



Adsorption and Desorption Characteristics of Cd²⁺ and Pb²⁺ by Micro and Nano-sized Biogenic CaCO₃

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The purpose of this study was to elucidate the characteristics and mechanisms of adsorption and desorption for heavy metals by micro and nano-sized biogenic CaCO₃ induced by *Bacillus subtilis*, and the pH effect on adsorption was investigated. The results showed that the adsorption characteristics of Cd²⁺ and Pb²⁺ are well described by the Langmuir adsorption isothermal equation, and the maximum adsorption amounts for Cd²⁺ and Pb²⁺ were 94.340 and 416.667 mg/g, respectively. The maximum removal efficiencies were 97% for Cd²⁺, 100% for Pb²⁺, and the desorption rate was smaller than 3%. Further experiments revealed that the biogenic CaCO₃ could maintain its high adsorption capability for heavy metals within wide pH ranges (3–8). The FTIR and XRD results showed that, after the biogenic CaCO₃ adsorbed Cd²⁺ or Pb²⁺, it did not produce a new phase, which indicated that biogenic CaCO₃ and heavy metal ions were governed by a physical adsorption process, and the high adsorptive capacity of biogenic CaCO₃ for Cd²⁺ and Pb²⁺ were mainly attributed to its large total specific surface area. The findings could improve the state of knowledge about biogenic CaCO₃ formation in the environment and its potential roles in the biogeochemical cycles of heavy metals.

Keywords: biogenic CaCO₃, heavy metals, adsorption, desorption, mechanism

INTRODUCTION

The main current environmental problems are the increasing atmospheric greenhouse effect and environmental pollution of large areas. Moreover, the increase of population and industrial or agricultural production makes such environmental issues more prominent. Heavy metal pollution in water and soil is already a global problem, and it is especially serious in soils (Zhao et al., 2014a). For example, the proportion of heavy metal pollution has exceeded 2.5% by land area, covering 2.32 million hectares in China, and the exceedances of permissible threshold values for Cd, Hg, As, Cu, Pb, Cr, Zn, and Ni are 7, 1.6, 2.7, 2.1, 1.5, 1.1, 0.9, and 4.8%, respectively (The Ministry of Environmental Protection, 2014; Zhao et al., 2014a; The Ministry of Land and Resources, 2015).

Microbial methods have become favored due to their low cost and environmentally—friendly nature (Lian et al., 2008; Kavamura and Esposito, 2010; Moreau et al., 2013; Santos et al., 2017), but the adsorbed heavy metals may re-enter the environment and cause re-pollution with the change in environmental conditions (Pavasant et al., 2006; Pan et al., 2007; Apiratikul and Pavasant, 2008; Tsekova et al., 2010). A sequestration method seems to be the most convenient and most commonly

chosen method (Lagadic et al., 2001; Babel and Kurniawan, 2003; Kobya et al., 2005; Ren et al., 2013); however, currently available heavy metals adsorbents remain limited, and most traditional adsorbents come with high utilization costs. Therefore, it is necessary to develop a new high-efficiency, low-cost, environmentally-friendly heavy metal adsorbent.

CaCO₃ is one of the most abundant bio-minerals found in nature, and it has aroused great interest in many branches of science. The biosynthesis of CaCO₃ is of great significance. It can promote carbon deposition, thus contributing to mitigate global warming (Dupraz et al., 2009; Mitchell et al., 2010; Phillips et al., 2013). CaCO₃ is reported to adsorb heavy metal ions in water or soil with good effect, and increasing the amount of CaCO₃ in the soil or water can significantly reduce the migration of heavy metals (Al-Degs et al., 2006; Yavuz et al., 2007; Aziz et al., 2008; Cai et al., 2010; Zhao et al., 2014a). However, the use of biogenic CaCO₃ combined with microbial technology to remediate heavy metal pollution, including the related process and the microscopic mechanism, has not yet been reported.

Natural CaCO₃ from limestone has limited further development prospects as a result of its low purity and efficiency. The traditional CO₂-bubble method for synthesizing CaCO₃ cannot sufficiently regulate the product size, morphology, or crystal type, and the cost is higher. But it is feasible to produce biogenic CaCO₃ particles with morphological diversity (such as: spherical, rhabditiform, flower, dumbbell-shape, reticular structure aggregates, etc.) and low cost by microbial mineralisation technology (Lian et al., 2006; Han et al., 2013; Cao et al., 2016). On this basis, developing the application of biogenic CaCO₃ in the treatment of heavy metals can not only deepen our understanding of the environmental significance of bio-mineralisation, but also develop a potential means with which to control heavy metal pollution.

