



# Removal of Mo(VI) from Aqueous Solutions using Pyrite and Cinder: Batch and Column Adsorption Studies

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## ABSTRACT

Removal of heavy metals from mine tailing effluent has been a long-standing environmental management issue in mining industry. In this study, removal of Mo(VI) from aqueous solutions was investigated using pyrite and cinder. Various parameters such as pH, agitation time and Mo(VI) concentration have been studied in batch experiments for the two materials firstly. The maximum adsorption of Mo(VI) occurred at pH 4.0 for cinder, and 3.0 for pyrite. Kinetic studies showed that Mo(VI) adsorption by the two materials generally obeyed a pseudo second-order model. Furthermore, application of Langmuir and Freundlich isotherm models to the adsorption equilibrium data showed that the adsorption behavior obeyed the Langmuir model. The adsorption capacity of cinder and pyrite was found to be 3.01 and 8.35 mg Mo(VI)/g adsorbent. Subsequently, three flow-through columns (Column 1#,  $V_{\text{pyrite}} : V_{\text{cinder}} = 2:1$ ; Column 2#,  $V_{\text{pyrite}} : V_{\text{cinder}} = 1:1$ ; Column 3#,  $V_{\text{pyrite}} : V_{\text{cinder}} = 1:2$ ) were operated for the removal of Mo(VI) for six months. Results indicated the average removal efficiency of Mo(VI) by Column 1# were 47.68%, by Column 2# were 50.03%, and by Column 3# were 23.34%, respectively. Therefore, the pyrite-cinder mixture ( $V_{\text{pyrite}} : V_{\text{cinder}} = 1:1$ ) proven to be a feasible and cost-efficient treatment technology for Mo(VI) removal.

## INTRODUCTION

Molybdenum (Mo) is considered as an essential trace element for both plants and animals. The provisionally recommended dietary intake is 75-250  $\mu\text{g}/\text{day}$  for adults and older children (Namasivayam & Sangeetha 2006). However, it would become toxic when the level of molybdenum concentration in water is above 5 mg/L (Moret & Rubio 2003). Chronic oral exposure can result in a high incidence of weakness, headache, growth retardation, sterility, and death (Namasivayam & Sangeetha 2006). Molybdenum pollution events have been reported for several years, such as in California's San Joaquin Valley (Zhang et al. 2005) and at the Wujintang reservoir in China (Yu et al. 2011). Due to the huge molybdenum-containing effluents from mining tailings without any pretreatment, such pollution has become a major water quality management problem in many regions of the world. However, most of the relevant research was concerned with the removal of cations (e.g.,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ) (Ikram et al. 2010, Kalesh & Nair 2005) and anionic complex species (e.g., cyanide, arsenate, chromate) (Moret & Rubio 2003). Molybdenum is generally found in two oxidation states in nature, Mo(IV) and Mo(VI) (Fox & Doner 2002). It may exist as  $\text{MoS}_2$  in reducing environments although the formation may be kinetically limited (Helz

1996). Mo (VI) dominates under oxidizing conditions and is commonly present as  $\text{MoO}_4^{2-}$  (Fox & Doner 2002). Therefore, removal of  $\text{MoO}_4^{2-}$  from wastewaters is of significant importance from an environmental point of view. From an economic standpoint, its recovery would be attractive because molybdenum is a precious metal with many industrial applications.

Different methods have been developed to remove metal ions from water samples including coprecipitation (Mamtaz & Bache 2001), reverse osmosis (Zhao et al. 2005) that generally need various and complicated equipments and reagents. Adsorption has been showing to be an economical alternative for removing metals from water (Afkhami & Conway 2002). The removal of  $\text{MoO}_4^{2-}$  from aqueous solutions has been studied using different adsorbents like sulfuric acid modified cinder (Lian et al. 2012), iron ore (Xu et al. 2006, Bostick et al. 2003),  $\gamma\text{-Al}_2\text{O}_3$  (Wu et al. 2000), carbon cloth (Afkhami & Conway 2002), magnetic chitosan resins (Elwakeel et al. 2009), and maghemite nanoparticles (Afkhami & Norooz-Asl 2009). However, more research for environmentally benign, cost effective, and efficient materials for Mo removal is desired.

