



Effects of water-washing pretreatment on bioleaching of heavy metals from municipal solid waste incinerator fly ash

Qunhui Wang^{a,*}, Jie Yang^b, Qi Wang^c, Tingji Wu^d

^a Department of Environmental Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian, Beijing 100083, China

^b Shanghai Academy of Environmental Sciences, 508 Qinzhou Road, Shanghai 200233, China

^c Chinese Research Academy of Environmental Science, Beijing 100012, China

^d School of Municipal and Environmental Engineering, Harbin Institute of Technology, 202 Haihe Road, Nangang, Harbin 150090, China

ARTICLE INFO

Article history:

Received 21 July 2007

Received in revised form 9 March 2008

Accepted 22 May 2008

Available online 2 July 2008

Keywords:

Heavy metals

Bioleaching

Water-washing pretreatment

Aspergillus niger

Fly ash

ABSTRACT

Previous studies demonstrated that the bioleaching of municipal solid waste incinerator fly ash by *Aspergillus niger* was an efficient “green technology” for heavy metals removal, however, it demanded a long operational period. In this study, water-washing was used as a fly ash pretreatment before the bioleaching process (one-step and two-step). This pretreatment extracted 50.6% of K, 41.1% of Na, 5.2% of Ca and 1% of Cr from the fly ash. Due to the dissolution of alkali chlorides which hold particles together, fly ash particles were smashed into smaller granules by the hydraulic flushing action caused by vibration. After the pretreatment, the lag phase and bioleaching period were reduced by 45 and 30%, respectively, in one-step bioleaching of 1% (w/v) fly ash. Meanwhile, the metals extraction yield both in one-step and two-step bioleaching was increased markedly, e.g. in two-step bioleaching, 96% Cd, 91% Mn, 73% Pb, 68% Zn, 35% Cr and 30% Fe was extracted from 1% water-washed fly ash, respectively. The reduction of the bioleaching period and improvement of metals extraction yield will likely allow the practical application of the bioleaching technology for heavy metals removal from fly ash.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Considering the lack of landfill space and the contamination to environment, municipal solid waste (MSW) is usually incinerated to reduce its volume and provide energy. However, the fly ash (abbreviated to FA in the following text) collected from the flue gas by the air pollution control (APC) devices [1] is potentially harmful to the environment due to the existence of leachable heavy metals (e.g. Cd, Cr, Mn and Pb). Therefore, the MSW incinerator (MSWI) FA is classified as a kind of hazardous waste in China. The toxic heavy metals leached from FA contaminate soil and groundwater when water flows through the uncontrolled landfill of FA. FA can also be identified as “artificial ore” [2] considering various recoverable metals in it (e.g. Cu, Zn and Fe).

Conventional treatments of MSWI FA such as immobilization with construction materials [1], chemical washing [3] and chloride evaporation [4] have been reported. Whereas, they generally demand high energy, require the use of hazardous chemical

reagents, and produce final products that exhibit the leaching behavior. Therefore, it is necessary to investigate an economical and efficient green technology for both the detoxification and the metals recovery from FA.

The application of bioleaching technology, a pollution-less approach with low cost and low energy consumption, used for metals extraction from low-grade ores, soil or mine tailings by chemolithotrophic bacteria, heterotrophic bacteria or fungi, has been reported [5–9]. *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* are commonly used for the bioleaching of sulfide minerals [10,11]. Furthermore, the bioleaching of FA using a pure or mixed culture of these two *Thiobacillus* spp. has been investigated intensively [12,13].

It is well known that *Aspergillus niger* metabolites various organic acids such as citric, oxalic and gluconic acid by aerobic fermentation using carbon sources. The safety of this fungus allows its application in the industrial fermentation of citric, oxalic or gluconic acids serving as the raw materials for food, pharmaceuticals and other industrial fields [14,15]. The bio-produced organic acids may be used as leaching agents to extract metals from fly ash. In 1996, Bosshard et al. [2] reported the bioleaching of MSWI fly ash by *A. niger* for the first time. The main agreed mechanisms of bioleaching were described as: (i) acidolysis; (ii) complexolysis; (iii) redoxolysis; (iv) bioaccumulation [2,5]. Wu and Ting [5]

* Corresponding author at: Department of Environmental Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing 100083, China. Tel.: +86 10 62332778; fax: +86 10 62332778.

E-mail address: wangqh59@sina.com (Q. Wang).

investigated the metals extraction efficiency from fly ash by *A. niger* using one-step and two-step bioleaching at various fly ash concentrations and compared them with the chemical leaching using commercial organic and inorganic acids. Xu and Ting [16] optimized the bioleaching conditions using the central composite design (CCD) and obtained empirical models. According to these studies, the acidolysis of bio-produced organic acids was considered as the principal mechanism in fungal bioleaching process. Therefore, *A. niger* may be used in the bioleaching of heavy metals from fly ash both in the one-step bioleaching (incubating the fungus with the fly ash) and the two-step bioleaching (pre-culturing the fungus for a couple of days before adding in the fly ash). Nevertheless, the bioleaching of fly ash by *A. niger* demand a long operational period of approximately 15–40 days [2,5,16].

Water-extractable alkali chlorides (e.g. NaCl, KCl and CaCl₂) are abundant in MSWI FA. The amphoteric heavy metals in FA such as Pb and Zn can also be extracted by water [17]. Hence, the water-washing pretreatment of FA before bioleaching process may reduce toxicities of FA to *A. niger* due to the extraction of chlorides, leachable salts, and amphoteric heavy metals, consequently reduce the bioleaching period.

