



Calcifying cyanobacterium (*Nostoc calcicola*) reactor as a promising way to remove cadmium from water



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ABSTRACT

Application of the conventional bioreactors based on biosorption for removal of heavy metals is limited because they can be broken through by heavy metals. The novel calcifying cyanobacteria reactors based co-precipitation of heavy metals with carbonate minerals induced by cyanobacteria may be a promising alternative technology to overcome the shortcomings of biosorption. In this study, removal of cadmium (Cd) from wastewater using three calcifying bacterium *Nostoc calcicola* reactors was investigated. *N. calcicola* can significantly increase aquatic phase pH in the reactor, associated with a decrease of dissolved inorganic carbon (DIC) content in the effluent. During the two-month operation of the bioreactors, over 98% of Cd removal was obtained with an initial Cd²⁺ concentration of 2.5 μM. Cd²⁺ was mainly sequestered in organic-bound fraction, followed by a small amount of carbonate and exchangeable fractions in the *N. calcicola* cell. A crystalline compound of Ca, C, and O, as well as a small amount of Cd on the surface of *N. calcicola* cell, was observed. The two-month high Cd removal efficiency of the *N. calcicola* reactors shows the calcifying cyanobacteria reactors have advantages over the conventional biosorption system, which can be shortly broken through for removal of heavy metals. Although the results revealed that calcifying cyanobacterium reactor is a promising way to remove Cd from water, assessment of its longer-term performance of heavy metal removal is needed.

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1. Introduction

Cadmium (Cd) can cause considerable environmental and health problems due to its mobility and high toxicity to plants, animals and human being because of its mobility and toxicity to plants and animals (Alloway, 1995; Xu et al., 2014). Wastewaters from a variety of industries, including plating, refinery, mine and electron devices industries, frequently contain high levels of Cd

and other heavy metals. Cd is also one of the most common toxic metals found in surface water and groundwater in many countries including China (Su et al., 2013). Many conventional methods such as chemical precipitation, coagulation and ion-exchange have been used to remove heavy metals from wastewaters. However, these methods sometimes become less effective and more expensive when the volume of wastewater containing low concentrations of metal ions (Kapoor and Viraraghavan, 1995). Biosorption of heavy metals by microbes, including bacteria, fungi, microalgae and cyanobacteria, has been proven to be effective in removing heavy metals from wastewater (Pan et al., 2005, 2009a,b) and it is more cost-effective and more environmental friendly than the conventional physical and chemical methods (Areco and dos Santos Afonso, 2010; Das et al., 2008; Muñoz and Guieysse, 2006). Biosorption of heavy metals using photosynthetic microbes such as cyanobacteria is most cost-effective because of their autotrophy. Thus, bioremediation of heavy metal pollution by algae and cyanobacteria has attracted increasing research interests

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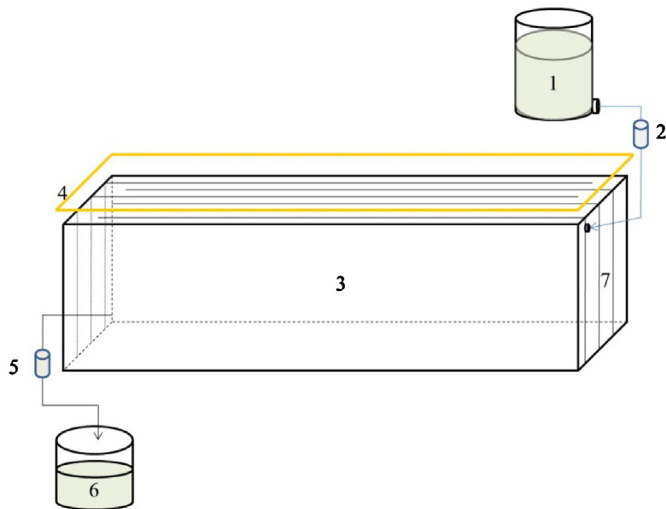


Fig. 1. Schematic of the cyanobacterial reactor ((1) Inlet bottle; (2) inflow regulator; (3) glass reactor; (4) fluorescent lamp; (5) flow regulator; (6) outlet bottle; and (7) deflector baffle).

(Gupta et al., 2001; Davis et al., 2003; Vilar et al., 2006; Akhtar et al., 2007; Bulgariu and Bulgariu, 2013). However, the practical application of biosorption is very limited because of some problems with the biosorption technology. The reactors packed with bioadsorbents may be broken through shortly. Furthermore, in a biosorption system considerable amount of heavy metal ions are adsorbed by the extracellular polymeric substances (EPS) during adsorption (Zhang et al., 2006, 2010, 2011; Pan et al., 2010) and the EPS bound metal ions may be released into water again due to dissociation of metal-EPS complexes or decomposition of EPS when some environmental factors change (Zhang et al., 2013; Song et al., 2015).