Pyrite is an acidogenic material that has rich resources in Liaoning province. Due to the main compositions of Fe and

Ca oxides, they have been undergone many investigations for Mo(VI) removal (Xu et al. 2006, Bostick et al. 2003). The mechanisms of Mo(VI) removal by pyrite include the process of adsorption and precipitation, moreover, the major mechanism is often determined by many factors, such as the chemical composition and the solution pH. This removal mechanism is similar to P removal by iron oxides. However, adsorbents based on iron oxides for P-removal were found the clogging phenomena in column tests for their easily aggregate together in water phase or moisture conditions that made the hydraulic conductivities of the column decreasing, and treatment efficiency decreasing finally in concomitance with clogging (Gustafsson et al. 2008). Sand has been used as a mixture to avoid clogging (Deng 2002), but sand is not an appropriate substrate due to its finer texture and stable physico-chemical properties (Meers et al. 2006). Therefore, to select substrates with conducive physico-chemical properties to Mo(VI) removal, while maintaining sufficient permeability is of utmost importance for infiltration systems. Few attempts have been tried to resolve these problems in column tests and keep steady Mo(VI) removal rate in long run. A mixture of pyrite and cinder as column media will be an approach.

Cinder is a solid waste generated from coal combustion in industry and district heating. In China, there are about 60 million tonnes of coal that is produced per annum in Liaoning province. It is deemed as an ideal material for the removal of pollutants with low cost in wastewater treatment due to the porous structure with rich oxides. Due to the complex porous structure and higher hydraulic conductivity, cinder is often mixed with other materials in soil treatment systems for improving the permeability and enhancing nitrogen removal (Zhang et al. 2005). It can also be used to immobilize cells or as filter media for advanced wastewater treatment because of the high specific surface for microbial attachment and growth (Li et al. 2005). However, cinder is prone to break down and clog, and it is often used as an additive in filter media. The mixture of pyrite and cinder as filter media for wastewater treatment could not only exert the higher Mo(VI) removal ability of pyrite, moreover, cinder is staple solid waste in China and its utilization is also make sense to waste reuse.

The objective of this work was to test the feasibility of the mixture of pyrite and cinder as adsorbent for the removal of Mo(VI). The solution pH, contact time and initial Mo(VI) concentration of pyrite and cinder were evaluated in batch experiments. Subsequently, three columns with different volume ratio of pyrite to cinder were operated for Mo(VI) removal, and an optimum mixture ratio of pyrite and cinder in the columns was investigated.

## MATERIALS AND METHODS

**Reagents and Instruments:** Pyrite was supplied by Huajian Co., Ltd., Hefei, China. Cinder was obtained from boiler room in Dalian University of Technology, Liaoning, China. The property and composition of these materials are presented in Table 1. For removing soluble material of the substrate surface, a deionization cleaning procedure was applied (Afkhani & Conway 2002). Then, the washed cinder was milled, rinsed, dried and pulverized to a particle size < 0.15 mm for testing after dried at 105°C, and kept in a plastic bag for further uses. Mo(VI) was added to suspensions using 100 mg/L stock solutions of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O. All other chemicals were of standard-grade.

A model Optima 2000 DV inductively coupled plasma spectrometer (Perkin Elmer Co., Americal) as background correction, and a model 7504 PC UV/visible spectrophotometer with 1 cm glass cells (Shanghai Xinmao Instrument Co., Ltd, Shanghai, China) were used for determination of Molybdenum concentration in the solutions. The surface characteristics of adsorbents were measured using scanning electron microscopy (FEI Quanta 200, Holland). The major elements in materials were obtained by an X-ray fluorescence spectrometer (SHIMADZU Co., Japan). As for the batch adsorption experiments, four instruments including a model DHG-9023A serious heating and drying oven (Shanghai Jinghong Laboratory Instrument Co., Ltd, Shanghai, China), a model PHS-3C pH meter (Shanghai Precision & Scientific Instrument Co., Ltd, Shanghai, China), an electronic balance model CP 153 (Ohaus instrument Co., Ltd, Shanghai, China) and an oscillator model KS (Ronghua instrument Co., Ltd, Jiangsu, China) were used collectively. In addition, all glassware were soaked in dilute nitric acid for 12 h and finally rinsed for three times with double distilled water prior to use.

