Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1140078

57 (2016) 23987–24003
October

Taylor & Francis
Taylor & Francis Group

Removal of cadmium from aqueous solution using waste shells of golden apple snail

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Received 5 January 2015; Accepted 26 December 2015

ABSTRACT

Golden apple snail (GAS) is one of the 100 worst invasive alien species. With the application of molluscicides to kill and control the spreading of these snails, a large amount of dead GAS shells are remained in many farms. This study ascertained the characteristics and removal of cadmium (Cd) by the GAS shell (GASS) powders and the associate mechanisms. Results showed that when the concentration of shell powder increased from 0.05 to 10.00 g/L, pH from 1.5 to 5.5, contact time from 2 to 100 min, and temperature from 10 to 50°C, the Cd removal efficiency from the solution increased gradually and reached an equilibrium condition. The Cd removal efficiency decreased as the initial Cd concentration increased from 5 to 500 mg/L. The changes in the amount of Cd removal conformed to the Langmuir model with a capacity of 81.301 mg/g. A thermodynamic analysis indicated that the Cd removal by the GASS powder was an endothermic and spontaneous process. Our study also revealed that the solution pH was affected greatly by the amount of GASS powder. The powder X-ray diffractometer (XRD) and scanning electron microscopy indicated that the $CdCO_3$ precipitated on the surface of GAS shells. The Cd removal was related to the ion exchange and the micro-precipitation with a depletion of aragonite and calcite. This study suggests that shells of GAS could be used as an effective biomaterial for Cd removal from contaminated water.

Keywords: Cadmium removal; Precipitation; Golden apple snail shell; Waste water; Sorption isotherm

1. Introduction

Golden apple snail (*Pomacea canaliculata*), a mollusk native from South America, has been listed as one of the 100 worst invasive alien species by Invasive Species Specialist Group of the World Conservation Union [1,2]. Golden apple snail (GAS) was introduced into Asia around 1980s for commercial purposes. Unfortunately, these snails escaped into water bodies

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such as rivers, canals, lakes, and paddy fields in South China [3]. In the paddy fields, these snails feed on seedlings and have resulted in the mass loss of rice production [4]. The GAS proliferates quickly and has spreading in the provinces of Hainan, Fujian, Yunnan, Guangdong, and Guangxi in China due to lack of natural enemies. The area of the “spreading” of GAS in 2011 was 1,217,434 km^2 in China [5]. Currently, many measures are used to kill the snails, including molluscicide application, manual capture, and egg picking [6]. As a result, large amount of GAS shell (GASS) are discarded as wastes. Molluskan shells are extensively utilized as an additional calcium carbonate source in construction application, poultry feeds, lime, and production [7]. However, in spite of their abundance in South China, the GASS have not been fully utilized.

The GAS grows very fast as compared to the local snails, sometimes the GASS height exceeds 47 mm or even larger, which is more sizeable compared with many local snails [8]. The GAS has a hard shell for life protection. During its growth, the GAS enlarges much faster than that of the local snail. Although the seashells originated from seafood wastes have been used as metal-removal biomaterials [7,9], the GASS has its own particular composition, structure, and characters. It has been reported that the GASS is used as an efficient catalyst for biodiesel production from palm oil [10], indicating their potential to be the valued-added materials.

Furthermore, the works carried out to date have shown that mollusk shells exhibited their own unique capacity to remove metal from aqueous solutions. The heavy metal removal efficiency of mollusk shells was influenced by many factors, including pretreatment method, metal type, reaction time, pH, and temperature [7,11,12]. Therefore, it is necessary to identify the factors mentioned above for maximizing the heavy metal removal efficiency when waste shells of GAS were used. Generally, heavy metal removal was closely related to diverse surface groups of adsorbents such as chitin, acetamido, alcoholic, carbonyl, phenolic, amido, and amino groups [13]. These groups greatly determined removal capacity, and were associated with adsorption mechanisms such as electrostatic adsorption, complexation adsorption, ion exchange, micro-precipitation, and metal hydroxide condensation [12,14,15].