Bioremediation based on co-precipitation of heavy metal ions with minerals produced by microbes shows great potential in immobilization of heavy metals from water (Gadd, 2000) since this method can overcome some limits of biosorption. When heavy metals are precipitated with the biogenic minerals, they are usually incorporated into the lattice of mineral crystals, and the lattice trapped heavy metals are geologically stable. A variety of microbially produced minerals such as calcite have been proven to be effective in immobilization of heavy metal ions (Gadd, 2000; Achal et al., 2011, 2012a,b,c, 2013; Li et al., 2015). Biomineralization based on non-photosynthetic or photosynthetic microbes induced calcite precipitation (MICP) is one of these promising techniques to immobilize toxic metals with additional advantages over current bioremediation techniques (Pan, 2009; Achal et al., 2011, 2012a,b,c, 2013). Some cyanobacteria (e.g., *Nostoc calcicola*) can efficiently produce calcium carbonate minerals around their cells during their photosynthesis (Kawaguchi and Decho, 2002; Obst et al., 2009) and are promising candidates for decontamination of heavy metals based on MICP. On one hand, the ambient CO_2 around the cyanobacterial cell is continuously consumed during photosynthesis, which increases water pH of the

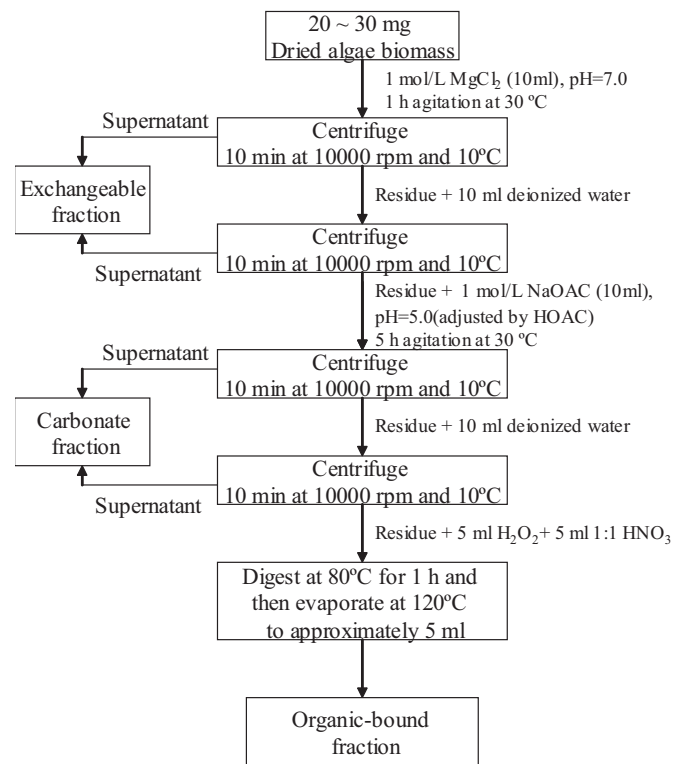


Fig. 2. Flow chart for analysis of Cd and Ca speciation in cyanobacterial biomass.

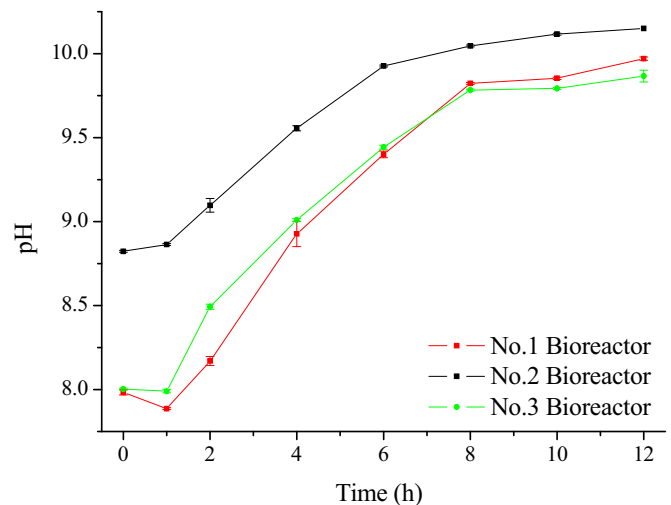


Fig. 3. Water pH change of three cyanobacterial reactors during 12 h of illumination time.

microenvironment near the cell. On the other hand, EPS on the surface of cell usually has strong binding capacity for cations such as Ca^{2+} (Pan, 2010). The increased pH and Ca concentration in the

Table 1
Chemical composition of tap water.