**Batch phosphate adsorption experiments:** Solution of Mo(VI) concentrations 10 mg/L and 2 g/L of adsorbent dose were used to examine the pH effect. The initial pH of the mineral suspensions containing Mo(VI) was adjusted to the range of 2.0-10.0 using 0.1 mol/L HCl or 0.1 mol/L NaOH additions, and the changed total volume was <2%. The point of zero charge (pzc) is one of the most important characteristics of an oxide surface, which corresponds to the pH value of the liquid surrounding oxide particles when the sum of surface positive charges balance the sum of surface negative charges. The pH of zero point charge (pH<sub>zpc</sub>) of the two materials was tested by the mass titration method, which demonstrated that the pH of the system will approach pH<sub>s</sub> = (pK<sub>1</sub>+pK<sub>2</sub>) pzc/2 under the limiting conditions of “infinite” mass/volume ratio (Noh & Schwarz 1988).

Adsorption kinetic tests were investigated by adding the four materials (2 g/L) to 50 mL Mo(VI) solutions (20 mg/L)

with a 0.1 mol/L NaCl solution at 20°C and pH  $4.0 \pm 0.3$ . Adsorption isotherms were developed by adding the four materials (2 g/L, respectively) to Mo solutions (0–40 mg/L Mo) at pH  $4.0 \pm 0.3$ . Sodium chloride (0.1 mol/L NaCl) was used as a background electrolyte to obtain a constant ionic strength that allows comparison among different experiments (Xu et al. 2006, Bostick et al. 2003). At the end of the adsorption equilibration time, the suspensions were filtered through 0.45  $\mu\text{m}$  pore size filters, and the residual molybdate ion was analyzed.

**Column Mo(VI) adsorption experiment:** Column adsorption tests on Mo(VI) removal were conducted at room temperature. Three columns were constructed of PVC tubes of 40 cm length and 10 cm inner diameter and filled with a 30 cm layer of the appropriate filter material. The bottom of the columns was filled with a 5 cm layer of gravel to prevent loss of material from the columns. The schematic diagram of the column is shown in Fig. 1. Considering the different Mo(VI) removal capacities of pyrite and cinder, the volume ratio of pyrite to cinder was tested in the experiments. Column 1# was designed as  $V_{\text{pyrite}} : V_{\text{cinder}} = 2:1$ , Column 2# was designed as  $V_{\text{pyrite}} : V_{\text{cinder}} = 1:1$ , and Column 3# was designed as  $V_{\text{pyrite}} : V_{\text{cinder}} = 1:2$ . The average Mo(VI) concentration of influent was 5.02 mg/L in the whole test. Because the pH of practical Mo(VI) effluent was alkaline, the simulated influent pH was maintained in range of 7.0–9.2 during the tests. The effluent was collected in a storage tank and then continuously pumped to each column by peristaltic pumps. The effect of different flow rates on Mo(VI) removal was also tested at a flow rate of 4.0 mL/min in the first three months, and 12.0 mL/min in the last three months. The effluent samples were collected weekly for Mo(VI) analysis.

**Analytical methods:** The thiocyanate photometric method was used to determine Mo(VI) concentrations in aqueous solution, which was performed by using a model 7504 PC UV/visible spectrophotometer with 1 cm glass cells (Shanghai Xinmao Instrument Co., Ltd, Shanghai, China). The principle for determining these measurements is based on a reduction reaction from Mo(VI) to Mo(V) by using stannous

chloride in acid condition, and then Mo(V) can be treated to prepare the salmon-pink complex compounds by thiocyanate. All adsorption experiments were performed in triplicate and the data were expressed as the average value.

## RESULTS AND DISCUSSION

**Chemical characteristics of the materials:** The chemical composition of the materials for this study is presented in Table 1. The pyrite was rich in Fe and S, representing 45.52 % and 49.05 %, respectively. Fe and S are known to play an important role in Mo(VI) retention (Xu et al. 2006). Mo(VI) reacts with iron oxides by ligand exchange forming inner-sphere complexes (Goldberg et al. 1996). Fe, Al and Ca oxides constituted 12.41 %, 17.26 % and 6.55 % of the cinder, respectively (Table 1). The ingredient of Al is also effective for Mo(VI) removal by ligand exchange. The cinder was also high in Si, however, it was previously reported that Si has little efficiency for Mo(VI) retention (Goldberg et al. 1996).

**Effect of pH:** Solution pH plays a critical role in the rate and mechanism of the removal of phosphate. It should be noted that the removal efficiency decreased with increasing pH and shows a maximum removal value at equilibrium pH 3.0 for pyrite and pH 4.0 for cinder (Fig. 2). This finding has been reported by several investigators (Moret & Rubio 2003, Afkhami & Norooz-Asl 2009, Moselhy et al. 2011), who have found that Mo(VI) adsorption is enhanced in the acidic range of pH. As mentioned by Afkhami et al. (2009), favorable effect of low pH can be attributed to the neutralization of negative charges on surface of the adsorbents by excess hydrogen ions, thereby facilitating the diffusion of Mo(VI) and its subsequent adsorption.

