the first several days when pH reduced to about 4.5. Then the concentration in effluent decreased rapidly until cadmium was leached completely. The maximum dissolution of cadmium delayed with the increase of the HRT. As for the minor metal cobalt (Fig. 4(c)), its concentration change in the effluent was similar to cadmium except for the longer time it took to finish the leaching.

The above phenomenon was due to the different phases in spent battery and different heavy metals solubility [23]. According to the higher solubility of cadmium hydroxide than nickel hydroxide and the higher reducing power of cadmium than nickel (i.e. elemental cadmium is easier oxidized than elemental nickel), the attack to anodic material by microorganisms and sulphuric acid was faster than that corresponding to cathodic material [24]. The solubilization rate constant of metal Ni^0 in the bioleaching process was also lower than the other metals [25].

It is noted that at the beginning of the leaching with the fresh medium (pH < 2.0) flowing into the leaching reactor, the rapid dissolution of nickel, cadmium and cobalt and a fast increase of pH (about 5.0) (Fig. 5) indicates that it was an acid dissolution. During the following continuous extraction, the rates of dissolution were lower with no significant increase in pH. The fast increase of pH was due to the first dissolution of the oxidized species (oxides and hydroxides) and the neutralization of the electrolyte (KOH). Then a later dissolution of species as elemental metals (especially for Ni^0) needed a longer time.

4. Conclusions

The spent Ni–Cd batteries were treated in a continuous flow two-step leaching system by the bio-sulphuric acid which was produced using the acidifying of sewage sludge. The electrodes of spent Ni–Cd battery were characterized. The bioleaching tests at different hydraulic retention time of the leaching reactor and process load were performed. The following conclusions can be drawn from this research.

(1) The XRD patterns of the active electrode materials confirmed the presence of Ni^0, Ni(OH)$_2$ and γ-NiOOH in the cathode; Cd^0, Cd(OH)$_2$ and KOH in the anode.
(2) The long HRT cannot enhance the dissolution of the metals Ni, Cd and Co in their oxide or hydroxide form. The HRT of 1–3 days was effective. pH was an essential factor that influences the metals dissolution. Most of the metals dissolution needed relative short time in the initial 5–10 days. It can be inferred that acid dissolution is the main mechanism of metals extraction at the initial bioleaching. Perhaps the direct microbial mechanism of oxidation existed due to existence of large amount of live thiobacilli in the leaching reactor.
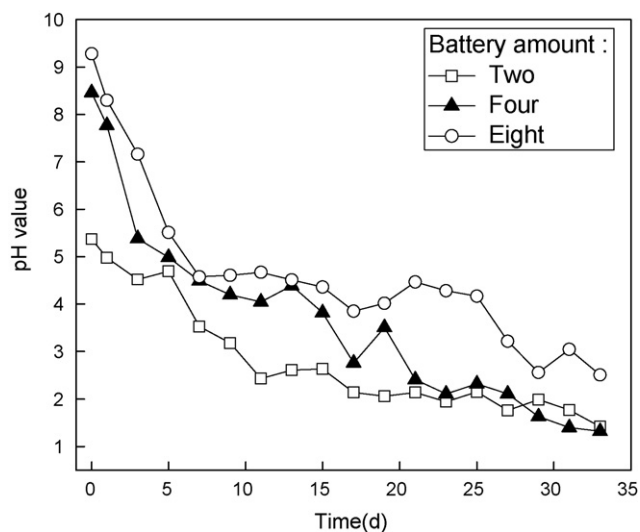

Fig. 7. Change of pH value in the leaching reactor with time at different process load.

(3) Metals Ni, Cd and Co can be completely dissolved in all loadings if enough time is given. The all time used was not proportionate with the increasing of the load. More concentrated metals solution can be obtained with higher load even though the pH during the leaching was higher.

Acknowledgement

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