Iron and lead ion adsorption by microbial flocculants in synthetic wastewater and their related carbonate formation

Minjie Yao[1,2], Bin Lian[1,3,*], Hailiang Dong[4,5], Jianchao Hao[3], Congqiang Liu[1]

1. State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China.
E-mail: yaominjiera@126.com
2. Key Laboratory of Environmental and Applied Microbiology, Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041, China
3. Jiangsu Key Laboratory for Microbes and Functional Genomics, Jiangsu Engineering and Technology Research Center for Microbiology,
College of Life Science, Nanjing Normal University, Nanjing 210046, China
4. State Key Laboratory of Geobiology and Environmental Geology, China University of Geosciences, Beijing 100083, China
5. Department of Geology and Environmental Earth Science, Miami University, Oxford, OH 45056, USA

Abstract

Although microbial treatments of heavy metal ions in wastewater have been studied, the removal of these metals through incorporation into carbonate minerals has rarely been reported. To investigate the removal of Fe^{3+} and Pb^{2+}, two representative metals in wastewater, through the precipitation of carbonate minerals by a microbial flocculant (MBF) produced by *Bacillus mucilaginosus*. MBF was added to synthetic wastewater containing different Fe^{3+} and Pb^{2+} concentrations, and the extent of flocculation was analyzed. CO_2 was bubbled into the mixture of MBF and Fe^{3+}/Pb^{2+} to initiate the reaction. The solid substrates were analyzed via X-ray diffraction, transmission electron microscopy and energy dispersive spectroscopy. The results showed that the removal efficiency decreased and the MBF adsorption capacity for metals increased with increasing heavy metal concentration. In the system containing MBF, metals (Fe^{3+} and Pb^{2+}), and CO_2, the concentrated metals adsorbed onto the MBF combined with the dissolved CO_2, resulting in oversaturation of metal carbonate minerals to form iron carbonate and lead carbonates. These results may be used in designing a method in which microbes can be utilized to combine CO_2 with wastewater heavy metals to form carbonates, with the aim of mitigating environmental problems.

Key words: *Bacillus mucilaginosus*; microbial flocculation; wastewater treatment; carbon dioxide fixation; mineral carbonation
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Introduction

With the rapid development of industries, excessive amounts of wastewater containing heavy metal ions and waste gases are discharged into the environment, causing environmental pollution and global warming. The removal of heavy metal ions from wastewater typically involves traditional chemical precipitation, redox reaction, ion exchange, adsorption, evaporation, electrolysis, and membrane methods (Kang et al., 2004, 2011; Kagramanov et al., 2010; Li et al., 2011; Mamba et al., 2009; Navarro et al., 2005). The microbiological method has been extensively used because of its cost effectiveness, superior performance, and environmental friendliness. The current microbial treatment of wastewater from domestic, brewage, dairy, and pharmaceutical sources largely depends on biosorption processes, including the removal of

suspended solids, organic material, and heavy metal ions (Abd-El-Haleem et al., 2008; Chen and Lian, 2005; Kang et al., 2005; Lian et al., 2008; Nadais et al., 2006; Xing et al., 2010; Yi and Lian, 2012). However, the ultimate fate of metal-loaded microbial substrates in these studies remains unclear. An alternative approach would be to permanently remove the metals through the precipitation of solid minerals. This approach would be more appealing if it could be combined with CO_2 fixation to concurrently remove CO_2 from the atmosphere.

CO_2 sequestration by mineral carbonation is a hot topic of research (Allen and Brent, 2010; Huijgen et al., 2005; Montes-Hernandez et al., 2007; Park and Fan, 2004; Voormeij and Simandl, 2004). The microbiological method of CO_2 fixation is particularly important because of its low cost and high efficiency relative to physical and chemical methods. Microbial fixation of CO_2 generally refers to the fixation of CO_2 into organic matter by

autotrophic organisms. CO_2 removal by heterotrophic organisms via precipitation of carbonate minerals, especially in combination with heavy metal removal, has received little attention in the past. One possible difficulty in precipitating heavy metal carbonate minerals is that metal ion concentrations in most wastewaters are not high enough to reach carbonate oversaturation. Hence, this method requires a preconcentration step through certain media to improve its feasibility. One such medium is microbial flocculant (MBF), which is noted for its exceptionally high sorption capacity.

MBF is a mixture of microorganisms and their secretion products. This type of flocculant not only has the traditional characteristics of chemical flocculation (Kang et al., 2005), but has the added advantages of high efficiency and safety with no pollution (Lian et al., 2008). Although the removal of heavy metal ions from wastewater using MBF has been studied (Chen and Lian, 2005; Kang et al., 2005; Lian et al., 2004), previous studies have targeted wastewater samples with low heavy metal concentrations. The primary mechanisms of bioadsorption include electrostatic attraction, surface complexation, ion exchange, redox, enzymatic action, and microdeposition. In addition, the characteristics of various adsorbents, the composition and structure of the cell wall and extracellular products, and the types of heavy metal ions all affect the bioadsorption mechanisms (Bai and Abraham, 2002; Tsezos and Volesky, 1982; Volesky et al., 1993; Wang, 2002; Wu and Li, 2001).