The  $\text{pH}_{\text{zpc}}$  of the pyrite and cinder is around 5.25 and 9.13, therefore, the almost complete removal of Mo(VI) occurred at equilibrium pH of 4.0 for cinder and 3.0 for pyrite. This may be due to the high protonation of adsorbents at high pH lowering the final pH, which controls the point of zero charge while reacting with Mo(VI) (Illies & Tombacz

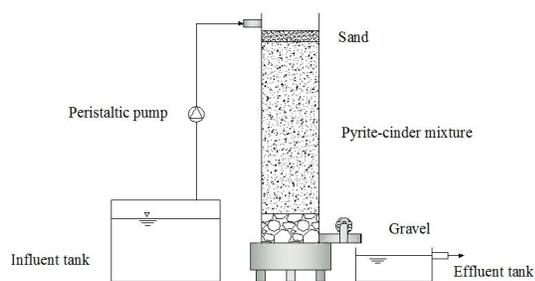


Fig. 1: Schematic diagram of laboratory based small column for fixed bed studies.

Table 1: Property and composition of the pyrite and cinder.

Property and composition	Pyrite	Cinder
Particle size (mm)	2.00–4.00	1.00–2.00
Bulk density ( $\text{g cm}^{-3}$ )	$1.42 \pm 0.2$	$0.97 \pm 0.2$
Surface area ( $\text{m}^2 \text{g}^{-1}$ )	0.37	8.63
The pH of zero point charge ( $\text{pH}_{\text{zpc}}$ )	$5.25 \pm 0.05$	$9.13 \pm 0.05$
$\text{Fe}_2\text{O}_3$ (%)	45.52	12.41
S (%)	49.05	-
$\text{Al}_2\text{O}_3$ (%)	-	17.26
CaO (%)	-	6.55
MnO (%)	-	2.28
$\text{SiO}_2$ (%)	2.11	69.29

Values are the means of duplicate determinations  $\pm$  standard deviation.

2006). Moreover, the speciation of molybdate anions are anionic polynuclear hydrolyzed species in the pH range 2.0-4.6:  $\text{Mo}_7\text{O}_{21}(\text{OH})_3^{3-}$ ,  $\text{Mo}_7\text{O}_{22}(\text{OH})_2^{4-}$ ,  $\text{Mo}_7\text{O}_{23}(\text{OH})^{5-}$ ,  $\text{Mo}_7\text{O}_{24}^{6-}$  (Namasivayam & Sangeetha 2006a, Afkhami & Norooz-Asl 2009). Therefore, the adsorbent surface is positively charged below the  $\text{pH}_{\text{zpc}}$ , and anion adsorption occurs. However, when at the final  $\text{pH} > \text{pH}_{\text{zpc}}$ , uptake of Mo(VI) decreases since at higher pH the adsorption surface sites are negatively charged which increases electrostatic repulsion between Mo(VI) and the adsorbent (Namasivayam & Sureshkumar 2009). The lower removal rate at  $\text{pH} < 3.0$  may be attributed to the higher concentration of  $\text{Cl}^-$  anions, which compete with the molybdate anions for interaction with the adsorbent active sites (Elwakeel et al. 2009).

**Adsorption kinetics:** Kinetic studies of Mo(VI) adsorption were performed to determine the time required to reach adsorption equilibrium. The optimum contact time for Mo(VI) adsorption by pyrite and cinder appears to be 150 min and 110 min, respectively. The sorption of Mo(VI) for all experiments is rapid during the initial stages of the sorption process, however, the rate of Mo(VI) adsorption becomes slower in latter stages. It can be attributed to the surface characterization of pyrite and cinder. As shown in Fig. 4, the cinder has larger pore structure and surface area, indicating that the faster adsorption rate for Mo(VI) by cinder than pyrite. Moreover, the surface area of cinder is  $8.63 \text{ m}^2/\text{g}$ , so Mo(VI) has to first encounter the boundary layer effect and then adsorb on the surface, and finally has to diffuse into the porous structure of the adsorbent which takes a longer time.