The adsorption of heavy metal ions is subject to many factors, such as contact time, temperature, pH, and so on. Since the surface charge of an adsorbent in a solution could be altered by changing its pH value, the pH is one of the most important factors affecting the adsorption process of metal ions (Farrah and Pickering, 1979; Chen et al., 1997; Abollino et al., 2003; Üçer et al., 2006; Wolthers et al., 2008; Meng et al., 2009; Ma et al., 2012). Here, the adsorption-desorption properties of Cd²⁺ and Pb²⁺ by CaCO₃ induced by *Bacillus subtilis* and the pH effect on adsorption were investigated. This study will improve our knowledge of biogenic CaCO₃ formation in the environment and its potential role in the remediation of heavy metals.

MATERIALS AND METHODS

Preparation of Micro and Nano-sized Biogenic CaCO₃ and Its Morphology and Chemical Composition Analysis

Experimental Strain

B. subtilis (GenBank accession number KT343639), derived from the National Research and Extension Centre of Microbial Fertilizer Technology of China, is the legal functional microbial fertilizer strain in China.

We inoculated two or three rings with *B. subtilis* in 200 mL LB liquid culture medium [tryptone 0.1% (W/V), yeast extract 0.5% (W/V), NaCl 1% (W/V), 6.5 ≤ pH ≤ 7.5], shaking-cultured for 10 h at 30°C and 180 rpm, to prepare the bacterial liquid [(7.75 ± 1.19) × 10⁷ cfu/mL]. We added 100 mL LB liquid medium (containing CaCl₂ 0.2 g) to a clean 250 mL conical flask. Afterwards, we inoculated 2 mL strain from the aforementioned bacterial liquid to form the experimental group, and set up 20 parallel, shaking-cultured samples (30°C, 180 rpm, for 7 days) to induce CaCO₃ synthesis. The culture solution was centrifuged at 8000 rpm for 15 min at 4°C, and then the centrifuged sediments were collected and dried at 55°C, then milled to 200 mesh size or finer by agate mortar in readiness for testing. To verify whether the acquisition of micro- and nano-sized biogenic CaCO₃ was successful, or not, we smeared the precipitate evenly on clean cover-glasses, drying naturally, then, subjected them to field emission scanning electron microscopy and energy dispersive spectrometry (FESEM-EDS) analysis. In addition, the XRD and TEM-SAED (selected area electron diffraction) methods were used to analyse the crystal structure of the precipitate.

The Adsorption and Desorption of Cd²⁺ and Pb²⁺ by Micro and Nano-sized Biogenic CaCO₃

To investigate the environmental remediation benefits of biogenic CaCO₃, the adsorption and desorption characteristics of two common heavy metal ions (Cd²⁺ and Pb²⁺) under the action of biogenic CaCO₃ were investigated. The Langmuir and Freundlich equations were used to fit an adsorption model, and this was then employed to obtain the maximum adsorption capacity of such heavy metals (Wang et al., 2007b; Mikutta et al., 2012; Musso et al., 2014).

Adsorption Experiments

Some 0.10 g biogenic CaCO₃ was added to a 50 mL polyethylene centrifuge tube containing 20 mL solution with different Cd²⁺ (CdCl₂), and Pb²⁺ (Pb(NO₃)₂) concentrations (0, 5, 10, 30, 60, 100, 150, 180, 220, and 260 mg/L: concentration based on actual measurements). The mixture was shaken at 25°C, and 100 rpm in a shaker for 24 h, and each group was tested as a set of three replicates. After shaking, the supernatant was separated by centrifuging at 8000 rpm for 15 min. The concentration of metal ions was determined by atomic absorption spectrometer (AAS, AA-6300C, Shimadzu). The adsorption amount of Cd²⁺ and Pb²⁺ by biogenic CaCO₃ (Q_e) was calculated based on Equation (1), the adsorption isotherms were obtained by use of C_e with Q_e, and the heavy metal adsorption rates were calculated by using of Equation (2), the formulae are as follows (Argun et al., 2007; Wang et al., 2007b; Lian et al., 2008; Ma et al., 2012; Yao et al., 2013; Zhao et al., 2014b; Liu et al., 2016):

$$Q_e(\text{mg/g}) = \frac{C_0 - C_e}{W1} \times V \quad (1)$$

$$\text{The rate of absorption (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where C₀ and C_e are the initial, and equilibrium concentrations of the metal ions (mg/L), respectively; V represents the volume of

equilibrium liquid in the centrifuge tube (L), and W_1 is the mass of biogenic CaCO_3 (g).

Experimental results were analyzed with reference to the Langmuir and Freundlich isotherms (Equations 3, 4), respectively (Grimm et al., 2008; Ma et al., 2012; Mikutta et al., 2012; Wang et al., 2015):

$$L: \frac{1}{Q_e} = \frac{1}{Q_m \cdot K_L} \cdot \frac{1}{C_e} + \frac{1}{Q_m} \quad (3)$$

$$F: \text{Log } Q_e = n_f \cdot \text{Log } C_e + \text{Log } K_f \quad (4)$$

Where C_e denotes the equilibrium concentration of metal ions in the supernatant (mg/L), Q_e is the adsorption amount of metal ions by biogenic CaCO_3 (mg/g), Q_m denotes the maximum adsorption amount of metal ions (mg/g), K_L is the adsorption coefficient of the Langmuir model (L/mg), K_f is the Freundlich constant, and n_f is the adsorption intensity constant of the Freundlich equation.