Element	Mn	Cu	Zn	Cr	Pb	Ni	Cd	Al	Ca	Co	Sr	Fe
Content (mg/L)	0.36	0.007	0.018	ND	0.004	0.15	0.085	2.64	19.9	0.045	0.12	0.62

microscale environment around the cell generates supersaturation of Ca^{2+} and carbonate ions and consequently induces precipitation of calcium carbonate minerals. During precipitation of carbonate minerals (e.g., calcite), metal ions with ion radius close to Ca^{2+} , such as Cd^{2+} and Cu^{2+} , may be incorporated into the calcite crystal by their replacement of Ca^{2+} in the lattice (Pan, 2009). This makes cyanoremediation (Mani and Kumar, 2014) based on calcifying cyanobacteria a better way to remove heavy metals than conventional biosorption.

N. calcicola is one of the nitrogen fixing cyanobacteria with strong calcification ability to form carbonate sediments (Arp et al., 1999). In addition, *Nostoc* is not toxic to animals and human being and some *Nostoc* species are edible. Therefore, *N. calcicola* can be safely used for bioreactor for removal of heavy metals. In addition, *Nostoc* cyanobacteria are nitrogen fixer, which can reduce feed cost of nitrogen. This study aims to (1) investigate the performance of calcifying *N. calcicola* reactors for Cd removal and

(2) reveal the removal mechanisms of Cd by cyanobacterial calcification.

2. Materials and methods

2.1. Cyanobacterium strain and culture

N. calcicola (CCAP1453/1), purchased from Scottish Association for Marine Science, was cultivated in batch culture of Jaworski's Medium (Thompson et al., 1988) at 25 °C and light intensity of 30 $\mu\text{mol}/(\text{m}^2 \text{s})$ with a 12 h/12 h light-dark cycle.

2.2. Bioreactor setup and start-up

Three identical cuboid reactors (R1, R2, and R3) were set up to evaluate the Cd removal performance in continuous mode. The reactors (Fig. 1) were made of plexiglass, with dimensions of