The purpose of this study was to introduce the water-washing pretreatment of the FA that might reduce the bioleaching period and improve the metals extraction yield. In this study, the FA was washed by deionized water before the bioleaching process. The raw FA (i.e. the FA without water-washing pretreatment) and the water-washed FA were bioleached by *A. niger* both in one-step and two-step bioleaching at various FA concentrations. The chemical and physical characteristics of the raw FA and the water-washed FA were compared. The pH values of the bioleaching suspensions were monitored. The metabolic organic acids and heavy metals in suspensions after bioleaching were also analyzed.

2. Materials and methods

2.1. Characteristics of raw FA

The raw FA in this study was obtained from a MSW incineration power plant with a capacity of 300 t/day located in Zhejiang province, China. The flue gas was treated with lime powder. Samples collected from the hop-pocket dust catcher were homogenized and dried in an oven at 105 °C for 24 h before use.

The raw FA for test was acid-digested according to US-EPA SW-846 3050B method, and the metals content was analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 5300DV). The elemental composition of the raw FA used in this study was shown in Table 1. The result indicated that Ca (111.6 mg/g) was the most abundant metal element

Table 1
Elemental composition of raw FA (analyzed by ICP-OES)

Element	Content (mg/g)
Al	39.79
Ca	111.62
Cd	0.06
Cr	0.18
Cu	0.55
Fe	22.51
K	44.76
Mg	14.85
Mn	0.75
Na	32.29
P	5.59
Pb	2.10
Zn	5.22

Table 2
Chemical component in raw FA (analyzed by XRF)

Component	Content (%)
CaO	24.36
SiO ₂	22.04
Cl	9.20
SO ₃	8.90
Al ₂ O ₃	7.79
K ₂ O	7.43
Na ₂ O	5.45
Fe ₂ O ₃	5.17
MgO	3.72
P ₂ O ₅	2.52
TiO ₂	1.50
ZnO	0.77
PbO	0.34
MnO	0.20
Cr ₂ O ₃	0.13
BaO	0.11
CuO	0.10
SnO	0.08
Br	0.07
SnO ₂	0.07
NiO	0.02
Co ₂ O ₃	0.02

in the raw FA due to the addition of the lime powder into the flue gas. Al, K, Fe, Na and Mg were all above 10 mg/g. Some toxic heavy metals, such as Cd, Cr, Cu, Mn, Zn and Pb were less than 10 mg/g. Furthermore, the X-ray fluorescence (XRF, SHIMADZU XRF-1700) analysis of the raw FA (Table 2) indicates that CaO and SiO₂ were the major compounds, and other metal elements formed mainly in oxides.

The BET surface area and the total pore volume of the raw FA (analyzed using ASAP2020 surface area and porosity analyzer, Micromeritics) was 8.57 m²/g and 0.01126 cm³/g, respectively. These results were in a good agreement with that in Xu and Ting (5.75 m²/g and 0.01927 cm³/g) [16].

The homogenized dry raw FA was washed by deionized water at a liquid-to-solid ratio (L/S) of 2 in a polythene vessel shaken by an end-over-end fashion at 30 ± 2 rpm for 60 min, the same vibration condition as TCLP (US EPA SW846 Method 1311). The suspension was filtered and the filtered ash was washed twice with deionized water, and then put into an oven drying at 105 °C for 24 h. The metal contents in the washing water supernatant and the filtered dry ash (water-washed FA) were analyzed using ICP-OES.

2.2. Fungal strain and inoculum preparation

A strain of *A. niger* (AS 3.40) was obtained from China General Microbiological Culture Collection Center (CGMCC), Institute of Microbiology, Chinese Academy of Science. In order to obtain sufficient spores, the fungus was inoculated on 3.9% (w/v) potato dextrose agar (PDA) at 28 °C for 6 days. The mature conidia were then washed off from the surface of the PDA medium using sterilized deionized water. The number of spores was counted using a hamocytometer and adjusted using sterilized deionized water to approximately 2 × 10⁷ spores/ml before every experiment. One milliliter of spore suspension was added to 100 ml sucrose medium. The sucrose medium was modified according to that of Bosshard et al. [2] as follows (g/l): sucrose (100), NH₄Cl (4), KH₂PO₄ (0.5), MgSO₄·7H₂O (0.025), KCl (0.05). All reagents were analytical grade. The culture medium was autoclaved at 121 °C for 20 min prior to inoculation.

2.3. Bioleaching experiments

Bioleaching experiments were carried out in 250 ml Erlenmeyer flasks containing 1, 2 and 4% (w/v) FA and 100 ml sucrose medium. Two different types of experiments were carried out. In one-step bioleaching, *A. niger* was incubated with the FA. In two-step bioleaching, *A. niger* was pre-cultured in sucrose medium without FA and then the FA was added after 2 days. The raw FA and water-washed FA were used both in the two types of experiments.

All flasks were sealed with four layers pledget and incubated under the condition of 30 °C and 140 rpm. Each flask experiment was carried out in duplicate. The fresh medium leaching and the deionized water leaching were also carried out as control experiments, under the same conditions as the bioleaching process. Two milliliters samples were taken by disposable sterilized pipettes at regular intervals for pH measurement. Subsequently, the volume was made up by sterile sucrose medium. At the end of bioleaching period (pH no longer decreased), the mixtures of *A. niger* and the FA were centrifuged at 10,000 rpm for 20 min. After filtration through 0.45 μm membrane filters, the heavy metals concentrations and the organic acids concentrations in supernatant were analyzed.