Desorption Experiments

We added 20 mL desorption liquid (Dong-Mei et al., 2003; Arias et al., 2006; Gherasim and Bourceanu, 2013; 1 mol/L NaNO_3 , pH = 7.0) to the centrifugal tube with the precipitates therein after adsorbing any Cd^{2+} or Pb^{2+} , then the samples were shocked at 25°C, and 100 rpm for 12 h. Afterwards, the samples were centrifuged at 8000 rpm for 15 min, and AAS was used to determine the Cd^{2+} or Pb^{2+} concentrations in supernatant (C_1). Each desorption experiment was conducted in triplicate.

The desorption amount of heavy metals (Q_{de}) (Equation 5) and the rate of desorption (Equation 6) were calculated as follows (Gao et al., 2003; Wang et al., 2007a; Zhao et al., 2014b):

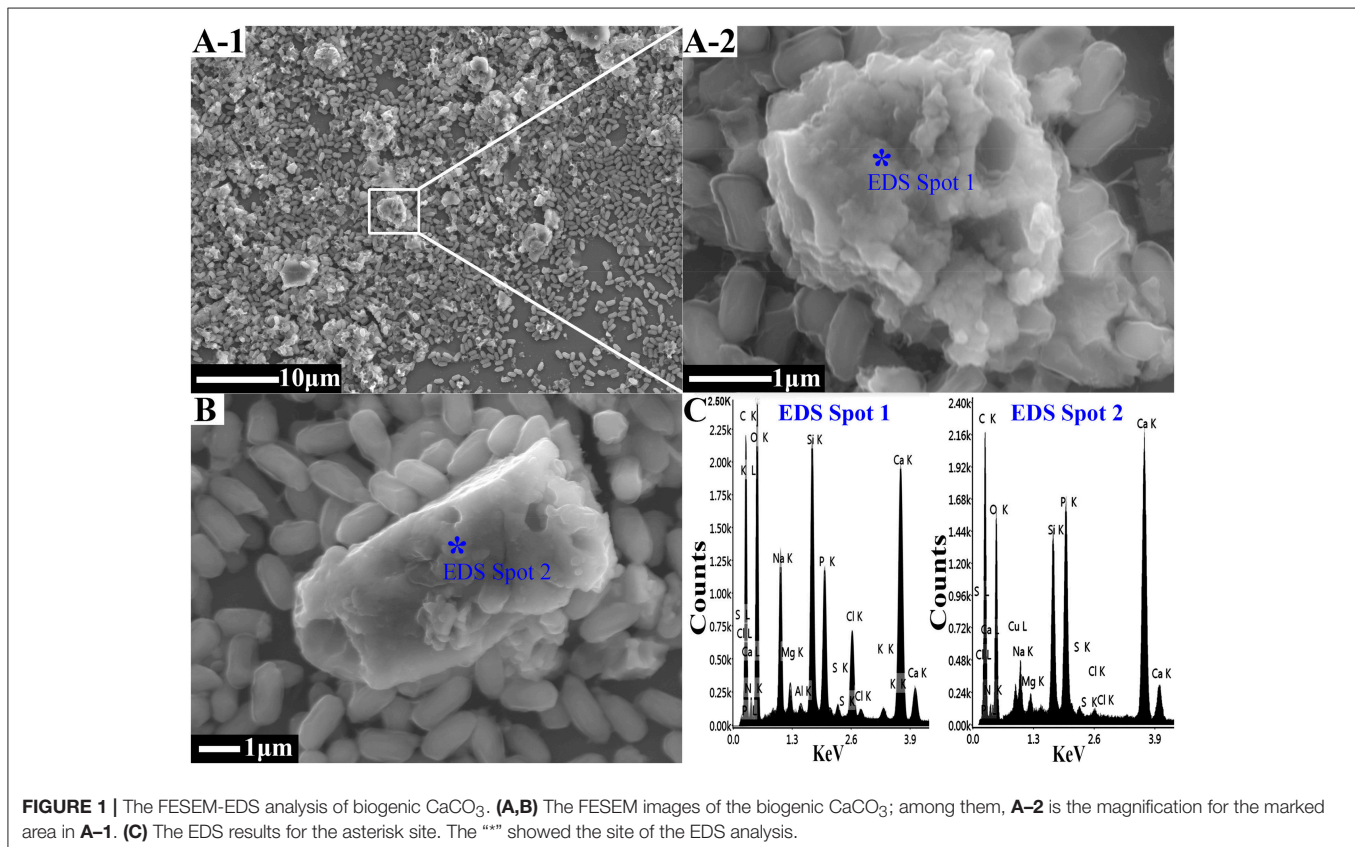
$$Q_{de}(\text{mg/g}) = \frac{C_1 \times V}{W_1} \quad (5)$$

$$\text{The rate of desorption (\%)} = \frac{Q_{de}}{Q_e} \times 100 \quad (6)$$

Where Q_{de} is the desorption amount of heavy metals (mg/g), V is the volume of desorption solution (L), C_1 represents the metal ion concentration of desorption supernatant (mg/L), and W_1 is the mass of biogenic CaCO_3 (g).