In the past, some researchers have reported that Cd can be removed with a variety of materials such as coal fly ash, bagasse fly ash, *Lycopodium clavatum* spores, olive stone waste, black gram husk, carbon nanotubes sheets, and eggshell waste [15–23]. To date, waste shells of GAS have not been considered as specialized materials owing to biomineralized origins, which likely enabled them to abstract metal ions from aqueous solutions. To develop low-cost and high-efficient metal adsorbents, waste shells of GAS may be a suitable choice in South China. It is meaningful to select the Cd, which is one of the well-known toxic heavy metals in contaminated water, to investigate the removal capacity of shells of GAS.

The aim of this study was to characterize the potential of GASS materials as agents for Cd removal from the aqueous solution and to clarify the mechanisms associated in this process. Results from this study would provide a means for heavy metal removal and invasive species waste utilization. In addition, exploration of waste shells of GAS to control water pollution provides an innovative idea in water treatment and an important practical way to use waste or harmful biological resources.

2. Materials and methods

2.1. Preparation of GASS materials

The GASS were collected from the paddy fields in South China Agricultural University, Guangzhou, China (23°14′34.61′′N, 113°38′06.73′′E). These shells with 10–40 mm heights determined with caliper were brushed to remove any adhered materials and crushed into large fragments. Crushed shell fragments were rinsed with purified water for 20 min and then washed with purified water for three times. The clean shell fragments were dried at 40℃ for 8 h in a constant-temperature dry oven (Shanghai Jinping Instrument Co.). Then, the dried shell fragments were pulverized into particles (Fig. 1) through a plastic sieve of 200-mesh and kept in desiccators at room temperature (25 ± 1℃) for further experiment. The surface area of the GASS powder was 2.0989 m^2/g estimated by Brunauer–Emmett–Teller (BET) method, which was obtained at liquid nitrogen temperature of −196℃ using a Beckman Coulter SA3100 surface area analyzer (USA).

2.2. Preparation of Cd solutions

The Cd stock solution (1.0 g/L) was prepared by dissolving 2.036 g of $CdCl_2 \cdot 2.5H_2O$ (Analytical grade, Tianjin Fuchen Chemicals Co., Ltd) in 1.0 L of purified water. The concentrations of Cd used in the experiment were obtained from stock solution by diluting with purified water in different volumes. All solutions were prepared with purified water produced by the purification system (Pine-Tree, Beijing Xiangshunyuan Co., Ltd), and then, adjusted to the required pH values by adding HCl (0.10 mol/L) or NaOH (0.10 mol/L). The pH was determined using a

Fig. 1. Shell of GAS and shell powder material (200 mesh).

Cyberscan 510 pH meter calibrated with the standard buffer solutions of different pH levels (4.01, 6.86, and 9.18).

2.3. Effect of different factors on Cd removal efficiency

Effects of different factors including amount, initial concentration, pH, contact time, and reaction temperature on Cd removal efficiency were investigated (Table 1). Each treatment was performed in triplicate, and the results were reported in the form of mean values and standard errors. The effect of GASS amount on Cd (100 mg/L) removal efficiency (Experiment 1 in Table 1) was investigated in a series of treatments, which were conducted at 30℃ in the solution with pH 3.5 for 60 min with different amounts (0.00, 0.05, 0.10, 0.20, 0.50, 1.0, 2.0, 3.0, 5.0, and 10.0 g/L) of GASS powder. The effect of initial Cd concentration on the Cd removal efficiency (Experiment 2 in Table 1) was also investigated in different treatments, which were conducted at different Cd concentrations (0, 5, 10, 20, 40, 60, 100, 150, 200, 300, 400, and 500 mg/L) at 30℃ in the solution with pH 3.5 and 2.0 g/L of GASS powder (treatment) and without GASS powder addition (the control) for 60 min. The effect of initial pH on the Cd (100 mg/L) removal efficiency (Experiment 3 in Table 1) was examined with different treatments, which were conducted with different pH values (1.5, 2.5, 3.5, 4.5, and 5.5) at 30℃ in the solution containing 2.0 g/L GASS (treatments) and without the GASS powder addition (the control) for 60 min. In this study, pH values less than 6.0 were selected in order to avoid metal hydroxide complexes formation [24]. The effect of contact time on the Cd (100 mg/L) removal efficiency (Experiment 4 in Table 1) was evaluated in different treatments, which were performed at 30℃ in the solution (pH 3.5) containing 2.0 g/L of GASS (treatments) and without GASS powder addition (the control) for different contact times (2, 5, 10, 20, 40, 60, 80, and 100 min). The effect of temperature on Cd (100 mg/L) removal efficiency (Experiment 5 in Table 1) was studied in treatments, which were performed in the solution (pH 3.5) containing 2.0 g/L GASS powder (treatments) and without GASS powder addition (the control) at different temperatures (10, 20, 30, 40, and 50℃) for 60 min.