In the present study, two kinetic models were tested in order to predict the adsorption data of Mo(VI) as function of time using a pseudo first order model and a pseudo second order model. According to Gupta et al. (2001), the pseudo first-order model can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \dots(1)$$

Where  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo first order rate constant,  $q_e$  and  $q_t$  ( $\text{mg}/\text{g}$ ) are the amounts of metal ion adsorbed at equilibrium and at time  $t$  (min), respectively. The values of  $k_1$  and  $q_e$  are calculated from the slope and the intercept of the plots of  $\ln(q_e - q_t)$  versus  $t$ , respectively. The pseudo second order model is expressed by equation (2):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots(2)$$

Where,  $k_2$  is the pseudo second order rate constant of adsorption ( $\text{g}/\text{mg}/\text{min}$ ). The values of  $k_2$  and  $q_e$  were calculated from the plots of  $t/q$  vs.  $t$ .

Accordingly,  $q_e$  values of pyrite ( $4.02 \text{ mg}/\text{g}$ ) and cinder ( $4.45 \text{ mg}/\text{g}$ ), calculated from the first-order model, do not generally agree with the experimental  $q_e$  values of pyrite ( $3.08$

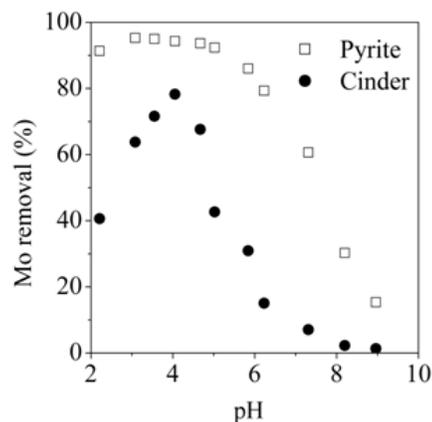


Fig. 2: Effects of varying equilibrium pH values on Mo(VI) adsorption.

$\text{mg}/\text{g}$ ) and cinder ( $1.21 \text{ mg}/\text{g}$ ), although the correlation coefficients of the first-order plots are high. Therefore, the pseudo-first-order model is not suitable for modeling the adsorption of Mo(VI) onto the pyrite and cinder. In contrast, the application of the pseudo second-order model leads to much better regression coefficients, all greater than 0.99. Furthermore, the calculated  $q_e$  values of pyrite ( $3.20 \text{ mg}/\text{g}$ ) and cinder ( $1.37 \text{ mg}/\text{g}$ ) are close to experimental values. Thus, these results indicate that the adsorption process studied generally followed the second-order kinetic model. Similar results have been observed in the adsorption of molybdate onto waste Fe(III)/Cr(III) hydroxide (Lian et al. 2012, Namasivayam & Prathap 2006).

**Adsorption isotherms:** The adsorption isotherms indicate how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The model parameters for both Langmuir and Freundlich models are given in Table 2. Both equations were suitable for the description of Mo(VI) sorption isotherm by pyrite and cinder, but the Langmuir equation was fitter than the Freundlich equation according to the correlation coefficients ( $R^2$ ). According to the coefficients of Langmuir isotherm, the maximum adsorption capacity of pyrite was  $8.35 \text{ mg Mo(VI)}/\text{g}$ , and that of cinder was only  $3.01 \text{ mg Mo(VI)}/\text{g}$ .

A lot of studies deal with the mechanism of heavy metal uptake by adsorbent materials. However, the conclusions of these studies are often contradictory. For instance, Elwakeel et al. (2009) and Moselhy et al. (2011) showed that Langmuir isotherm equation is well suited for modeling the sorption kinetics of Mo(VI) onto various adsorbents. On the other hand, Afkhami et al. (2009) and Namasivayam & Sangeetha (2006a) have shown Langmuir and Freundlich models were both successful in modeling the adsorption of Mo(VI) on different adsorbents. In conclusion, it appears from literature

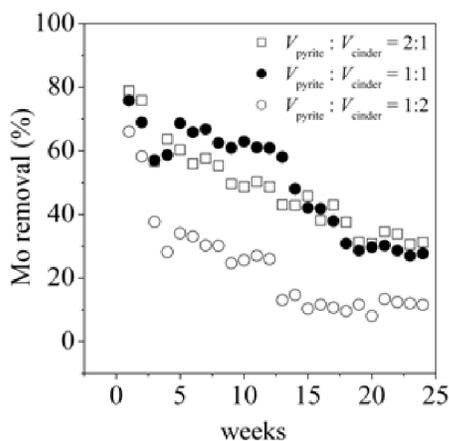


Fig. 3: Mo(VI) removal through pyrite and cinder columns.

that the adsorption isotherm is strongly dependent on the type of adsorbent material.