The Mechanism of Adsorption

To elucidate the adsorption mechanism of biogenic CaCO_3 , we collected the biogenic CaCO_3 before and after adsorbing Cd^{2+} or Pb^{2+} , and dried it at 55°C. Afterwards, using FTIR (NEXUS670, Thermo Nicolet), XRD (Ultima IV Multipurpose, Rigaku), FESEM-EDS, and soft X-ray microscopy techniques were used to analyse the changes in structures, morphologies and elemental compositions. Meanwhile, the adsorption and desorption of Cd^{2+} (74 mg/L) and Pb^{2+} (94 mg/L) by vaterite biogenic CaCO_3 (prepared in LB liquid medium containing 0.8 g CaCl_2 , referenced in Section Preparation of Micro and Nano-sized Biogenic CaCO_3 and Its Morphology and Chemical Composition Analysis) were also studied, and the structural changes of



vaterite before, and after, adsorbing Cd^{2+} or Pb^{2+} were analyzed by XRD.

The Comparison of Adsorption and Desorption for Heavy Metals by Biogenic CaCO_3 and Bacterial Cells

We added 100 mL LB liquid medium to a clean 250 mL conical flask, sterilized it at 115°C for 20 min, then inoculated 2 mL strain from the bacterial liquid mentioned above in the experimental group, set up 10 parallel trials, and subjected them to shaking-culturation at 30°C and 180 rpm for 7 days. Then, the culture solution was centrifuged at 8000 rpm for 15 min at 4°C , whereafter, the bacterial cells were collected and dried at 55°C , and then milled to 200 mesh or finer, by agate mortar in readiness for testing.

The biogenic CaCO_3 including CaCO_3 and bacterial cells was used to clarify the advantages of biogenic CaCO_3 for heavy metals the adsorption. The adsorption and desorption experiments of Cd^{2+} (74 mg/L), and Pb^{2+} (94 mg/L) by biogenic CaCO_3 and bacterial cells were carried out using the method described in section The Adsorption and Desorption of Cd^{2+} and Pb^{2+} by Micro and Nano-sized Biogenic CaCO_3 .

The Effect of pH on Adsorption of Biogenic CaCO_3 for Heavy Metals

To study the influence of pH on the removal efficiency, 0.05 g biogenic CaCO_3 was placed into a 50 mL polyethylene centrifuge tube containing 20 mL solution with different pH values (1, 2, 3, 4, 5, 6, 7, and 8) of 83.13 mg/g Cd^{2+} (CdCl_2), or 99.30 mg/g

Pb^{2+} ($\text{Pb}(\text{NO}_3)_2$), respectively. The mixture was shaken at 25°C and 100 rpm for 24 h, and each group was replicated three times. The supernatant was obtained by centrifuging at 8000 rpm for 15 min. The concentrations of Cd^{2+} or Pb^{2+} in the supernatant were determined by AAS, and the heavy metal adsorption rates were calculated by use of Equation (2).

RESULTS AND DISCUSSION

The Morphological and Elemental Composition Analysis of Biogenic CaCO_3 Sediments

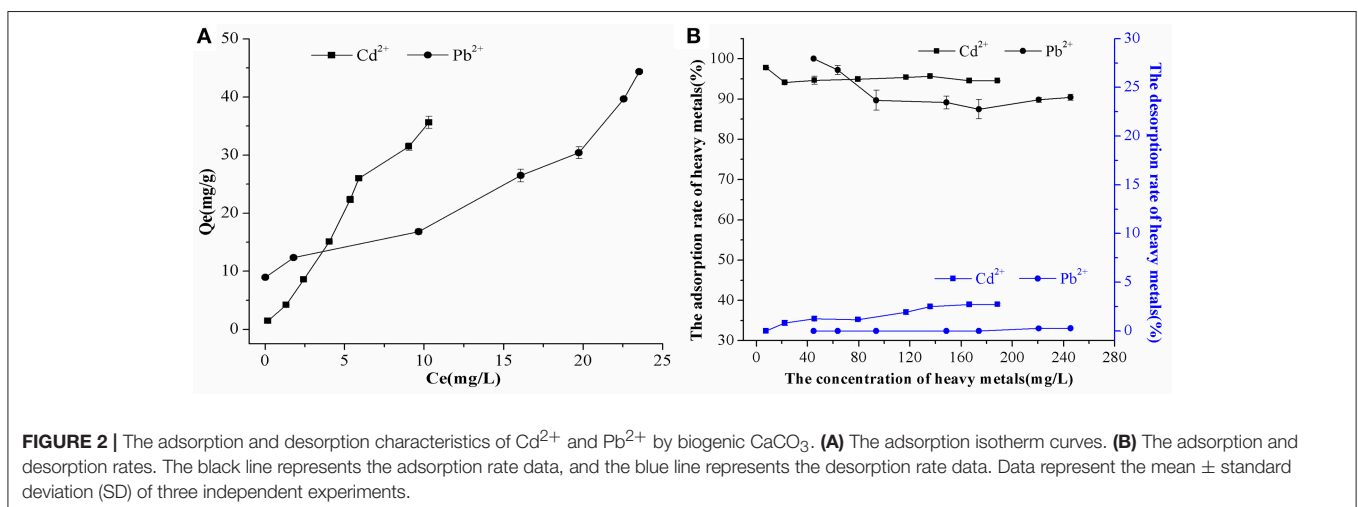
Different morphologies of crystals in the sediments were observed by using FESEM. These morphologies included cauliflower-like forms, scaly aggregates, and various irregular aggregates of sediment (part of them shown in **Figures 1A,B**). EDS was used to determine the main component as being CaCO_3 (**Figure 1C**). The biogenic CaCO_3 exhibited its porous surface, corner-incomplete form, and visible irregular fine lines on its surface, thus it had both a larger internal and external specific surface area and pore volume.