2.4. Analytical methods

The metals concentrations in suspension were analyzed using ICP-OES (PerkinElmer Optima 5300DV) at the following wavelengths (nm): Cd (228.802), Cr (267.716), Cu (327.393), Fe (238.204), Mn (257.61), Pb (220.353) and Zn (206.2). The tested samples were filtered through a 0.45-μm membrane filter before analysis. The metals extraction yield and the total metals extraction yield were calculated as following equations:

$$\text{Metals extraction yield} = \frac{C_S V_S}{C_F M_F} \times 100\% \quad (1)$$

$$\text{Total metals extraction yield} = \frac{\sum C_S V_S}{\sum C_F M_F} \times 100\% \quad (2)$$

where C_S is metal concentrations in bioleaching suspension, V_S is the volume of the bioleaching suspension, i.e. 100 ml, C_F is the metal content in FA (mg/g) and M_F is the mass of added FA.

The total metals included Cd, Cr, Cu, Fe, Mn, Pb and Zn.

The concentrations of bio-produced organic acids (i.e. citric, oxalic and gluconic acid) were analyzed using ion chromatography (ICS-3000 system, DIONEX). This IC system included an IonPac AG11 AS11 column using KOH as the effluent at a flow rate of 1.2 ml/min at 30 °C. The signal was monitored by a conductive detector.

3. Results and discussion

3.1. Growth of *A. niger* in the absence of FA

Fig. 1 shows the changes in pH and biomass concentration during the growth of *A. niger* in the absence of FA. The pH dropped from 5.2 to 2.3 drastically in 24 h and thereafter gradually decreased to 1.3 after 240 h. The biomass concentration (dry cell weight/volumes of culture medium (g/l)) increased slightly during 48 h and attained the maximum value (19.1 g/l at average value) after 96 h cultivation and then remained relatively constant up to 240 h. The changes in pH during the bioleaching process was considered as a significant parameter of the growth of the fungus due to the significant negative correlation ($r = -0.81$, $P < 0.01$) between biomass and pH.

It was difficult to measure the precise biomass concentration of *A. niger* in the presence of FA due to the mixture of the mycelium and FA granules. Therefore, only the pH values of the suspension were

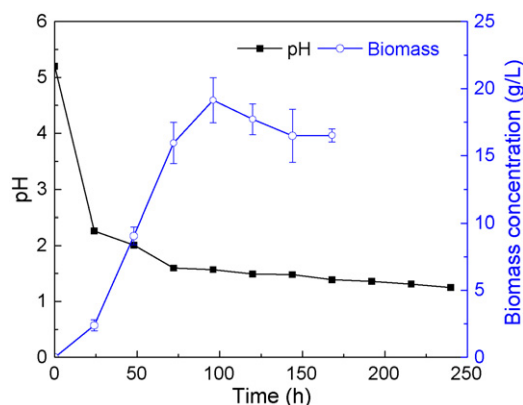


Fig. 1. Changes in pH and the biomass concentration during the growth of *A. niger* in the absence of FA.

detected during the growth of *A. niger* with FA (i.e. the one-step and two-step bioleaching).

3.2. One-step bioleaching experiment

3.2.1. Effect of water-washing pretreatment on pH

It was observed that the pH at the beginning of the incubation of *A. niger* with FA remained relatively invariable for many hours which was considered as the “lag phase” (the adaptive duration of *A. niger* to the FA in culture medium) [2,5]. The changes in pH during the growth of *A. niger* in the presence of raw FA and water-washed FA at various FA concentrations were shown in Fig. 2, which were considered as the indicator of the bioleaching process [2].

In the case of 1% (w/v) raw FA, the pH decreased steadily from 7.9 to 2.5 after a lag phase of 264 h (11 days) and thereafter remained constant up to 720 h (30 days). At 2% FA concentration, the lag phase and the final pH was 408 h and 4.7, respectively. Differently, the pH with 4% FA kept relatively invariable at about 8 for 720 h (30 days), as a result of the fungal death under the formidable condition caused by a relatively high concentration of the raw FA. On the other hand, in the case of water-washed FA, the initial and final pH was similar to that of raw FA. However the lag phases in one-step bioleaching of 1 and 2% water-washed FA were shorter than that of the raw FA at the same fly ash concentrations. Especially at 4% FA concentration, *A. niger* germination in the presence of the water-washed FA resulted in the pH decrease, as compared to the fungal death in the presence of the raw FA.

3.2.2. Effect of water-washing pretreatment on organic acids production

As acidolysis of bio-produced organic acids played an important role in bioleaching mechanisms [2], it was necessary to determine the organic acids concentrations in suspension and the results were listed in Table 3. *A. niger* secreted 3.95 mM citric acid and 24.31 mM gluconic acid after 240 h of incubation in the absence of FA.