A comparison of the Mo(VI) adsorption capacity ( $q_m$ ) of some adsorbents based on the Langmuir isotherm constants has been made. The  $q_m$  for Mo(VI) on chelating resin (Kalal et al. 2011) and acid treated Fe(III)/Cr(III) hydroxide (Namasivayam & Prathap 2006) are 4.20 mg/g (pH 6.5) and 7.35 mg/g (pH 4.0), respectively. Besides, the  $q_m$  for Mo(VI) on pyrite (41.7 m<sup>2</sup>/g) (Bostick et al. 2003) is 12.47 mg/g (pH 4.0-7.0). This indicates that the surface area of adsorbents and lower pH is important for Mo(VI) removal.

The essential characteristics of the Langmuir isotherm model can be expressed in terms of a dimensionless constant,  $R_L$ , defined by Hall et al. (1996) as equation (3):

$$R_L = \frac{1}{1 + bC_0} \quad \dots(3)$$

Where,  $C_0$  is the initial Mo(VI) concentration (mg/L),  $R_L$  is a positive number whose value reveals the feasibility of the sorption process. The process is irreversible if  $R_L = 0$ , favorable if  $R_L < 1$ , linear if  $R_L = 1$  and unfavorable if  $R_L > 1$ . The values of  $R_L$  for pyrite and cinder are found to lie between 0.05-0.55 and 0.08-0.64, which signifies that the adsorption module is favorable at all the concentrations tested.

**Removal of Mo(VI) in column experiments:** Three columns flow-through adsorption tests were conducted for nearly 180 days. The Mo(VI) concentrations of every week are shown in Fig. 3. It showed that Mo(VI) after the columns 1# and 2# were largely reduced comparing to the column 3#. The constant effluent concentration of the pyrite-cinder columns at the beginning of operation were mainly due to the higher Mo(VI) sorption capacity, when the adsorbent mixture was fresh and the sorption sites were free for Mo(VI). Column 2# had higher Mo(VI) removal efficiency than

Table 2: Langmuir and Freundlich isotherm parameters.

Parameters	Pyrite	Cinder
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b}$	
$q_m$ (mg g <sup>-1</sup> )	8.35	3.01
$b$ (L mg <sup>-1</sup> )	1.52	1.03
$R^2$	0.9978	0.9951
Freundlich	$\ln q_e = \frac{1}{n} \ln C_e + \ln k$	
$K$	3.96	4.58
$n$	6.83	2.50
$R^2$	0.8517	0.9359

Column 1# in first three months, although higher amounts of pyrite were added in Column 1#. It was because fractional adsorption was dependent on Mo(VI) contents taken by the influent at the initial time when the amount of pyrite was sufficient for adsorption. With time going on, Mo(VI) removal rate of Column 1# was gradually higher than Column 2# due to higher amount of pyrite. But finally the difference was not evident. For half year, the average removal rate of Mo(VI) by Column 1# was 47.68%, and by Column 2# was 50.03%, respectively. It can be known from the results that the mixture of pyrite and cinder as filter media was feasible for Mo(VI) removal.

Regarding to the influence of hydraulic retention time, three columns showed similar trend. Except for Column 3#, removal efficiencies of Mo(VI) did not decline apparently as hydraulic loading increased. Moreover, over the operating days, effluent pH in Columns 1# and 2# varied mainly from 5.2 to 7.8. Comparing to influent pH, there was slight pH drop (about 1.4-1.8 unit) in the effluent. This is mainly caused by the acid production of oxidation reaction in pyrite.

In order to study the particles surfaces before and after adsorption, scanning electron microscopic (SEM) images for the samples of raw adsorbents and adsorbents from Column 2# were obtained at the terminative time of test. The micrographs are presented in Fig. 4. The micrograph of raw adsorbents showed the significant difference on the surface of cinder and pyrite. More micropores existed in the surface of cinder and relatively smooth on the surface of pyrite, which can also explain why cinder had higher speed rate of removal for Mo(VI) than pyrite in the first place.