The Adsorption and Desorption of Biogenic CaCO_3 for Cd^{2+} and Pb^{2+}

Although both Freundlich and Langmuir equations could be used to fit the isothermal adsorption process of Cd^{2+} and Pb^{2+} by biogenic CaCO_3 , the fitting effect of Langmuir adsorption isotherm equation was more favorable, which suggested that the adsorption process was a single-molecule adsorption process (Mikutta et al., 2012; Wang et al., 2015). The maximum adsorption amounts of Cd^{2+} and Pb^{2+} by biogenic CaCO_3 were 94.340 and 416.667 mg/g, respectively (**Table 1**). CaCO_3 is an important mineral that is ubiquitous in soils, shallow grand water aquifers and marine sediments which has good adsorption properties for heavy metals (Davis et al., 1987; Garcia-Sánchez and Alvarez-Ayuso, 2002; Al-Degs et al., 2006; Lee et al., 2007; Yavuz et al., 2007). Yavuz et al. (2007) found that the maximum adsorption capacities of Cd^{2+} and Pb^{2+} by natural CaCO_3 were

TABLE 1 | Isotherms coefficients according to Langmuir and Freundlich.

Elements	Langmuir			Freundlich		
	K_L (L/g)	Q_m (mg/g)	R^2	$\text{Log}K_F$ (L/g)	n_f	R^2
Cd^{2+}	0.033	94.340	0.994	0.531	1.056	0.981
Pb^{2+}	0.004	416.667	0.953	0.255	0.976	0.914