The treatment of wastewaters with high concentrations of heavy metals remains a difficult problem. The use of MBF adsorption of heavy metal ions and its subsequent ability to fix CO_2 has been rarely reported. The MBF produced by *Bacillus mucilaginosus* has been shown to lower the turbidity of sewage, to treat pharmaceutical wastewater, and to decolorize colored solutions (Lian et al., 2004, 2008). This flocculant has also been shown to lower concentrations of heavy metal ions (to less than 100 mg/L) from wastewater (Chen and Lian, 2005; Lian et al., 2004; Zhao et al., 2008).

The objective of this article was to investigate the ability of MBF produced by *B. mucilaginosus* to adsorb high concentrations of Fe^{3+} and Pb^{2+} from synthetic wastewaters and to precipitate iron and lead carbonates through fixation of atmospheric CO_2. The efficiency of metal removal by MBF was quantified via chemical methods, and carbonate precipitates were determined via X-ray diffraction and electron microscopy.

1 Materials and methods

1.1 MBF

The GY03 strain, isolated from a farmland soil in the nearby suburbs of Guiyang City, Guizhou Province, China, was identified as *B. mucilaginosus* by its morphology and 16S rDNA sequence (Lian et al., 2004, 2008). The

activated strain was inoculated into a 250 mL triangular flask containing 100 mL nitrogen medium (10.0 g sucrose, 0.3 g yeast extract, 0.5 g $(NH_4)_2SO_4$, 1.0 g $MgSO_4 \cdot 7H_2O$, 0.5 g $CaCO_3$, 1.0 g K_2HPO_4, 1000 mL distilled water, pH 7.0–7.5, autoclaved for 20 min at 121°C), cultured on a shaker at 29°C and 150 r/min for 5 days. The experiment was repeated twice to collect sufficient biomass. A total of 10 mL bacterial culture was inoculated into a nitrogen-free medium (5.0 g sucrose, 0.5 g $MgSO_4 \cdot 7H_2O$, 0.1 g $CaCO_3$, 2.0 g Na_2HPO_4, 0.005 g $FeCl_3$, 7.0 g glass dust, 1000 mL distilled water, pH 7.0–7.5) for more polysaccharide production and cultured on a shaker at 29°C and 150 r/min for 5 days (Chen and Lian, 2005; Lian et al., 2004, 2008). The resulting viscous bacterial culture was used for the subsequent metal adsorption experiments.

1.2 Wastewater and CO_2 source

Wastewater in typical mining areas contains high concentrations of heavy metal ions, with Fe^{3+} concentrations above 1000 mg/L (Zhao et al., 2008). In this study, synthetic wastewaters with high concentrations (100 to 1000 mg/L) of heavy metals was prepared and treated using the microbial method. Samples of synthetic wastewater containing Fe^{3+} and Pb^{2+} were prepared using analytical-grade $FeCl_3 \cdot 6H_2O$ and $Pb(NO_3)_2$, respectively, and a series of concentrations, namely, 171, 273, 576, 797 and 999 mg/L (final concentration) for Fe^{3+} and 88, 264, 462, 726 and 917 mg/L (final concentration) for Pb^{2+} were used.

The CO_2 used in the carbonate precipitation experiment was produced by a gas generator in the laboratory by reacting marble with 15% hydrochloric acid (analytical grade).

1.3 Fe^{3+} and Pb^{2+} adsorption experiments

A total of 10 mL MBF was added into a 250 mL triangular flask containing 90 mL synthetic wastewater with different concentrations of Fe^{3+} and Pb^{2+}. The mixtures were incubated on a shaker at 29°C and 150 r/min for 15 min. The samples were then kept set aside overnight. The concentrations of Fe^{3+} and Pb^{2+} remaining in the wastewater supernatant were determined via atomic absorption spectroscopy (AAS, PE-5100, Perkin-Elmer, USA) after centrifugation, and the pH of the supernatant was obtained. Three parallel samples were prepared for each metal concentration.

The adsorption extent (R, the extent of Fe^{3+} and Pb^{2+} removal from the solutions) and adsorption capacity (Q, the amount of adsorbed Fe^{3+} and Pb^{2+} in mg by 1 L MBF) were calculated using the following formula (Lian et al., 2008; Mo and Lian, 2011; Yao and Lian, 2009):

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

$$Q = \frac{(C_0 - C_e)V_0}{V} \tag{2}$$

where, C_0 (mg/L) is heavy metal ion concentration in the original wastewater; C_e (mg/L) is heavy metal ion concentration remaining in wastewater after adsorption by MBF, V (mL) is volume of the MBF (10 mL), and V_0 (mL) is total volume of the reaction solution (100 mL).