The organic acids in suspensions after the bioleaching of the raw FA and the water-washed FA (in one-step and two-step) were also analyzed (Table 3). In general, *A. niger* secreted less organic acids with the increase of FA concentration, which was dissimilar to the results in Wu and Ting [5]. It was presumably due to the lower tolerance of AS 3.40 to the FA than that of *A. niger* in Wu and Ting. At 1% FA concentration, *A. niger* produced 2.23 mM of citric acid, 0.66 mM of oxalic acid and 60.7 mM of gluconic acid after 720 h of incubation with the raw FA. In contrast, the fungus produced 1.44 mM of citric acid, 1.36 mM of oxalic acid and 66.8 mM of gluconic acid after 480 h of incubation with the water-washed FA. The water-washing pretreatment improved the production of

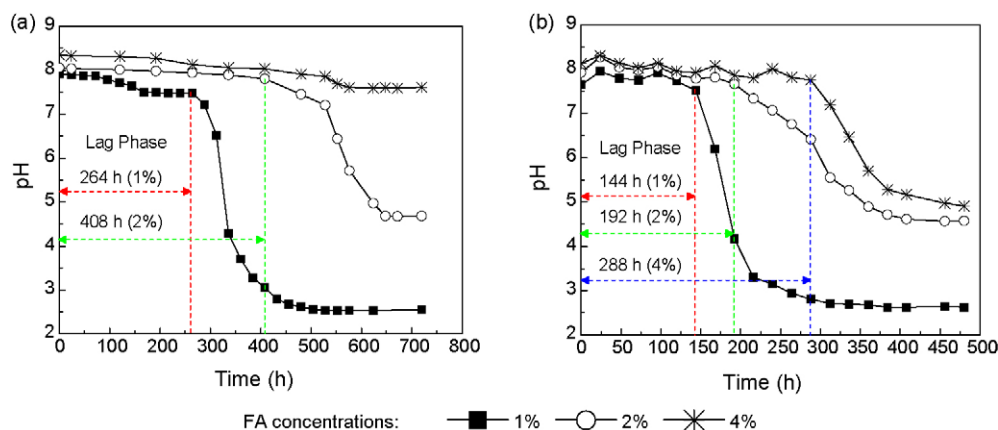


Fig. 2. Changes in pH during the growth of *A. niger* in the presence of raw FA (a) and water-washed FA (b) at various FA concentrations in one-step bioleaching.

the organic acids but not evident. A similar result was also noted at 2% FA concentration. At 4% FA concentration, no organic acid was detected in the bioleaching of the raw FA because of the fungal death. Differently, 0.31 mM oxalic acid and 0.28 mM gluconic acid were secreted by *A. niger* after 480h incubation with 4% water-washed FA, which caused the pH decrease described above.

3.2.3. Effect of water-washing pretreatment on metals extraction yield

Fig. 3 shows the metals extraction yield in one-step bioleaching of the raw FA and water-washed FA at various FA concentrations. In general, the increase in the FA concentration led to the decrease in the metals extraction yield. The higher concentration of FA increased the heavy metals toxicities to the fungal growth and decreased the organic acids production as listed in Table 3. Moreover, the higher content of heavy metals in higher concentration of FA resulted in the less metals extraction yield as calculated according to Eq. (1). The metals extraction yield in control experiments (i.e. the deionized water leaching and the fresh medium leaching) were negligible, except for Cr (about 9% Cr was extracted by deionized water).

Generally, the water-washing pretreatment improved the metals extraction yield in one-step bioleaching for all analyzed metals (Cd, Cr, Cu, Fe, Mn, Pb and Zn) except for Mn. It was not well understood that the metal extraction yield of Mn in one-step bioleaching was not improved by water-washing pretreatment. More details need to be studied in the future. In bioleaching of 1% raw FA the extraction yield of Cd, Zn, Pb and Cu was 67.5, 44.1, 19.3 and 18.9%, respectively. After the water-washing pretreatment, the extraction yield of these metals increased to 98.8, 61.7, 28.4 and 55.9%, respectively. A similar phenomenon was observed at 2% FA concentration, although the metals extraction yield decreased with the increase of FA concentrations. The metals extraction yield of 4% water-washed FA was similar to that of 2% water-washed FA. In contrast, the met-

als extraction yield of 4% raw FA was lower than 5% for almost all analyzed metal ions which correspond to no detected organic acids secreted by *A. niger* (Table 3).

3.2.4. Function of water-washing pretreatment

It was evident that the water-washing pretreatment slightly increased the organic acids production but remarkably reduced the lag phase of fungi growth and improved the metals extraction yield in one-step bioleaching. In order to understand the function of water-washing pretreatment, the chemical compositions and the SEM photographs of the FA with and without water-washing pretreatment were studied.

Fig. 4 illustrates the metal partitions in the washing water and water-washed FA. The results indicated that water extracted 50.6% of K, 41.1% of Na, 5.2% of Ca and 1.1% of Cr, although the extraction yield of other metals were negligible. The high extraction yield of K and Na resulting from the readily removed alkali chlorides (KCl and NaCl) was similar to the result in K.S. Wang et al., where more than 50% of K and Na were extracted [17]. Whereas, the extraction yield of Ca in this study was 5.2% and less than that in K.S. Wang et al. (20.8% of Ca was extracted) [17]. It was probably due to the dominance of insoluble calcium oxide [17] in the FA used in this study. The extraction of alkali chlorides presumably reduced the toxic effect of water-washed FA to the fungi, which resulted in a shorter lag phase and a faster bioleaching process.