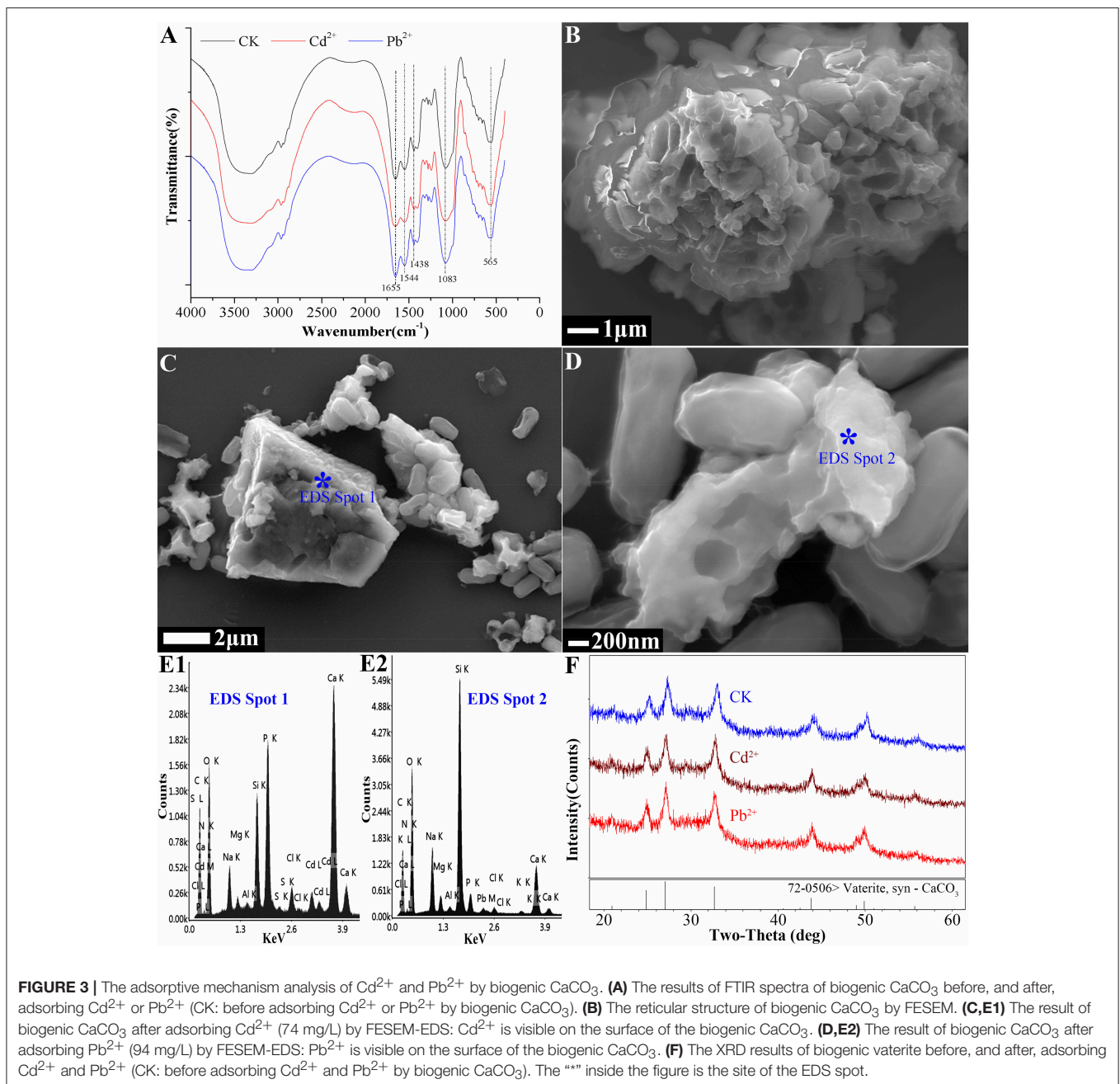
determined as 18.52 and 19.92 mg/g, respectively. This research on the adsorption of heavy metals with biogenic CaCO_3 induced by the strain (as a legal strain used in microbial fertilizer) is the first report, and the maximum adsorption capacities of biogenic CaCO_3 for heavy metals are apparently higher than that of natural calcite ($p < 0.01$), which suggests a considerable potential to immobilize or passivate heavy metals in contaminated soil.

Figure 2A showed that the adsorption amount (Q_e) of Cd^{2+} or Pb^{2+} on biogenic CaCO_3 increased with increasing Cd^{2+} or Pb^{2+} concentration in the equilibrium solution (C_e). When the concentration of Cd^{2+} or Pb^{2+} was between 5 and 260 mg/L, the rate of adsorption of heavy metals on biogenic CaCO_3

was as high as 87–100%, while the rate of desorption remained steady at 0.1–3% (**Figure 2B**), which suggest that biogenic CaCO_3 has a high adsorption capacity for heavy metals and carries little environmental risk. The results provide evidence that bacterial fertilizer and biogenic CaCO_3 may play important roles in various environments, and indeed more than previously acknowledged.

The Adsorption Mechanism

The FTIR results showed that it did not undergo a chemical precipitation reaction to produce new substances after the CaCO_3 had adsorbed Cd^{2+} (74 mg/L) or Pb^{2+} (94 mg/L)



(Figure 3A); which indicated that the reaction between the biogenic CaCO_3 and Cd^{2+} or Pb^{2+} was mainly based on physical adsorption. The FESEM-EDS analysis showed that the adsorbed Cd^{2+} and Pb^{2+} were visible on the surface of biogenic CaCO_3 (Figures 3C,E1,D,E2). Chemical CaCO_3 morphology is essentially a diamond-shaped cubic structure with smooth surfaces (Lian et al., 2006; Xiao et al., 2015; Cao et al., 2016), but the biogenic CaCO_3 surface is porous, micro and nano-sized, the edge is incomplete, and it can stack to form a fragmented structure or form a reticular aggregate with other different forms of CaCO_3 according to FESEM and soft X-ray microscopy analysis (Figures 1A,B,3B, Supplementary Video 1); thus it has a larger internal and external specific surface area and pore volume, which can provide more adsorption sites and accommodation spaces for heavy metals. The XRD and TEM-SAED results indicated that the biogenic CaCO_3 used in this test was mainly amorphous CaCO_3 (Figure 4), and according to the reports that the amorphous CaCO_3 surface area is 20 times that of other crystalline forms of CaCO_3 (Yan and Lu, 2012), therefore, it exhibits strong adsorption properties for Cd^{2+} and Pb^{2+} .