1.4 Carbonate precipitation experiments

After the adsorption of Fe^{3+} (999 mg/L) and Pb^{2+} (917 mg/L) by the MBF and the removal of the supernatant, viscous floc materials at the bottom of the flasks were reacted with excess CO_2 gas for 2 min. The CO_2 gas was introduced into the bottom of the flasks via a glass tube connected by a rubber tube. The flasks were then sealed with plastic wrap after CO_2 bubbling was stopped and set aside for 1 day at room temperature. The control samples consisted of three different concentrations of Fe^{3+} (171, 576 and 999 mg/L) and Pb^{2+} (88, 462 and 917 mg/L) in synthetic wastewater. These samples were reacted with CO_2 for 2 min without MBF. The pH and concentrations of the heavy metal ions in the supernatant were measured after the CO_2 bubbling was stopped, and the mixture was set aside for 1 day at room temperature. Three parallel samples were run for each test.

At the end of the experiments, sediments were collected after the particles were settled via gravity for 1 day, dried at 60°C and ground into powder. The powder samples were pressed and analyzed via powder X-ray diffraction (XRD, D/Max-2200, Rigaku, Japan) with Cu$K\alpha$ at 40 kV and 20 mA, and at 3°/min scan rate. The mineral phases were identified using the Joint Committee on Powder Diffraction Standards .

The samples were further analyzed via transmission electron microscopy (TEM, TEM-2000FXII, JEOL, Japan) and energy dispersive spectroscopy (EDS, Link ISIS, Oxford, UK) wih 180 kV. The powder samples were dispersed with ethanol, and placed on Cu grids, and dried in air. The magnification range was 2000–10000. The EDS results provided a means for mineral identification.

2 Results

2.1 Effect on the pH of Fe^{3+}- and Pb^{2+}-containing wastewater adsorbed onto MBF

The pH changes (**Fig. 1**) indicated the importance of MBF in Fe^{3+} and Pb^{2+} adsorption from synthetic wastewater. The pH of the Pb^{2+}-containing wastewater apparently decreased, whereas that of the Fe^{3+}-containing wastewater did not show any significant change after treatment by MBF. For both untreated and treated samples, the pH decreased with increasing heavy metal ion concentrations.

2.2 Adsorption efficiency of Fe^{3+} and Pb^{2+} onto MBF

The adsorption extents of Fe^{3+} and Pb^{2+} in wastewater (**Fig. 2**) showed a decreasing trend with increasing Fe^{3+} and Pb^{2+} concentrations. The extent of the adsorption
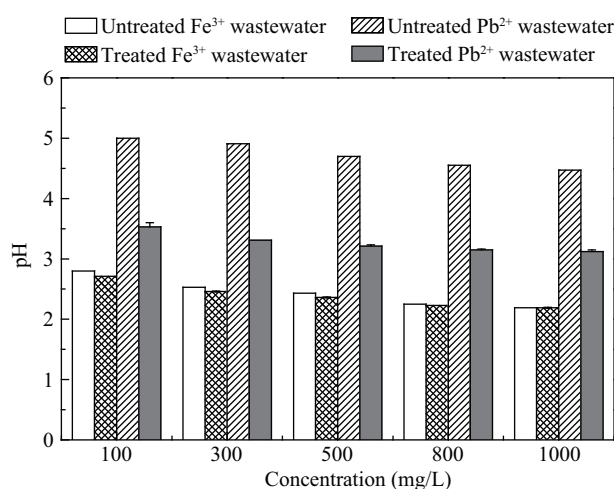

Fig. 1   Change in pH before and after Fe^{3+} and Pb^{2+} sorption by microbial flocculant (MBF). Volume of wastewater was 90 mL, the total volume (with 10 mL MBF) was 100 mL.

reached a minimum as the Fe^{3+} and Pb^{2+} concentrations further increased. The adsorption capacity increased with increasing Fe^{3+} and Pb^{2+} concentrations, suggesting that the adsorption capacity of MBF was not reached at the biggest.

2.3 Reaction of wastewater Fe^{3+} and Pb^{2+} with CO_2 in the absence of MBF

The pH did not change after the reaction of Fe^{3+}-containing wastewater with CO_2 and stayed within the 2.22–2.53 range, whereas the pH of Pb^{2+}-containing wastewater changed from 5.16–5.52 down to 4.06–4.65 after the reaction with CO_2, indicating that a significant amount of CO_2 dissolved in the wastewater. However, the Fe^{3+} and Pb^{2+} concentrations in wastewater showed little change (± 0.5%). No precipitates were formed during these experiments.