As shown in Fig. 5a, FA particles presented amorphous shapes, e.g. sphere, claviform, lumpishness and particle aggregations. According to Wu and Ting [5], the non-porous structure of FA probably resulted in the low specific surface area. The SEM image of the water-washed FA (Fig. 5b) shows relatively less materials on the surface of particles as compared to that of the raw FA. Guo et al. [18] analyzed the composition of particles covering the surface of FA using SEM-EDX and noted that the spherical particles were covered by soluble sodium chloride (NaCl), which explained the

Table 3
The concentrations of organic acids bio-produced by *A. niger* after bioleaching process

Organic acids (mM)	One-step bioleaching						Two-step bioleaching						In absence of FA (240 h)
	Raw FA (% (w/v))			Water-washed FA (% (w/v))			Raw FA (% (w/v))			Water-washed FA (% (w/v))			
	1	2	4	1	2	4	1	2	4	1	2	4	
Citrate	2.23	ND	ND	1.44	ND	ND	1.43	3.90	0.09	11.40	8.73	9.68	3.95
Oxalate	0.66	ND	ND	1.36	ND	0.31	0.36	0.54	ND	2.04	2.59	0.60	ND
Gluconate	60.70	0.42	ND	66.80	1.33	0.28	11.80	30.60	0.36	17.5	30.10	19.30	24.31
Total	63.59	0.42	ND	69.60	1.33	0.59	13.59	35.04	0.45	30.94	41.42	29.58	28.26

ND: not detected.

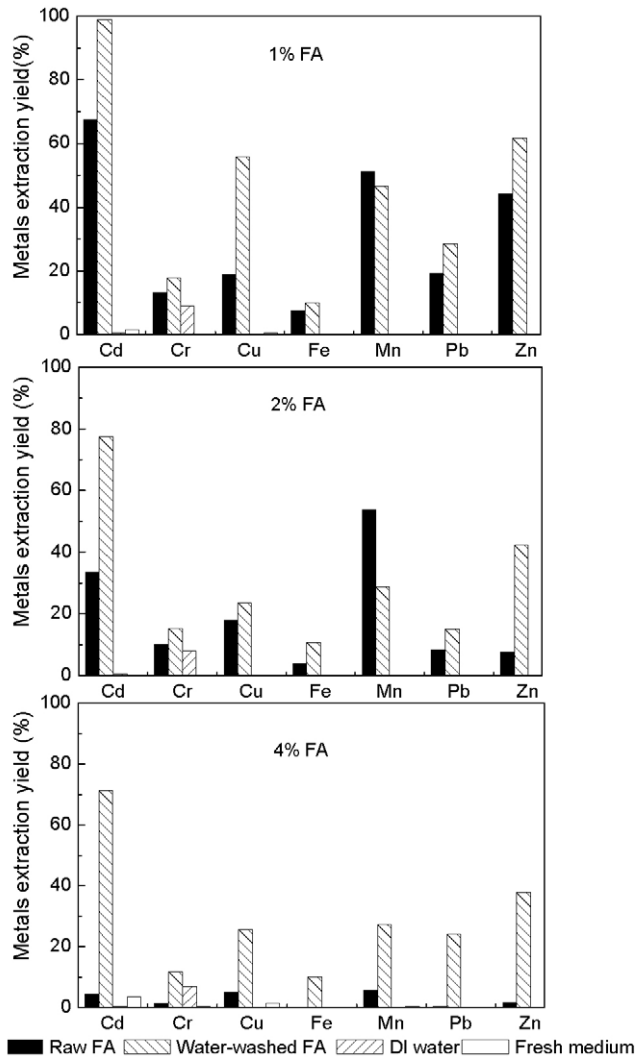


Fig. 3. Metals extraction yield of raw FA and water-washed FA at various FA concentrations in one-step bioleaching.

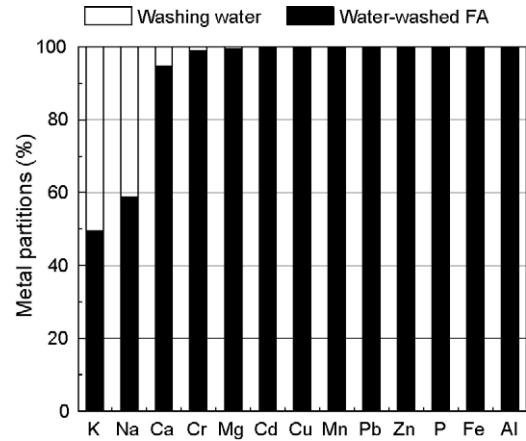


Fig. 4. Metal partitions in washing water and water-washed FA.

reduction of materials on the surface of water-washed FA. As compared to the SEM images of the raw FA (Fig. 5a), more fragmental particles appeared in that of the water-washed FA (Fig. 5b).

According to Bruckard et al. [19], the size distribution (P_{80}) of water-washed electric arc furnaces (EAFs) dust was lower than that of unwashed dust, and it was presumably due to the removal of soluble salts which help to hold together some of the particles. In addition, the action of hydraulic flushing action caused by an end-over-end vibration during the water-washing pretreatment also facilitated the smashing of FA particles into smaller granules. Most heavy metals in FA were packed in crystal lattices of the silicate or the aluminosilicate [18]. The heavy metals in smaller granules of the water-washed FA reacted more sufficiently with the bio-produced organic acids, which was in favor of the metals extraction.