Since there were no diffraction peaks observed from the amorphous biogenic CaCO_3 in the XRD result (Figure 4A), to clarify the adsorptive mechanism of biogenic CaCO_3 for heavy metals, vaterite-type biogenic CaCO_3 was used to adsorb Cd^{2+} (74 mg/L) or Pb^{2+} (94 mg/L), and the adsorption rates were

98.42 and 100%, respectively, moreover, the desorption rates were all zero. The XRD results revealed that, there was no new phase diffraction peak after the biogenic vaterite had adsorbed the Cd^{2+} and Pb^{2+} (Figure 3F), which also showed that the reaction between the biogenic CaCO_3 and Cd^{2+} or Pb^{2+} was mainly based on physical adsorption. It was also indicated that the Cd^{2+} or Pb^{2+} was stable in the mineral as a result of binding to the CaCO_3 surface adsorption sites, or entry to the CaCO_3 crystal pores. Consequently, biogenic CaCO_3 offered better adsorption properties for heavy metals. Our findings suggested that the biogenic CaCO_3 could be expected to be developed into a new type of heavy metals adsorbent, and might achieve the dual environmental benefits of carbon sequestration and heavy metal immobilization.

The Comparison of Adsorption and Desorption of Cd^{2+} and Pb^{2+} by Biogenic CaCO_3 and Bacterial Cells

Figure 5 illustrates that the adsorption rate of Cd^{2+} (74 mg/L) and Pb^{2+} (94 mg/L) by biogenic CaCO_3 , was significantly higher than that of the bacterial cells, and the desorption rate was significantly smaller than that of the desorption rate of bacterial cells ($p < 0.01$), it suggested that the adsorption of CaCO_3 crystal for heavy metals was dominant and its environmental risk was

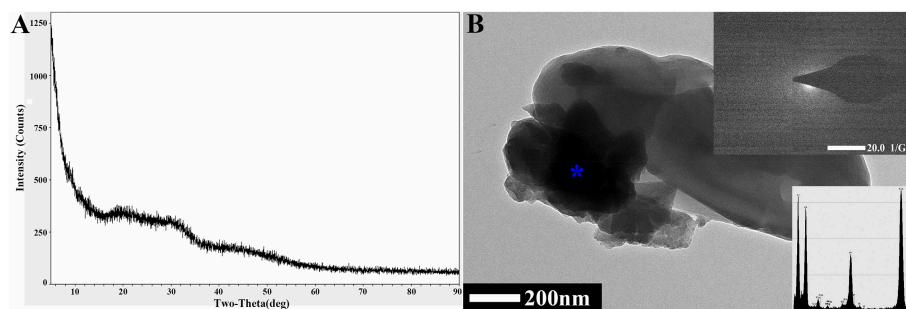


FIGURE 4 | The detection and analysis of biogenic CaCO_3 by XRD and TEM-SAED. **(A)** XRD detection. **(B)** TEM-SAED analysis. The “*” in the figure is the site of the EDS analysis.

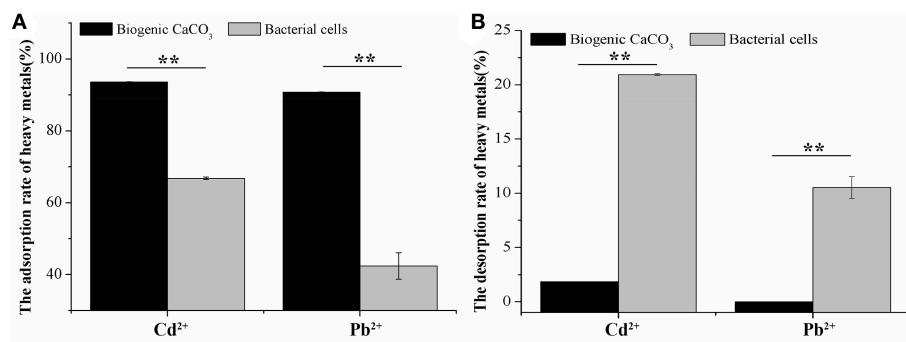
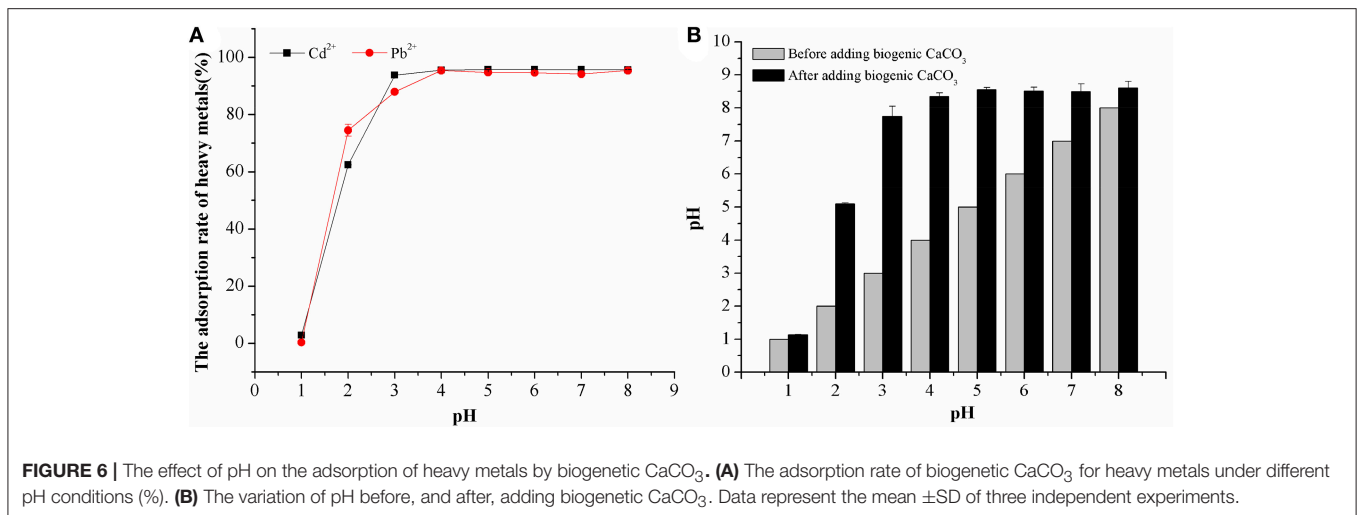