### 2.4 Carbonate formation in the presence of MBF

The MBF with adsorbed Fe^{3+} was yellow and homogeneous. After reacting with CO_2, the mixture turned brown, and solid precipitates appeared (**Fig. 3**).

2.5 XRD, TEM and EDS evidence of carbonate formation

The XRD peaks (not shown here) for the iron and lead carbonates were not well-resolved from the background, possibly because of the amorphous nature and small amounts of the metal carbonates formed.

The presence of iron and lead carbonates was confirmed via TEM and EDS (**Table 1**, **Fig. 4**). TEM results showed several iron and lead carbonates in the Fe^{3+}- and Pb^{2+}-adsorbed MBF samples that reacted with CO_2. However, in the corresponding control experiments (without reaction with CO_2), no iron and lead carbonates were found. EDS results identified Fe, C, and O and Pb, C, and O as the major elements in iron carbonate and lead carbonate,

◆ Adsorption extent   —— Adsorption capacity
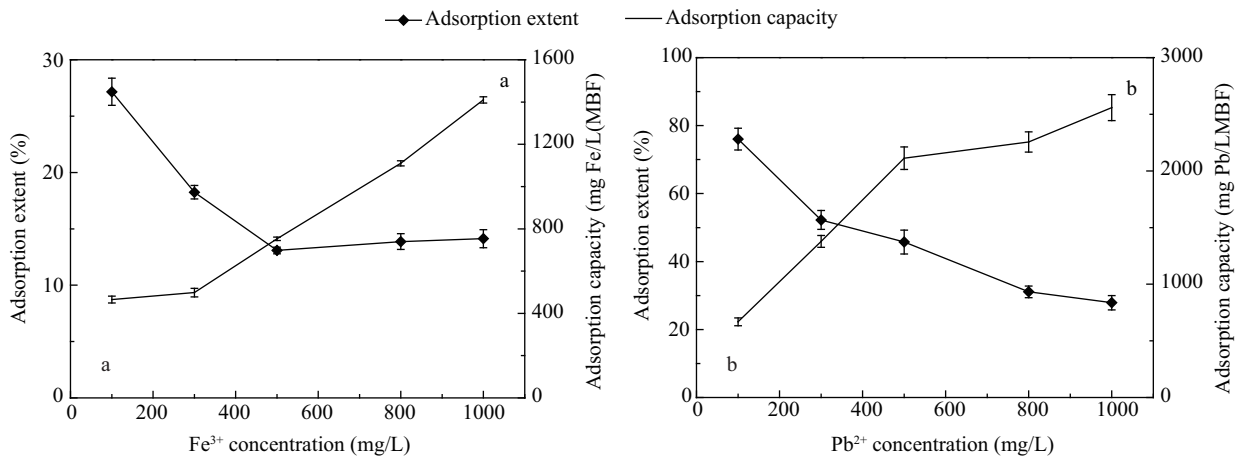
Fig. 2 Adsorption extent and capacity of Fe^{3+} (a) and Pb^{2+} (b) containing wastewater onto MBF. Volume of the MBF was 10 mL, the total volume was 100 mL.
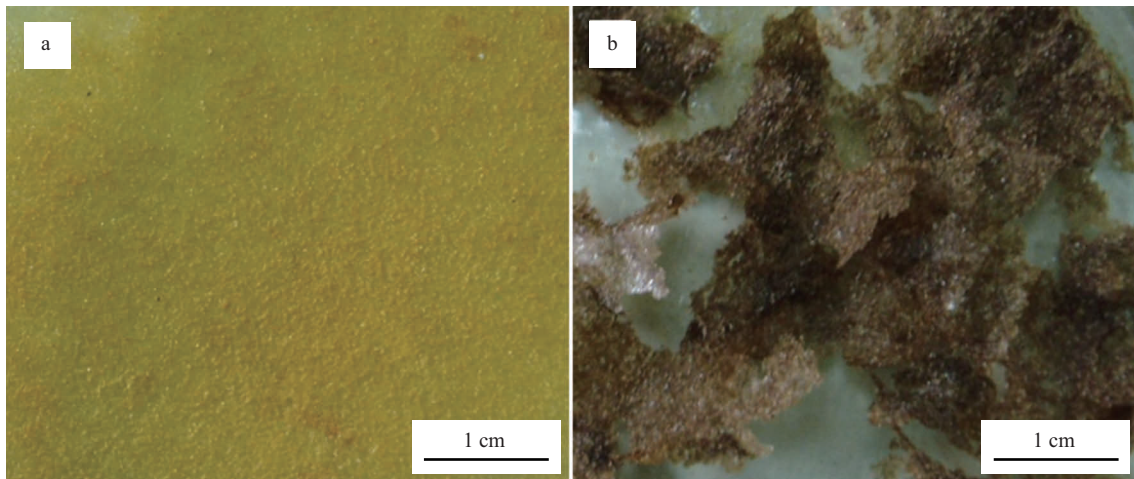
Fig. 3   Changes in the MBF with adsorbed Fe^{3+} before (a) and after (b) reacting with CO_2. Drying temperature: 60°C.

respectively. Under TEM, the carbonates appeared as irregularly shaped grains, and abundant flocculent materials were observed in close association with the carbonates (**Fig. 4**), suggesting that the iron carbonate and lead carbonate crystals were in the process of formation.