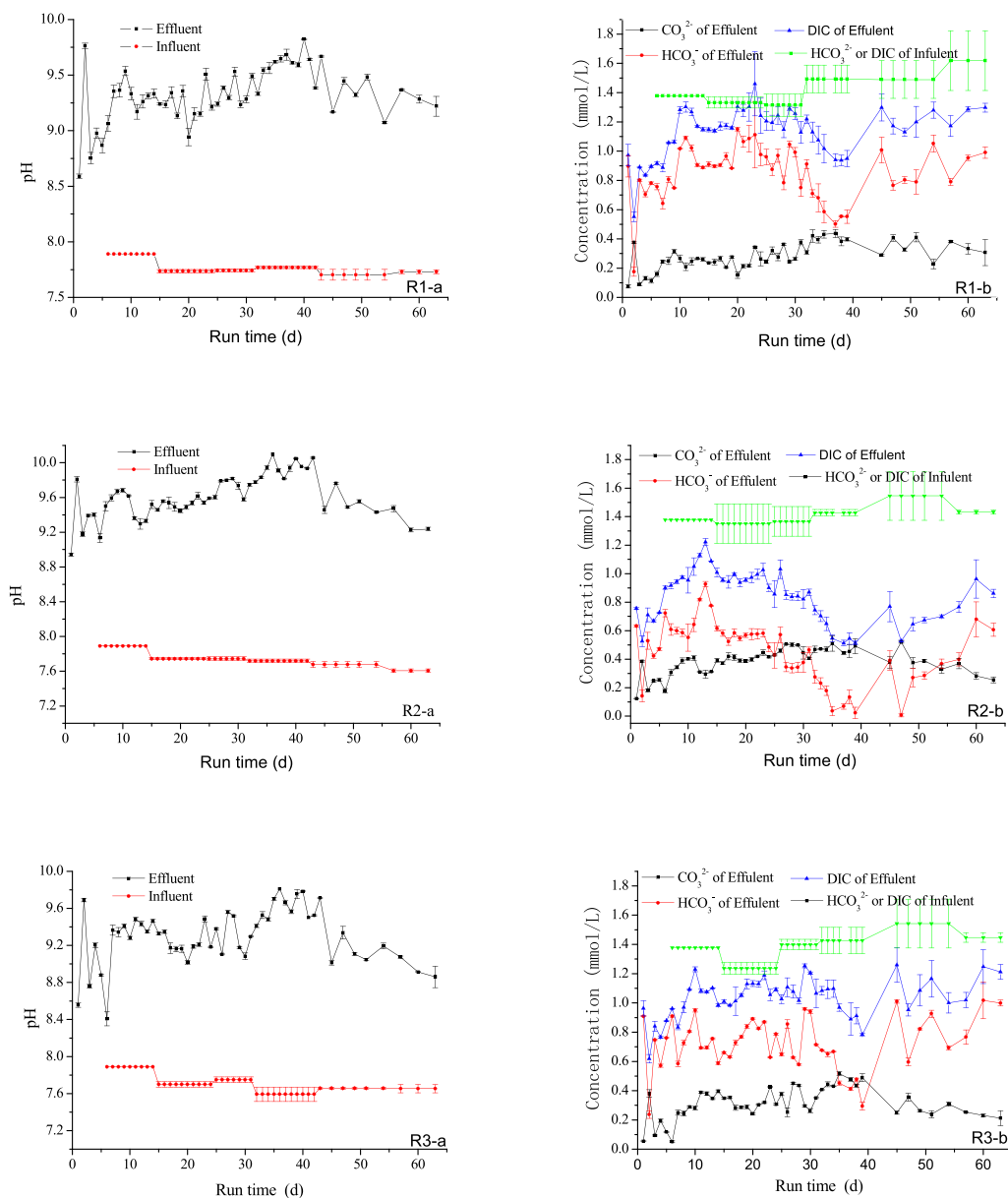


Fig. 4. Water pH of three bioreactors during their two months of operation (R1-a, R2-a, R3-a); concentrations of CO_3^{2-} , HCO_3^- and DIC of three bioreactors during their two months operation (R1-b, R2-b, R3-b).

100 cm × 10 cm × 7.8 cm and a working volume of 7500 mL. Six deflector baffles (95 cm × 7.8 cm) were fixed perpendicularly to the bioreactor bottom at equal spacing interval to increase the carrier surface for *N. calcicola* and the flow path was thus increased to 7 m. Four 110 cm-long fluorescent lamps were used as light source. The distance between the upper surface of the reactor and fluorescent lamps is 4 cm to achieve an illumination intensity of $30 \mu\text{mol m}^{-2} \text{s}^{-1}$ on the top surface of the reactors. The photoperiod for bioreactors was 12 h:12 h (light:dark). In order to avoid the effect of vaporization, the bioreactors were covered with glass plates.

After two months of cultivation in the reactors, *N. calcicola* biofilms formed on the interior walls of the reactors. Artificial wastewater was prepared by adding certain amount of CdCl_2 and CaCl_2 in boiled tap water. The chemical composition of boiled tap water is shown in Table 1. The initial pH of the boiled tap water was 8.0 for reactors 1 and 3 and 8.7 for reactor 2. During the operation of the reactor, pH was not adjusted. The reactors were operated in fed-batch mode, and wastewater was fed with a hydraulic retention time of 10 days. Ca^{2+} concentration in R1, R2, and

R3 was 0, 2.5, and 5 mM, respectively. Cd^{2+} concentration of the artificial wastewater for all reactors was set as $2.5 \mu\text{M}$ because Cd^{2+} concentration in real wastewater usually ranged from a few μM to tens of μM (Kulkarni and Kaware, 2013). The reactors were operated at 25°C , and water samples at 0 (the inlet), 1, 3, and 7 m (the outlet) from the feed wastewater inlet were collected periodically.

2.3. Analytical methods for water samples and light intensity

Concentrations of CO_3^{2-} and HCO_3^- and pH of the water samples were determined immediately after sampling using an automatic potentiometric titrator (Metrohm-titrator 702 SM Titrino, Switzerland) equipped with a glass electrode (Metrohm 6.0130.100); 0.0294 M H_2SO_4 (Sigma, AR) was used as the titrant (Allison et al., 2010). Concentrations of Ca^{2+} and Cd^{2+} in the water samples were determined by ICP-MS (ELAN DRC II, PerkinElmer, USA) (Zhang et al., 2014). The ICP-MS instrument was calibrated by the Agilent multi-element calibration standard-2A. The water