2.4. Cd removal with GASS powder

All experiments were conducted in the 100-mL Erlenmeyer flasks containing 30 mL solution in batches with or without the Cd. The GASS powder was added to each flask, which was shaken at 200 rpm using a vibratory shaker (KYC 100C Shaker, Shanghai Fuma Test Equipment Co., Ltd). The solution obtained from each treatment and control was centrifuged at 4,500× *g* for 5 min to collect the supernatant using a centrifuge (SIGMA 3K18, Germany). The concentration of Cd was determined using a Spectra AA 220FS/220Z atomic absorption spectrophotometer. The Cd removal efficiency (R) was calculated using Eq. (1) below:

$$R = \frac{C_i - C_r}{C_i} \times 100\% \tag{1}$$

Table 1
The Cd removal experimental conditions by GASS

Experiment	Experimental conditions under different influencing factors						
	Control	GASS Amount (g/L)	Initial Cd concentration (mg/L)	Initial pH	Contact time(min)	Reaction temperature (°)	Agitation speed (rpm)
1	No GASS	0.05, 0.10, 0.20, 0.50, 1.0, 2.0, 3.0, 5.0, 10.0	100	3.5	60	30	200
2	No GASS	2.0	5, 10, 20, 40, 60, 100, 150, 200, 300, 400, 500	3.5	60	30	200
3	No GASS	2.0	100	1.5, 2.5, 3.5, 4.5, 5.5	60	30	200
4	No GASS	2.0	100	3.5	2, 5, 10, 20, 40, 60, 80, 100	30	200
5	No GASS	2.0	100	3.5	60	10, 20, 30, 40, 50	200

where R is the removal efficiency (%), C_i is the initial concentration (mg/L), C_r is the residual concentration (mg/L) after reaction.

2.5. The solution pH change with GASS powder addition

Changes in solution pH at an interval of 5 minutes from 0 to 60 min during Cd removal at different concentrations of GASS powder (i.e. 0.05, 0.10, 0.20, 0.50, 1.0, 2.0, 3.0, 5.0, and 10.0 g/L) were monitored in this experiment. Meanwhile, the solution pH at 2 min was also measured to estimate the possible quick pH change. The solution pH was measured using a pH meter at 100 mg/L Cd with initial solution pH 3.5 and temperature of 30˚C. Based on the solution pH at different times, the pH change (r) was calculated in Eq. (2) below:

$$r = \frac{\mathrm{pH}_t - \mathrm{pH}_i}{t} \tag{2}$$

where pH_t is the solution pH at time t (min) and pH_i is the initial solution pH.