3.2.5. Two-step bioleaching experiment

According to the preliminary research, the pre-culturing of *A. niger* for 2 days avoided the lag phase in two-step bioleaching, allowing the spores to germinate to mycelia and metabolized organic acids, which were represented as a rapid increase in biomass and a fast decrease in pH (Fig. 1). Considering the improvement of water-washing pretreatment on the metals extraction yield in one-step bioleaching, the two-step bioleaching experi-

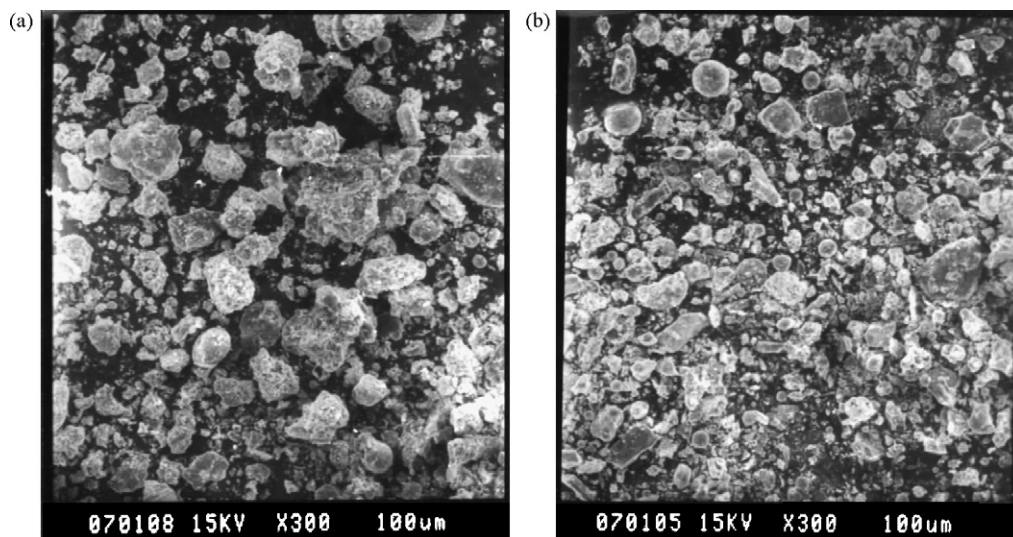


Fig. 5. Scanning electron micrographs of raw FA (a) and water-washed FA (b) (300 \times magnification).

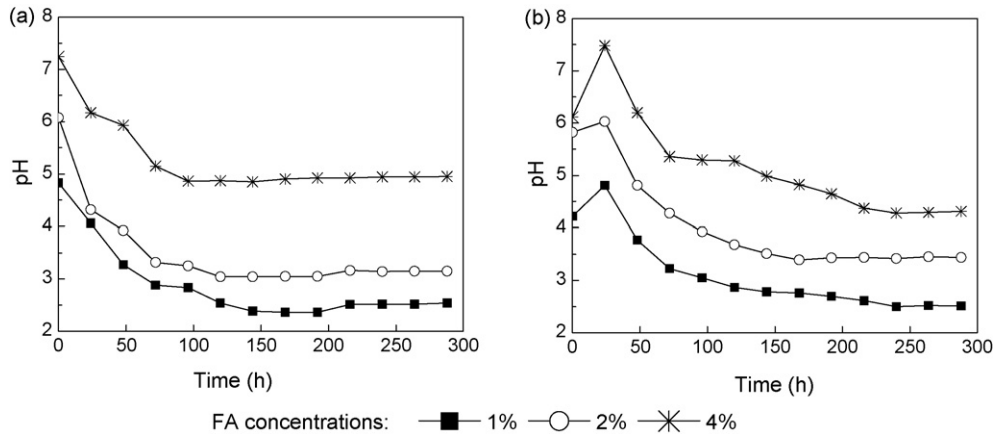


Fig. 6. Changes in pH during the growth of *A. niger* in the presence of raw FA (a) and water-washed FA (b) at various FA concentrations in two-step bioleaching.

ments of the raw FA and water-washed FA were also conducted, respectively.

3.2.6. pH changes

As shown in Fig. 6, the increase of FA concentrations led to an increase in the initial and final pH of the suspension. A lower initial pH was observed in two-step bioleaching because the protons in organic acids neutralized the alkali oxides in FA. At 1% raw FA, there was a gradually decrease in pH from 4.8 to 2.5 within 120 h and it kept constant afterwards. Apart from the higher initial and final pH, similar trends in pH changes were observed at 2 and 4% raw FA. In the case of water-washed FA, the pH increased within 24 h because of the proton consumption while converting the oxides in FA into soluble metal salts. After that, the pH decreased steadily due to the amount of protons produced by *A. niger* exceeded the demand for this reaction [3]. As mentioned above, the lag phase occurred neither in two-step bioleaching of the raw FA nor in that of the water-washed FA.

3.2.7. Organic acids production

As shown in Table 3, the fungi secreted more organic acids in two-step bioleaching of water-washed FA than that of raw FA. Especially at 4% FA concentration, 9.68 mM of citrate and 19.3 mM of gluconate were detected in suspension of water-washed FA as against negligible organic acids in that of raw FA. The increase of organic acids production was presumably due to the addition of the less toxic water-washed FA.

3.2.8. Metals extraction yield

Fig. 7 shows the metals extraction yield of the raw FA and the water-washed FA in two-step bioleaching at various FA concentrations. Due to the increase in organic acids production described above, the metals extraction yield of the water-washed FA was evidently higher than that of the raw FA at various FA concentrations, except for Cu. The maximum metals extraction yield was obtained in bioleaching of 1% (w/v) water-washed FA (i.e. 96% for Cd, 91% for Mn, 73% for Pb, 68% for Zn, 35% for Cr and 30% for Fe). It was noteworthy that the increase of FA concentrations brought a slight decrease in the metals extraction yield of the water-washed FA rather than a significant one in that of the raw FA, which was due to the higher organic acids concentration of the former. For example, at 4% FA concentration, 71.2% of Cd, 39.1% of Mn, 38.6% of Zn, 26% of Pb, 18.7% of Cr and 12.1% of Fe were leached from the water-washed FA compared to lower than 7% for all metals leached from the raw FA.