FIGURE 5 | The adsorption and desorption of Cd^{2+} or Pb^{2+} by biogenic CaCO_3 and bacterial cells. **(A)** The rate of adsorption (%). **(B)** The rate of desorption (%). The “**” indicates statistically significant differences between the two treatments (t -test, $*p < 0.05$, $**p < 0.01$). Data represent the mean \pm SD of three independent experiments.



very low, but the adsorption rate of bacterial cells for heavy metals was not only low, but also the adsorbed heavy metals would be released to the environment easily, therefore, it posed a higher environmental risk. This also suggested that the biogenic CaCO₃ had a larger specific surface area and rich reticular structures which contributed to its high adsorption and low desorption performance. This significant retaining ability of heavy metal ions indicates the remarkable efficiency of biogenic CaCO₃ as an adsorbent.

The Effect of pH on Adsorption of Biogenic CaCO₃ for Heavy Metals

The results in **Figure 6A** demonstrate the effects of pH on Cd²⁺ and Pb²⁺ adsorption by biogenic CaCO₃. The adsorption rate of these heavy metals was quite low at pH ≤ 1, as biogenic CaCO₃ could not exist at such a low pH value. At pH values from 1.0 to 4.0, the adsorption percentage increased rapidly with increasing pH; thereafter (pH > 4) it did not change to any significant extent with further increases in pH and the adsorption percentage was stable at around 95% (**Figure 6A**). Similar experimental results, such as those from Ma et al. (2012) who used chemogenic CaCO₃ for the adsorption of Cd²⁺ and Pb²⁺ and Merrikhpour and Jalali (2012) who used natural CaCO₃ for Cd²⁺, Pb²⁺, Cu²⁺, Zn²⁺ adsorption, etc., can also obtain good adsorption effect when starting from an acidic pH value. Furthermore, we found that the pH value of the adsorption system was increased after adding biogenic CaCO₃, and the final pH value after adsorption is around 8.61 (**Figure 6B**), which should be attributable by the biogenic CaCO₃ and alkaline metabolites produced by *B. subtilis*. In addition, the adsorption percentages of Cd²⁺ and Pb²⁺ at pH 8 were 16.22 and 41.23% when we did not add biogenic CaCO₃, which were significantly lower than biogenic CaCO₃ adsorption percentages ($p < 0.01$). This indicated that the adsorption rate of heavy metals was mainly influenced by the biogenic CaCO₃ rather than the formation of heavy metal hydroxides in alkaline conditions. In summary, the high adsorption capability of the biogenic CaCO₃ within a wide pH range (3–8) indicated its potential application in the control of the fate of heavy metals in the natural environment.

CONCLUSIONS

The Langmuir isotherm was preferred to describe the adsorption characteristics of Cd²⁺ and Pb²⁺ by biogenic CaCO₃ which suggested that the adsorption process was a single molecule layer adsorption process, and the maximum adsorption amounts (Q_m) of Cd²⁺ and Pb²⁺ were 94.340 and 416.667 mg/g, respectively. Moreover, biogenic CaCO₃ could maintain a high adsorption capability for heavy metals within a wide pH range. The biogenic CaCO₃ and heavy metal ions formed a physical adsorption process, and the high efficiency and stability of the adsorption of biogenic CaCO₃ for Cd²⁺ and Pb²⁺ were mainly attributed to its large total specific surface area and their porous structure. These findings revealed a new perspective on the remediation of heavy metal pollution by using biogenic CaCO₃.

AUTHOR CONTRIBUTIONS

BL: designed this study; RL, YG, and LC: performed the laboratory work; RL, YG, LC, and BL: analyzed the data; RL and BL: wrote this manuscript; All authors have read and approved the final manuscript.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fmicb.2018.00041/full#supplementary-material>

Supplementary Video 1 | The video of biogenic CaCO₃ by soft x-ray microscopy.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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