3 Discussion

3.1 Adsorption of Fe^{3+} and Pb^{2+} in wastewater by MBF

The MBF produced by *B. mucilaginosus* has high adsorption efficiency and can cause a pH increase at low heavy metal ion concentrations (below 100 mg/L) in wastewater

**Table 1**   TEM and EDS analyses of the carbonates

Sample	Mineral composition
MBF	Quartz, calcite (mostly)
MBF + adsorbed Fe^{3+}	Quartz (mostly), calcite (little), iron carbonate (rare)
MBF + adsorbed Fe^{3+} + CO_2	Iron carbonate (many)
MBF + adsorbed Pb^{2+}	Calcite (mostly), lead carbonate (rare)
MBF + adsorbed Pb^{2+} + CO_2	Lead carbonate (many)

(Lian et al., 2004; Zhao et al., 2008; Chen and Lian, 2005). In this study, a similar type of MBF has been demonstrated to adsorb high concentrations of heavy metals in the synthetic wastewater. The pH of the Fe^{3+}- and Pb^{2+}-containing wastewater decreased after metal adsorption by MBF, possibly because of the following ion exchange and charge neutralization reaction:

$$A^{n+} + nH_2O \rightleftharpoons nH^+ + A(OH)_n \downarrow \qquad (3)$$
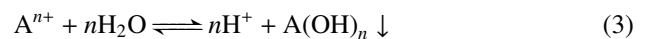
where, A^{n+} is metal cations.

The MBF produced by *B. mucilaginosus* is mainly an anionic flocculant (Konhauser and Urrutia, 1999; Zhao et al., 2008), which has a larger specific surface and would be expected to come in contact with heavy metal cations and form hydroxides in an aqueous solution through charge neutralization, adsorption, and other mechanisms over the course of the experiment. The A^{n+} in the solution would be adsorbed and $A(OH)_n$ precipitated by MBF, driving the Reaction (3) to the right direction and resulting in a decrease in the pH values. Considering Fe^{3+} hydrolysis is stronger than Pb^{2+} hydrolysis, the lower pH value was
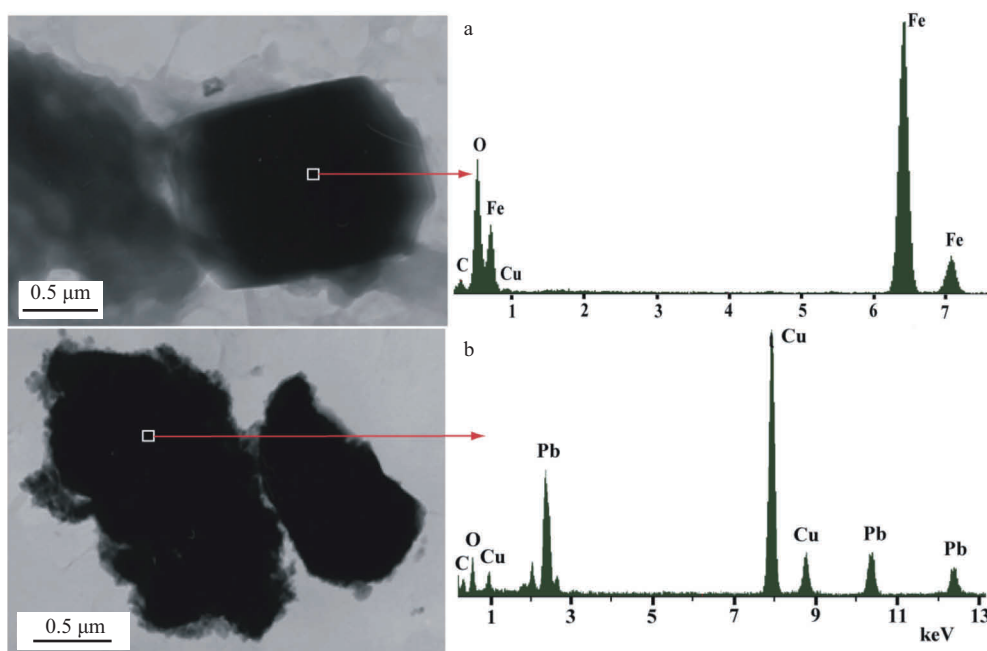
Fig. 4 Transmission electron microscopy (TEM) image and energy dispersive spectrum (EDS) showing iron carbonate and lead carbonate in the sample of MBF with adsorbed Fe^{3+} (a) and Pb^{2+} (b) after reacting with CO_2. TEM image magnification for Fe^{3+} is $\times$ 20,000 and for Pb^{2+} is $\times$30,000; EDS full scale = 2.74 k counts for Fe^{3+} and 1.89 k counts for Pb^{2+}; the Cu peaks were from the TEM grid.

expected in the solution containing Fe^{3+} (**Fig. 1**).