3.2.9. Improvement effects of water-washing pretreatment on bioleaching process

The water-washing pretreatment reduced the lag phase in one-step bioleaching (Figs. 2 and 8) and enhanced the total metals extraction yield at various FA concentrations (Fig. 8). Moreover, the water-washing pretreatment led to a faster one-step bioleaching, i.e. 20 days compared to 30 days without pretreatment. As shown in Fig. 8a, more shortened lag phase (i.e. the difference of the lag phase between the raw FA and water-washed FA) was obtained at higher

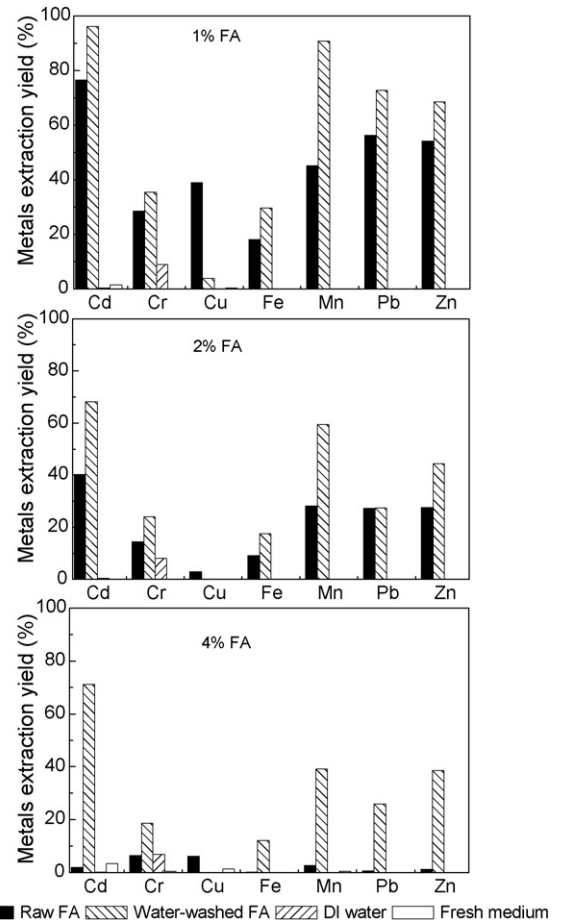


Fig. 7. Metals extraction yield of raw FA and water-washed FA at various FA concentrations in two-step bioleaching.

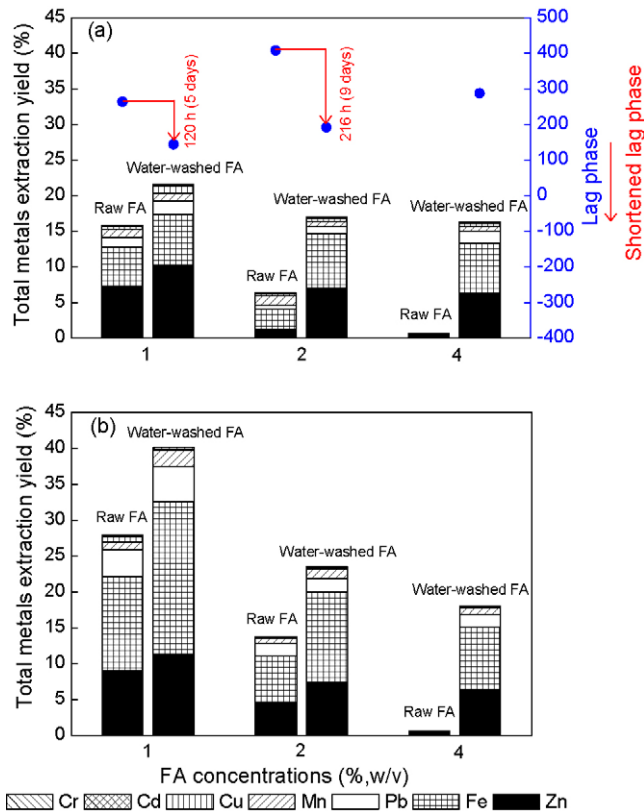


Fig. 8. The shortened lag phase in one-step bioleaching (a) and the total metals extraction yield of the raw FA and water-washed FA at various FA concentrations in one-step (a) and two-step bioleaching (b).

FA concentrations. The differences of the total metals extraction yield between the raw FA and water-washed FA both in one-step and two-step bioleaching (Fig. 8) had a similar rule as the shortened lag phase. The greatest increase of the total metals extraction yield was found at 4% FA concentration, where it increased from 1 to 16% in one-step bioleaching (Fig. 8a) and from 1 to 18% in two-step bioleaching (Fig. 8b). However the optimum FA concentration for bioleaching was observed at 1% (w/v) both in one-step and two-step bioleaching. This result was in agreement with that in Wu and Ting [4], and the authors attributed it to the fact that the FA concentration was the main factor in bioleaching process [4].

The results demonstrated that both the one-step and two-step bioleaching extracted metals effectively from the water-washed FA. Considering the high yield of total metals extraction, the two-step bioleaching process with the water-washing pretreatment was preferable.

4. Conclusions

The high concentration of alkali chloride and heavy metals in FA inhibited the fungal growth and resulted in the lag of the pH value drop (i.e. the increase of the lag phase) as well as a delay of bioleaching process.