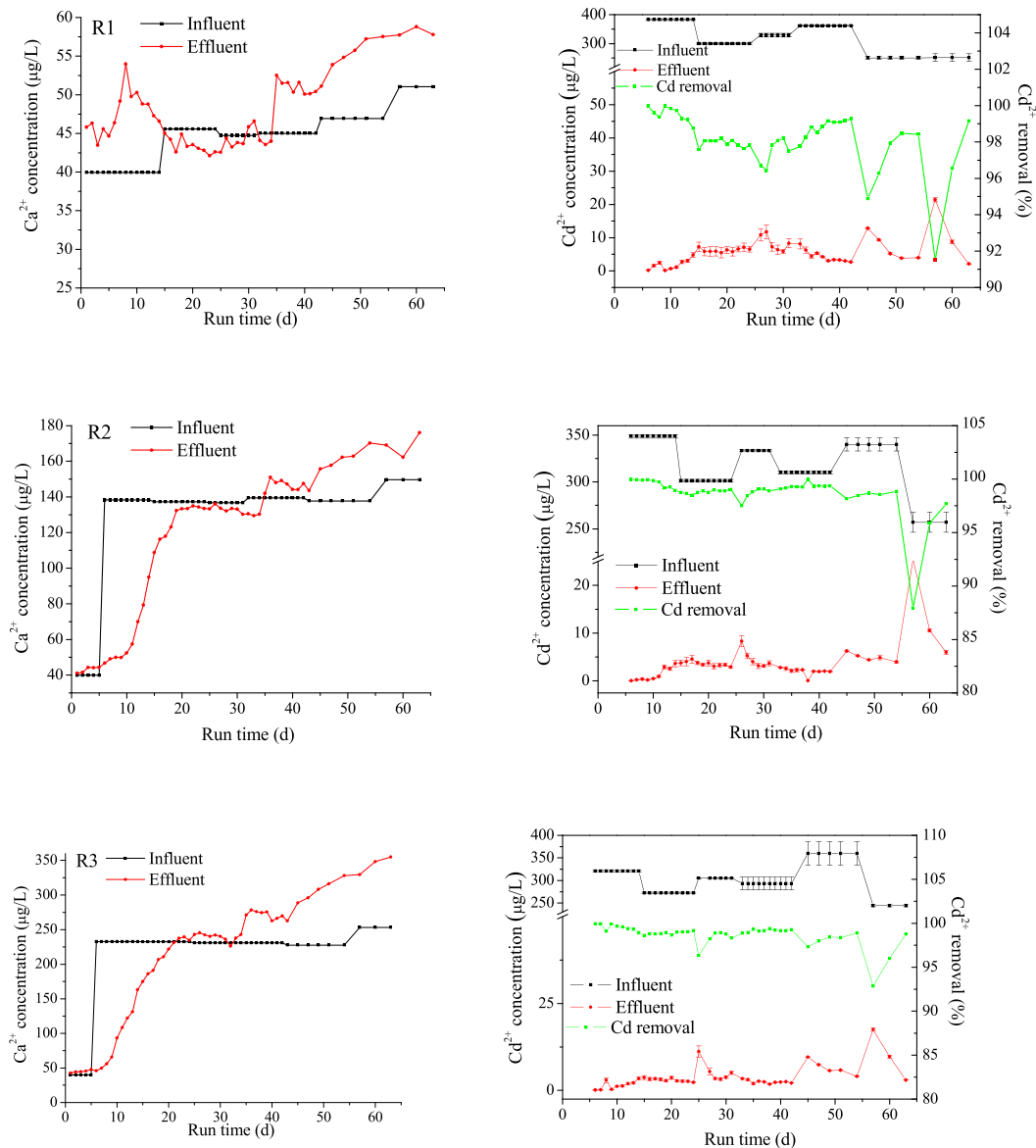


Fig. 5. Ca^{2+} concentration of the influent and effluent of the three bioreactors during their two months of operation (R1-a, R2-a, R3-a); Cd^{2+} concentration of the influent and effluent and Cd^{2+} removal of the three bioreactors during their two months of operation (R1-b, R2-b, R3-b).

samples were filtrated through a 0.22 μm acetate cellulose membranes (Beihua Liming Inc., Beijing, China), and then acidized by concentrated nitric acid of analytical grade (purity >95%) for measurement. Light intensity on the top surface of reactors was measured by a radiation illuminance meter (Model ESM-Q1, Ecotron Scientific Inc.).

2.4. Speciation analysis of Ca and Cd in algal biomass

On the 50thd of running, a certain amount of attached cyanobacterial biomass at 0, 1, 3, and 7 m from the water inlet was obtained from each reactor and subjected to freeze-drying (Labconco IEC 61010-1, USA). Afterward, 20–40 mg of dry biomass was analyzed to determine the exchangeable, carbonate bound and organic bound fractions of Cd and Ca in *N. calcicola* biomass (Siong and Asaeda, 2009). The extraction steps were shown in Fig. 2.

The Cd and Ca contents in the extract of each step were simultaneously determined by ICP-MS (Zhang et al., 2014), and then calculated into the content of the algal biomass.

The freeze-dried algal biomass was fixed on the carbon plate and sprayed with gold. The samples were analyzed using a scanning electron microscope (SEM, ZeissSuper 55VP, Germany) coupled with an energy dispersive X ray spectrometer (EDX, Bruker XFlash 5010, Germany) (Achal et al., 2013).

3. Results and discussion

3.1. pH changes in the effluent

The pH of the three reactors increased from 8–8.7 to 9.7–10 within 8 h and thereafter remained stable (Fig. 3). This finding suggests the strong photosynthetic activity of *N. calcicola* under the light. When dissolved inorganic carbon (DIC) in the

wastewater was consumed during photosynthesis, OH^- was released (Merz-Preiß and Riding, 1999), thereby causing an increase of pH. Extensive studies showed that water pH increased due to photosynthesis of cyanobacteria or algae (Shiraishi, 2012; Bundeleva et al., 2014).