The pH of the Fe^{3+}- and Pb^{2+}-containing wastewaters decreased with the increasing heavy metal ion concentrations, because the increased amount of Fe^{3+} and Pb^{2+} resulted in increased binding with OH^-. As a result, a higher amount of H^+ was released to the aqueous solution, leading to the pH decreases. Unlike the Pb^{2+}-containing wastewater (pH 4.47–5.00), because the pH value was already low (2.19–2.80) in Fe^{3+}-containing wastewater, and pH decrease was not as apparent as in Pb^{2+}-containing wastewater (**Fig. 1**). Considering that the bacteria had thick capsules on their cell surfaces, the resulting adsorption may largely have been through surface adsorption by those capsules.

The decreased extent of adsorption of MBF with the increasing heavy metal ion concentrations suggests that at high metal ion concentrations, the transport of ions from the bulk solution to MBF surfaces, as opposed to the amount of adsorption sites on the MBF surfaces, may be the rate-limiting step in metal adsorption. This explanation is further supported by the increased adsorption capacity of MBF with increasing metal concentrations. The adsorption sites on MBF were apparently not saturated with the metal concentrations used in this study. These data suggest that the optimal adsorption capacity of MBF should be higher than 1410 mg/L for Fe and 2560 mg/L for Pb (**Fig. 2**).

Langmuir isotherm and Freundlich isotherm (Gabr et al., 2009; Kularatne et al., 2009) can be expressed, respectively, as following Eqs. (4) and (5):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{4}$$

$$\ln q_e = K_F + \frac{1}{n}\ln C_e \tag{5}$$

where, C_e (mg/L) is the equilibrium concentration of solute, q_e (mg) is the equilibrium amount of solute adsorbed per unit mass of adsorbent, q_m (mg/g) is the adsorption capacity, K_L and K_F are adsorption constants. The results showed that the adsorption capacity increased when the Pb^{2+} concentration increased. This increase was rapid at lower Pb^{2+} levels and tended to be saturated at higher levels, suggesting that the adsorption curve was in accordance with the Langmuir model:

$$\frac{C_e}{q_e} = 0.0004C_e + 0.0333 \qquad R^2 = 0.9884\,(n = 6) \tag{6}$$

For the Fe^{3+}-containing wastewater, the adsorption curve was not in accordance with the Langmuir. This result was similar to those reported by Hao et al. (2011).

3.2 Role of MBF in carbonate formation

No carbonates were formed in the control group without MBF. Conversely, iron and lead carbonates precipitated in the presence of MBF, suggesting that MBF played a key role in the formation of these minerals. These data suggest that the MBF served as the medium for mineral carbonation through CO_2 fixation.

Our data suggest the following carbonate formation mechanism: CO_2 dissolved in the aqueous solution and formed carbonate ions (CO_3^{2-}) due to the disassociation reaction. The resulting carbonate anions combined with the preconcentrated Fe^{3+} and Pb^{2+} on the MBF. The nucleation

of iron and lead carbonates may have initiated on the MBF and cell surfaces, a phenomena commonly observed on bacterial surfaces (Konhauser, 1997; Konhauser et al., 1993, 2002; Konhauser and Urrutia, 1999). Considering that the pH value of the viscous floc materials (bacterail-mineral complex) has some buffering capacity (Mo and Lian, 2011), and the carbonic anhydrase secreted by *B. mucilaginosus* (Zhang et al., 2011) can catalyze the following Reaction (7), which promotes carbonate formation.

$$H_2O + CO_2 \rightleftharpoons HCO_3^- + H^+ \qquad (7)$$

MBF can be applied to the removal of heavy metal ions from wastewater as well the formation of carbonate minerals through a reaction with CO_2. While one role of MBF may be to adsorb heavy metal ions for wastewater to meet various discharge standards, another function may serve as a medium for the nucleation of carbonate mineral crystals. In general, crystal growth from the liquid or gas phases involves three stages (Gabrielli et al., 1999): (1) oversaturation or overcooling of phases, which serve as the medium; this stage requires a pre-concentration step by the MBF because of its exceptionally high sorption capacity; (2) the nucleation stage, in which the adsorbed metal cations are electrostatically bound to the anionic surfaces of the bacterial cell and to the surrounding extracellular polymers for the CO_2 dissolution, in which they subsequently serve as nucleation sites for crystal growth; and (3) the growth phase, wherein the metal ions adsorbed by MBF form carbonate minerals. The formation of carbonate minerals can remove heavy metal ions from wastewater and permanently induce sequestration of CO_2 from the waste gas.