The readily removed alkali chlorides in the raw FA were extracted through the water-washing pretreatment, which resulted in the reduction of the inhibition of the FA to the fungal growth. In one-step bioleaching, *A. niger* grew only at 1–2% (w/v) raw FA, the fungal growth was observed even in the presence of 4% (w/v) water-washed FA. After the pretreatment, both the lag phase and the bioleaching period were reduced in the one-step bioleaching. The one-step bioleaching period

was shortened to 20 days compared to 30 days without the pretreatment.

The dissoluble alkali chlorides on the surface of FA particles held together some of the FA particles. Their extraction made the FA particles easier to be smashed into smaller granules by the hydraulic flushing action. Therefore, the heavy metals in silicate or alumino-silicate of FA granules reacted with the bio-produced organic acids more sufficiently, which explained the increase of the metals extraction yield after the water-washing pretreatment.

The water-washing pretreatment of FA in this paper enabled a faster bioleaching process in one-step bioleaching and a higher metals extraction yield both in one-step and two-step bioleaching. It may allow this green technology to practical application as an alternative to conventional physicochemical methods for removal of hazardous heavy metals from MSWI FA.

Acknowledgement

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (NSFC, no. 20577047).

References

- [1] C. Ferreira, A. Ribeiro, L. Ottosen, Possible applications for municipal solid waste fly ash, *J. Hazard. Mater.* B96 (2003) 201–216.
- [2] P.P. Bosshard, R. Bachofen, H. Brandl, Metal leaching of fly ash from municipal waste incineration by *Aspergillus niger*, *Environ. Sci. Technol.* 30 (1996) 3066–3071.
- [3] K.J. Hong, S. Tokunaga, Y. Ishigami, T. Kajiuchi, Extraction of heavy metals from MSW incinerator fly ash using saponins, *Chemosphere* 41 (2000) 345–352.
- [4] M. Tateda, M. Ike, M. Fujita, Comparative evaluation of processes for heavy metal removal from municipal solid waste incineration fly ash, *J. Environ. Sci.: China* 10 (1998) 458–465.
- [5] H.Y. Wu, Y.P. Ting, Metal extraction from municipal solid waste (MSW) incinerator fly ash—chemical leaching and fungal bioleaching, *Enzyme Microb. Technol.* 38 (2006) 839–847.
- [6] C.N. Mulligan, M. Kamali, B.F. Gibbs, Bioleaching of heavy metals from a low-grade mining ore using *Aspergillus niger*, *J. Hazard. Mater.* 110 (2004) 77–84.
- [7] C.N. Mulligan, R. Galvez-Cloutier, Bioleaching of copper mining residues by *Aspergillus niger*, *Water Sci. Technol.* 41 (2000) 255–262.
- [8] I.M. Castro, J.L.R. Fietto, R.X. Vieira, M.J.M. Trópia, L.M.M. Campos, E.B. Paniago, R.L. Brandão, Bioleaching of zinc and nickel from silicates using *Aspergillus niger* cultures, *Hydrometallurgy* 57 (2000) 39–49.
- [9] S.K. Mandal, P.C. Banerjee, Iron leaching from China clay with oxalic acid: effect of different physico-chemical parameters, *Int. J. Miner. Process.* 74 (2004) 263–270.
- [10] E. Donati, G. Curutchet, C. Pogliani, P. Tedesco, Bioleaching of covellite using pure and mixed cultures of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*, *Process Biochem.* 31 (1996) 129–134.
- [11] L. Falco, C. Pogliani, G. Curutchet, E. Donati, A comparison of bioleaching of covellite using pure cultures of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* or a mixed culture of *Leptospirillum ferrooxidans* and *Acidithiobacillus thiooxidans*, *Hydrometallurgy* 71 (2003) 31–36.
- [12] C. Brombacher, R. Bachofen, H. Brandl, Development of a laboratory-scale leaching plant for metal extraction from fly ash by *Thiobacillus* strains, *Appl. Environ. Microb.* 64 (1998) 1237–1241.
- [13] T. Ishigaki, A. Nakanishi, M. Tateda, M. Ike, M. Fujita, Bioleaching of metal from municipal waste incineration fly ash using a mixed culture of sulfur-oxidizing and iron-oxidizing bacteria, *Chemosphere* 60 (2005) 1087–1094.
- [14] E. Schuster, N. Dunn-Coleman, J.C. Frisvad, P.W.M. van Dijck, On the safety of *Aspergillus niger*—a review, *Appl. Microbiol. Biotechnol.* 59 (2002) 426–435.
- [15] N. Jain, D.K. Sharma, Biohydrometallurgy for nonsulfidic minerals—a review, *Geomicrobiol. J.* 21 (2004) 135–144.
- [16] T.J. Xu, Y.P. Ting, Optimisation on bioleaching of incinerator fly ash by *Aspergillus niger*—use of central composite design, *Enzyme Microb. Technol.* 35 (2004) 444–454.
- [17] K.S. Wang, K.Y. Chiang, K.L. Lin, C.J. Sun, Effects of a water-extraction process on heavy metal behavior in municipal solid waste incinerator fly ash, *Hydrometallurgy* 62 (2001) 73–81.
- [18] Y.W. Guo, W. Wang, X.B. Gao, W. Qiao, Microstructure characteristic and X-ray energy dispersive microanalysis of MSW incineration fly ash, *J. Fuel Chem. Technol.: China* 33 (2005) 703–707.
- [19] W.J. Bruckard, K.J. Davey, T. Rodopoulos, J.T. Woodcock, J. Italiano, Water leaching and magnetic separation for decreasing the chloride level and upgrading the zinc content of EAF steelmaking baghouse dusts, *Int. J. Miner. Process.* 75 (2005) 1–20.