3.2. pH, CO_3^{2-} , HCO_3^- , and DIC changes in the reactors

During the operation period, the pH of R1, R2, and R3 effluents increased to 9.2, 9.6, and 9.3, respectively, much higher than 7.7 of the influents (Fig. 4), indicating that the photosynthesis of algae increases the pH (Small and Adey, 2001). The much lower DIC concentrations in the effluents compared with those of the influents suggest the efficient use of DIC by *N. calcicola* for photosynthesis. The changing trend of CO_3^{2-} concentration was consistent with the pH of the effluent, whereas HCO_3^- concentration showed an opposite changing trend to CO_3^{2-} concentration. This finding implies that CO_3^{2-} in the aquatic phase is mainly caused by the hydrolysis of HCO_3^- at high pH (Ramaraj et al., 2015).

3.3. Changes of Ca^{2+} concentration and Cd^{2+} removal

After 6 d, tap water was replaced with wastewater influent in R2 and R3, whereas R1 was maintained for background control. The results showed that Ca^{2+} concentrations in the effluent were higher than those in the influent during the late operation stage. This finding may be attributed to the fact that Ca fixed by cyanobacterial cells was partially released because of death of algal cells. The content of the three reactors was oversaturated with Ca^{2+} and supported normal metabolism, and then induced CaCO_3 deposits (Obst et al., 2009).

Cadmium ions were efficiently removed by over 98% in the three reactors. During operation, Cd^{2+} concentration was reduced

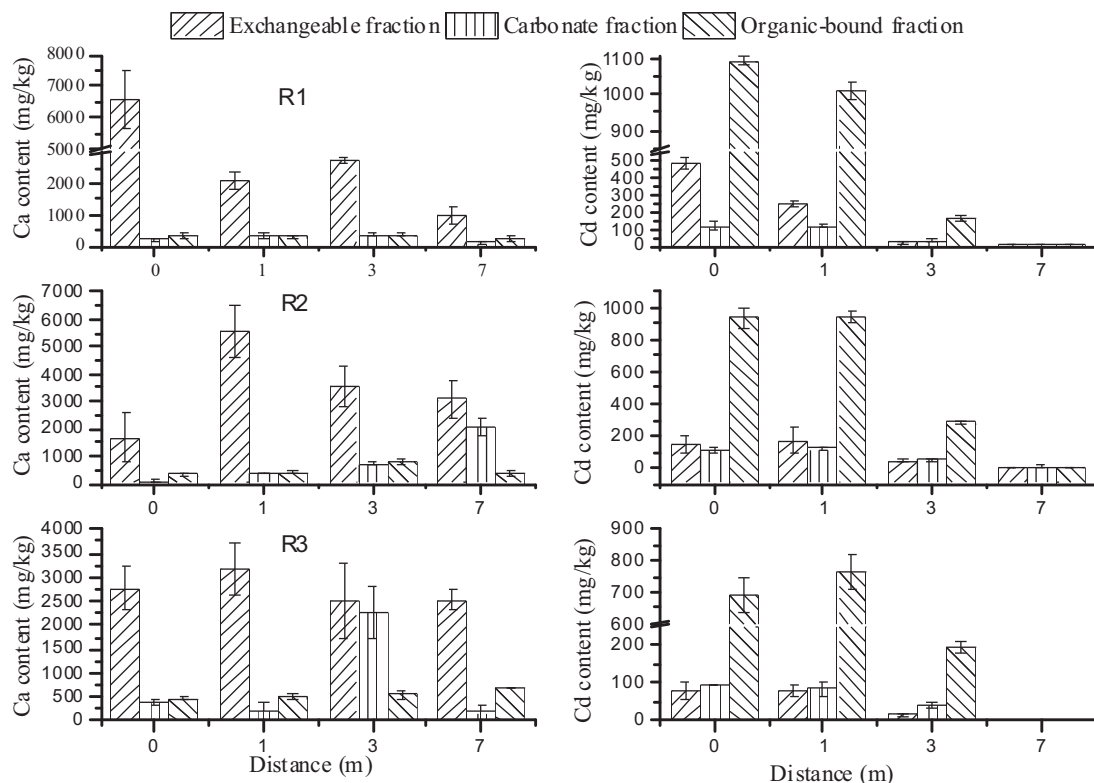


Fig. 6. Exchangeable, carbonate and organic-bound fractions of Ca and Cd in cyanobacterial biomass at different distances from the inlet of the three bioreactors R1, R2 and R3.

remarkably from 326.1 $\mu\text{g/L}$ to 5.6 $\mu\text{g/L}$ in R1, 319.6 $\mu\text{g/L}$ to 3.9 $\mu\text{g/L}$ in R2, and 301.5 \pm 30.9 $\mu\text{g/L}$ to 4.4 $\mu\text{g/L}$ in R3. Cd^{2+} removal by these bioreactors are better than some other bioreactors such as membrane bioreactors (MBR). For example, Mahmoudkhani et al. (2014) reported that the membrane bioreactor provided a Cd^{2+} removal of 84% at an initial Cd concentration of 0.48 mg/L. Some other bioadsorbents showed higher removal of Cd but these bioreactors were broken through shortly (Tahir and Iram, 2012). In the present study, although more than 98% of Cd^{2+} was removed and Cd^{2+} concentration in the effluent is close to water quality standard for Cd^{2+} , more work should be done in the future to optimize the bioreactor to increase its performance.