3.3 Implications for heavy metal and CO_2 removal by MBF

The results indicate that MBF is an efficient medium for heavy metal removal from wastewater. These adsorbed metals were incorporated into the carbonate mineral structures upon CO_2 bubbling into the metal-laden MBF. Compared with traditional methods, the treatment of heavy metal-laden wastewater using MBF is an easy and effective method of removing heavy metal ions. The method is further optimized when coupled with carbonate mineral formation. Abundant carbon dioxide is available from industrial waste gas, and carbonate minerals are thermally stable and are not easily degraded. Therefore, the proposed method can potentially be used for heavy metal removal and CO_2 sequestration using MBF.

4 Conclusions

The MBF produced by *B. mucilaginosus* removed high concentrations of Fe^{3+} and Pb^{2+} from wastewater, and the adsorption extent was closely related to the wastewater

pH and the Fe^{3+} and Pb^{2+} concentrations. Iron and lead carbonates were observed in the Fe^{3+} and Pb^{2+}-adsorbed MBF samples reacted with CO_2, but not in the control samples (without MBF), suggesting that MBF played a key role in carbonate formation. This study demonstrates a permanent method of heavy mental ion removal from wastewater using MBF. MBF not only removed heavy mental ions via adsorption from wastewater, but also formed carbonate minerals by combining with CO_2, which can address further problems in waste management.

References

Abd-El-Haleem D A M, Al-Thani R F, Al-Mokemy T, Al-Marii S, Hassan F, 2008. Isolation and characterization of extracellular bioflocculants produced by bacteria isolated from qatari ecosystems. *Polish Journal of Microbiology*, 57(3): 231–239.

Allen D J, Brent G F, 2010. Sequestering CO_2 by mineral carbonation: stability against acid rain exposure. *Environmental Science and Technology*, 44(7): 2735–2739.

Bai R S, Abraham T E, 2002. Studies on enhancement of Cr(VI) biosorption by chemically modified biomass of *Rhizopus nigricans*. *Water Research*, 36(5): 1224–1236.

Chen Y, Lian B, 2005. Ability of *Bacillus mucilaginosus* GY03 strain to adsorb chromium ions. *Pedosphere*, 15(2): 225–231.

Gabr R M, Gad-Elrab S M F, Abskharon R N N, Hassan S H A, Shoreit A A M, 2009. Biosorption of hexavalent chromium using biofilm of *E. coli* supported on granulated activated carbon. *World Journal Microbiology and Biotechnology*, 25(10): 1695–1703.

Gabrielli C, Maurin G, Poindessous G, Rosset R, 1999. Nucleation and growth of calcium carbonate by an electrochemical scaling process. *Journal of Crystal Growth*, 200(1-2): 236–250.

Hao J C, Deng Y N, Cao W C, Lian B, Liu C Q, 2011. Removal of Fe^{3+} in simulated wastewater by *Bacillus mucilaginosus*, *Aspergillus niger*, zeolite and their different combination. *Chinese Journal of Environmental Engineering*, 5(7): 1507–1512.

Huijgen W J J, Witkamp G J, Comans R N J, 2005. Mineral CO_2 sequestration by steel slag carbonation. *Environmental Science and Technology*, 39(24): 9676–9682.

Kagramanov G G, Farnosova E N, Kandelaki G I, 2010. Heavy metal cationic wastewater treatment with membrane methods. In: Water Treatment Technologies for the Removal of High-Toxicity Pollutants. Springer Press, the Netherlands. 177–182.

Kang O L, Ramli N, Said M, Ahmad M, Yasir S M, Ariff A, 2011. *Kappaphycus alvarezii* waste biomass: A potential biosorbent for chromium ions removal. *Journal of Environmental Sciences*, 23(6): 918–922.

Kang S Y, Lee J U, Kim K W, 2005. Metal removal from wastewater by bacterial sorption: Kinetics and competition studies. *Environmental Technology*, 26(6): 615–624.

Kang S Y, Lee J U, Moon S H, Kim K W, 2004. Competitive adsorption characteristics of Co^{2+}, Ni^{2+}, and Cr^{3+} by IRN-77 cation exchange resin in synthesized wastewater. *Chemosphere*, 56(2): 141–147.

Konhauser K O, 1997. Bacterial iron biomineralisation in nature. *FEMS Microbiology Reviews*, 20(3-4): 315–326.

Konhauser K O, Fyfe W S, Ferris F G, Beveridge T J, 1993. Metal sorption and mineral precipitation by bacteria in two Amazonian River systems – Rio-Solimoes and Rio-Negro, Brazil. *Geology*, 21(12): 1103–1106.