By a comparison of the SEM images of the fresh pyrite surface (Fig. 4c) and after 24 weeks of exposure to the Column 2# (Fig. 4d), significant differences in surface morphology can be observed. The surfaces of the fresh pyrite are flat and have some small steps and no erosion pits were observed. However, the surfaces after 24 weeks of exposure to the Column 2# are quite different. Different patterns of erosion

pits can be identified, including clusters of pits and pearl-string-like chains (Fig. 4d). These erosion pits are roughly of the size of *Thiobacillus ferrooxidans* (Lu et al. 2006). The erosion of pyrite by *Thiobacillus ferrooxidans* has been observed by many different authors (Sanhueza et al. 1999, Rodriguez-Leiva & Tributsch 1988). They reported that the bacteria attached to the surface of pyrite caused erosion sites to be left as pits of approximately the same dimension of the bacteria. The erosion of the mineral surface occurred probably in the contact area below the cell that leads to the formation of the erosion pits. Therefore, a conclusion can be drawn from the observation of the pyrite surfaces that *Thiobacillus ferrooxidans* might have oxidized the pyrite by corroding the surfaces, which play an important role in Mo(VI) removal by pyrite. Therefore, although higher amount of pyrite in Column 1#, it did not show significant superiority for Mo(VI) removal. The micrograph (Fig. 4b) and (Fig. 4d) indicated that the pores of the adsorbents have been covered with adsorbate after a long-term operation, but the potential for longer operation was still existed due to the incompleteness occupied adsorption sites on the substrates surface.

## CONCLUSIONS

Based on the chemical composition of the pyrite and cinder and the appropriate solution pH, Fe content and S content contributed primarily to Mo(VI) immobilization in pyrite, and Al content contributed primarily to Mo(VI) immobilization in cinder. The maximum adsorption occurred at pH 3.0 for pyrite and pH 4.0 for cinder. The equilibrium adsorption data showed a good fit to Langmuir isotherm, and the maximum adsorption capacity of cinder and pyrite was found to be 3.01 and 8.35 mg Mo(VI)/g, respectively. Kinetic studies referred that Mo(VI) adsorption reaction by pyrite and cinder was a second-order rate model.

Results of three flow-through columns experiments indicated the feasibility of the mixture of pyrite and cinder for Mo(VI) removal. The columns with volume ratio of pyrite to cinder as 1:1 and 2:1 were better in the test because of the higher Mo(VI) removal efficiency for a long time. Due to the low cost and high adsorptive capacity, the pyrite-cinder mixture ( $V_{\text{pyrite}} : V_{\text{cinder}} = 1:1$ ) possess the potential to be utilized for cost-effective Mo(VI) removal.

The investigations of other cation and anion concentrations in the solution during Mo(VI) adsorption experiments should be explored further, which are important in study of the feasibility and the contribution mechanism for Mo(VI) removal by the mixture of pyrite and cinder. In addition, the long-term performance characteristics of pyrite and cinder columns need to be evaluated further before it can be recommended for critical application requiring guaranteed performance.

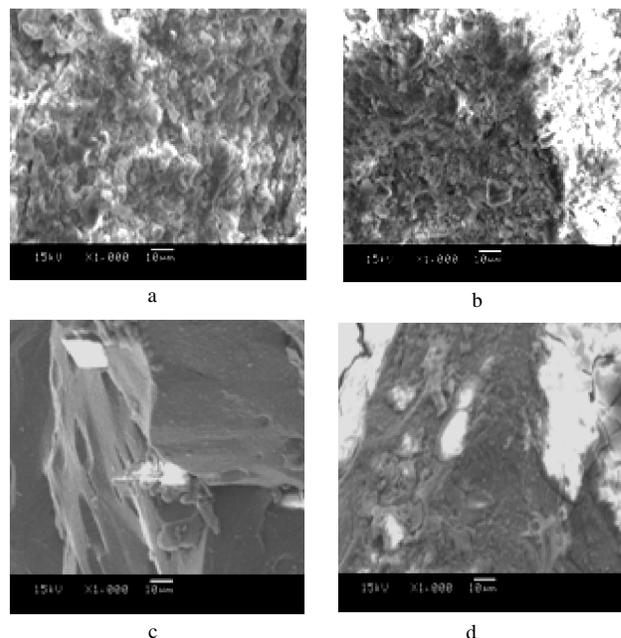


Fig. 4: SEM images of the cinder and pyrite. (a) cinder, (b) Mo(VI)-loaded cinder, (c) pyrite, (d) Mo(VI)-loaded pyrite.

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