The results elaborated that Ca^{2+} in tap water is sufficient as an element source for normal algal reactor. Additional Ca source is not required in the current study for bioreactors R1, R2 and R3. It provides the view of cost-down in further application of similar type of reactors in cyanoremediation of Cd^{2+} contaminated water.

3.4. Morphology changes of Ca and Cd in algae biomass

Ca in cells mainly existed in exchangeable fraction at different positions in the three reactors (Fig. 6). In R2 and R3, Ca content in the cells increased first, and then decreased with the increase of distance from the reactor inlet. A small difference was observed between the content of carbonate-bound Ca and organic-bound Ca at 0 and 1 m away from the inlet.

Cd in cells occurs mainly in the form of organic-bound fraction in all the three reactors, implying that Cd^{2+} was principally absorbed into the cells. The amount of Cd in the cells gradually declined with increasing distance from the inlet, and reached the minimum at outlet of the reactors. This finding agreed well with the Cd^{2+} removal data in Fig. 5. The occurrence of Cd in carbonate fraction indicates that some Cd^{2+} was removed because of its co-precipitation with calcium carbonate (Achal et al., 2011, 2012a, b, c, 2013). In R1, the exchangeable fraction of Cd was significantly higher than that of carbonate fraction (at $p = 0.05$). In R2 and R3, the exchangeable and carbonate fractions were comparable. The