Konhauser K O, Schiffman P, Fisher Q J, 2002. Microbial mediation of authigenic clays during hydrothermal alteration of basaltic tephra, Kilauea Volcano. *Geochemistry, Geophysics, Geosystems*, 3(12): 1–13.

Konhauser K O, Urrutia M M, 1999. Bacterial clay authigenesis: a common biogeochemical process. *Chemical Geology*, 161(4): 399–413.

Kularatne R K A, Kasturiarachchi J C, Manatunge J M A, Wijeyekoon S L J, 2009. Mechanisms of manganese removal from wastewaters in constructed wetlands comprising water hyacinth (*Eichhornia crassipes* (Mart.) Solms) grown under different nutrient conditions. *Water Environment Research*, 81(2): 165–172.

Li Y H, Xia B, Zhao Q S, Liu F Q, Zhang P, Du Q J et al., 2011. Removal of copper ions from aqueous solution by calcium alginate immobilized kaolin. *Journal of Environmental Sciences*, 23(3): 404–411.

Lian B, Chen Y, Yuan S, Zhu L J, Liu C Q, 2004. Study on the flocculability of metal ions by *Bacillus mucilaginosus* GY03 strain. *Chinese Journal of Geochemistry*, 23(4): 380–386.

Lian B, Chen Y, Zhao J, Teng H H, Zhu L J, Yuan S, 2008. Microbial flocculation by *Bacillus mucilaginosus*: Applications and mechanisms. *Bioresource Technology*, 99(11): 4825–4831.

Mamba B B, Nyembe D W, Mulaba-Bafubiandi A F, 2009. Removal of copper and cobalt from aqueous solutions using natural clinoptilolite. *Water SA*, 35(3): 307–314.

Mo B B, Lian B, 2011. Hg(II) adsorption by *Bacillus mucilaginosus*: mechanism and equilibrium parameters. *World Journal of Microbiology and Biotechnology*, 27(5): 1063–1070.

Montes-Hernandez G, Renard F, Geoffroy N, Charlet L, Pironon J, 2007. Calcite precipitation from CO_2-H_2O-$Ca(OH)_2$ slurry under high pressure of CO_2. *Journal of Crystal Growth*, 308(1): 228–236.

Nadais H, Capela I, Arroja L, 2006. Intermittent vs continuous operation of upflow anaerobic sludge bed reactors for dairy wastewater and related microbial changes. *Water Science and Technology*, 54(2): 103–109.

Navarro R R, Wada S, Tatsumi K, 2005. Heavy metal precipitation by polycation-polyanion complex of PEI and its phosphonomethylated derivative. *Journal of Hazardous Materials*, 123(1-3): 203–209.

Park A H A, Fan L S, 2004. CO_2 mineral sequestration: physically activated dissolution of serpentine and pH swing process. *Chemical Engineering Science*, 59(22-23): 5241–5247.

Tsezos M, Volesky B, 1982. The mechanism of uranium biosorption by *Rhizopus arrhizus*. *Biotechnology and Bioengineering*, 24(2): 385–401.

Volesky B, May H, Holan Z R, 1993. Cadmium biosorption by *Saccharomyces cerevisiae*. *Biotechnology and Bioengineering*, 41(8): 826–829.

Voormeij D A, Simandl G J, 2004. Geological, ocean, and mineral CO_2 sequestration options: A technical review. *Geoscience Canada*, 31(1): 11–22.

Wang J L, 2002. Biosorption of copper(II) by chemically modified biomass of *Saccharomyces cerevisiae*. *Process Biochemistry*, 37(8): 80–86.

Wu J, Li Q B, 2001. Study on mechanism of lead biosorption by phanerochaete chrysosporium. *Acta Scientiae Circumstantiae*, 21(3): 291–295.

Xing W, Guo W S, Ngo H H, Cullum P, Listowski A, 2010. Integration of inorganic micronutrients and natural starch based cationic flocculant in Primary Treated Sewage Effluent (PTSE) treatment. *Separation Science and Technology*, 45(5): 619–625.

Yao M J, Lian B, 2009. Microbial flocculability on wastewater containing high concentration heavy metal ions. *Environmental Science and Technology*, 32(11): 1–4.

Yi Z J, Lian B, 2012. Adsorption of U(VI) by *Bacillus mucilaginosus*. *Journal of Radioanalytical and Nuclear Chemistry*, 293(1): 321–329.

Zhang Z C, Lian B, Hou W G, Chen M X, Li X, Li Y, 2011. *Bacillus mucilaginosus* can capture atmospheric CO_2 by carbonic anhydrase. *African Journal of Microbiology Research*, 5(2): 106–112.

Zhao H X, Lian B, Xie Z H, Chen Y, Zhu L J, 2008. Water quality analysis and microbial treatment to the colliery area of Kaili in Guizhou Province, China. *Acta Mineralogica Sinica*, 28(1): 71–76.