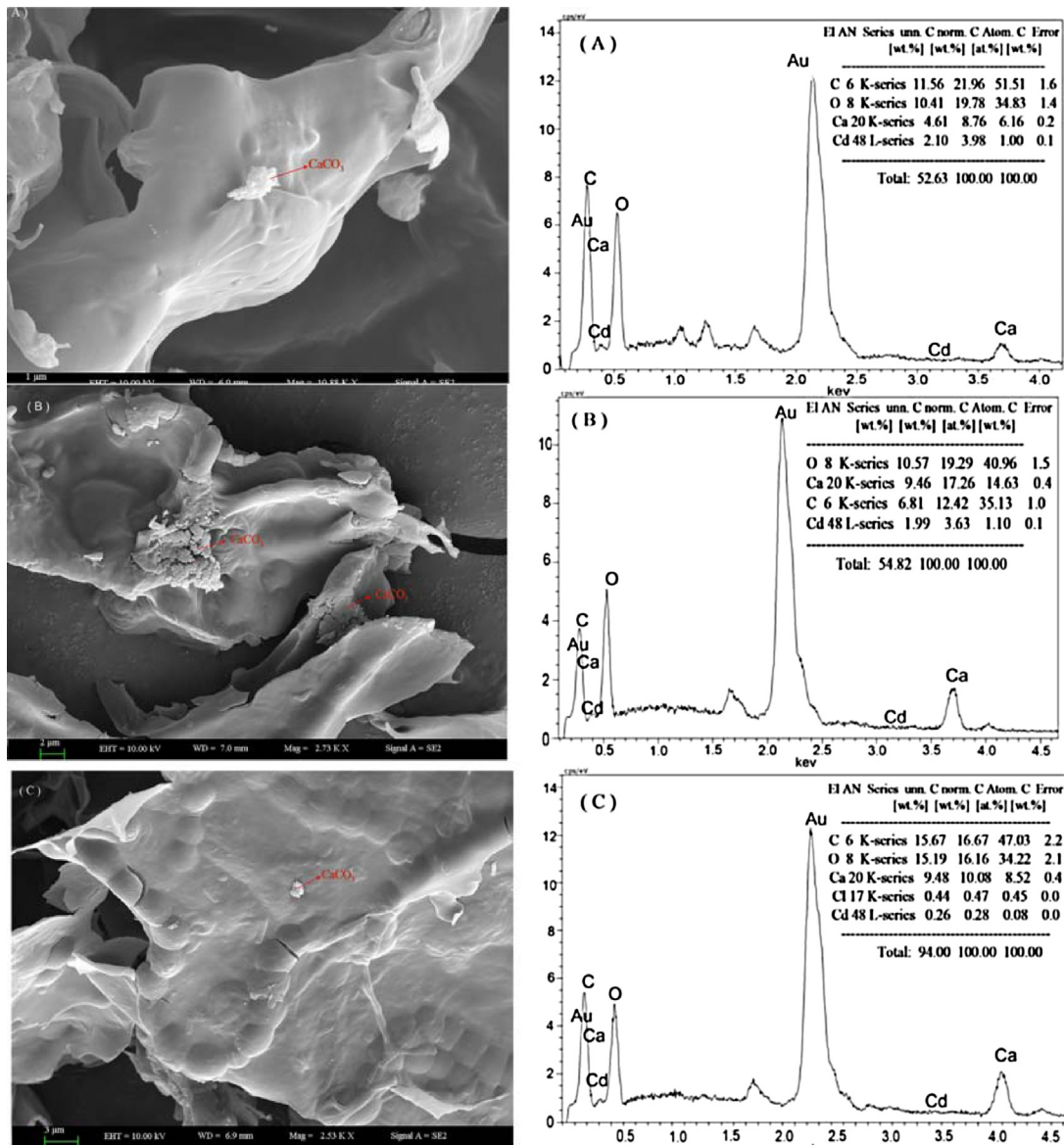


Fig. 7. Exemplified SEM images (left) and EDX spectrogram (right) of *N. calcicola* from three bioreactors R1 (A), R2 (B) and R3 (C).

higher carbonate fraction may be due to the incorporation of Cd into calcite which was formed when additional of Ca was fed and higher pH in R2 and R3 than R1 (Fig. 4) (Liang et al., 2013). Higher pH led to higher concentration of CO_3^{2-} . The average CO_3^{2-} concentrations of R2 and R3 are 0.38 and 0.31 mM, respectively, higher than that of R1 (0.29 mM).

3.5. Speciation analysis of Ca and Cd in cyanobacterial biomass

Crystalline precipitates were observed around *N. calcicola* cells (Fig. 7). EDX analysis revealed that the crystals are composed of C, O, Ca, Au and Cd. The high content of Au is attributed to the gold spraying on the surface of the sample during the sample preparation. Thus, the crystalline materials are mainly CaCO_3 , which are formed extracellularly by *N. calcicola*. This finding is consistent with the formation of CaCO_3 by *Synechococcus* (Obst et al., 2009). The small amount of Cd in the carbonate crystals implied that Cd was removed from water partly as precipitates of CdCO_3 or co-precipitates with CaCO_3 . In a MBR biosorption system Cd was principally removed by its extracellular adsorption (Mahmoudkhani et al., 2014).

Ca is helpful in removing Cd in the cyanobacterial reactor. First, Ca is a necessary co-factor of oxygen evolution complex of photosynthetic organisms (Vrettos et al., 2001) and an essential macroelement for metabolism. Thus, the photosynthesis of *N. calcicola* was enhanced under Ca-rich condition, which favors the removal of Cd. Ca-rich condition favored precipitation of CaCO_3 . The ionic radius of Cd^{2+} , Cu^{2+} and Pb^{2+} are close to that of Ca^{2+} and these ions can enter the lattices or defects of CaCO_3 crystals during precipitation of CaCO_3 induced by *N. calcicola* (Thakur et al., 2006; Pan, 2009; Achal et al., 2011). In other words, heavy metal ions can be removed through precipitation with CaCO_3 by a mechanism mediated by cyanobacteria. The calcite crystal, one of the common calcium carbonate crystal shapes, is highly stable in the ambient environment. Thus, after the ions, such as Cd^{2+} , Cu^{2+} , and Pb^{2+} are incorporated into the lattice of the calcite crystal, they are stably immobilized in the environment (Pan, 2009). Our findings suggest that bioreactor based on precipitation of CaCO_3 induced by *N. calcicola* is a potential cost-effective method for removing Cd.

4. Conclusion

N. calcicola can significantly increase the aquatic pH in reactor and decrease the DIC content in the effluent. Cd can be removed effectively by *N. calcicola* reactors during the two-month operation. Cd species in *N. calcicola* biomass was dominated by organic-bound fraction, followed by small amount of carbonate-bound and exchangeable fractions, indicating that the crystallization of CaCO_3 induced by *N. calcicola* contributes to the removal of Cd in the reactors. The long-term efficient operation shows that calcifying cyanobacterium reactor can overcome some limit of breakthrough of biosorption reactor and is a promising way for removing Cd from water. Furthermore, *N. calcicola* is a photosynthetic bacterium and an efficient photosynthetic bacterium and nitrogen fixer and there are enough other mineral nutrients in natural water, almost no operation cost is needed for the *N. calcicola* bioreactor. However, because considerable Cd was immobilized as the organic-bound fraction, which implies the re-release of Cd after cell death, long-term performance of heavy metal removal by such bioreactor should be assessed in the future study. In addition, it is also necessary to elucidate the types of calcification, which is important for understanding the mechanisms underlying heavy metal removal by calcifying cyanobacteria or algae and stability of the immobilized heavy metals.

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