2.6. Isotherm construction and thermodynamic parameters analysis

The most widely used models of Langmuir and Freundlich were selected to construct the Cd sorption isotherms in this study. The Cd removal capacity (Q, mg/g) was calculated in Eq. (3), where C_i was the initial Cd concentration (mg/L), C_r was the residual Cd concentration in solution at equilibrium (mg/L), V was the solution volume (L), and W was the amount of GASS powder (g):

$$Q = \frac{(C_i - C_r) \times V}{W} \tag{3}$$

The Langmuir model [25] was given in Eq. (4), where a was the constant related to the active sites (L/mg), and b was the maximum amount of Cd ions per unit of GASS powder (mg/g). The Freundlich model [26] was represented in Eq. (5), where K and n represented Freundlich constant related to removal capacity and intensity, respectively.

$$\frac{1}{Q} = \frac{1}{abC_r} + \frac{1}{b} \tag{4}$$

$$\log Q = \log K + \frac{1}{n} \log C_r \tag{5}$$

Thermodynamic analysis of the adsorption process with GASS is necessary to judge whether the process is spontaneous or not. Thermodynamic parameters, including ΔG (Gibbs free energy change), ΔH (enthalpy change), and ΔS (entropy change), were used to assess properties of the Cd removal reactions in this experiment, which were calculated through the Eqs. (6)–(8) below [27]:

$$\Delta G = -RT \ln K_e \tag{6}$$

$$\Delta G = \Delta H - T\Delta S \tag{7}$$

$$\ln K_e = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{8}$$

where R is the universal ideal gas constant (8.314 J/mol/K), T is the Kelvin temperature (K), and K_e is the equilibrium constant. The $\ln K_e$ vs. $1/T$ is plotted to determine the values of ΔH and ΔS from the slope and the intercept.

2.7. Analysis of GAS shell material and precipitate

The raw GASS powder and precipitates obtained from different treatments were tested using different instruments. After the addition of GASS powder (2.0 g/L) into the 200-mL Erlenmeyer flasks containing 60 mL of Cd solution (100 mg/L, pH 3.5), the flasks were shaken at 200 rpm for 60 min at 30˚C. Precipitates were collected by centrifuging the solution at 4,500× *g* for 5 min using a centrifuge (SIGMA 3K18, Germany). Raw GASS powder and precipitates obtained were both dried at 40 ± 1˚C in a constant-temperature oven for 24 h, and then, kept in desiccators at room temperature (25 ± 1˚C) for further analysis. The GASS powder was analyzed for microstructure and element composition using a scanning electron microscopy (SEM) (SEM, XL-30-ESEM, Netherlands FEI) equipped with an energy-dispersive X-ray spectrometer (EDX), and all parameters for analysis were in default settings. The raw GASS powder and precipitates were also analyzed for functional groups using Fourier transform infrared spectrometer (FTIR, VERTEX 70 BRUKER Germany) with the method of potassium bromide pellet. The infrared spectra were recorded from KBr disks over the wavenumber range of 4,000–400 cm^{-1}. The GASS powder was also tested using the powder Bruker X-ray diffractometer (XRD, Model D8 ADVANCE Germany), and the X-ray diffraction patterns were recorded at Ni-filtered CuKα with a LynxExe detector (40 kV; 40 mA; 2θ range 0˚–80˚; step size 0.02˚).

2.8. Statistical analysis

Data were analyzed using SPSS statistical analysis software (version 11.5). For each factor in different gradients including GASS powder amount, initial Cd concentration, solution pH, contact time, and reaction temperature, the variance analysis (ANOVA) method was applied to compare the effects of GASS powder addition on the Cd removal efficiency. The statistical significance between the control (without addition of GASS) and the treatments for different factors including GASS amount, initial Cd concentration, solution pH, contact time, and reaction temperature was also evaluated by the *t*-test at p = 0.05 and 0.01. Data from each treatment and the control were showed in mean and standard error.

3. Results and discussion

3.1. Effect of GASS powder on Cd removal and solution pH

Effects of the amount of GASS powder on Cd removal efficiency and solution pH under different treatments were shown in Fig. 2. When GASS powder concentrations increased from 0.05 to 10 g/L, the Cd removal efficiency improved from 21.7 to 99.2%. There were no significant differences in Cd removal efficiency among the GASS concentration at 2.00, 3.00, 5.00, and 10.00 g/L (p > 0.05), which all exceeded 98% with pH above 8.0 at 60 min. In contrast, there were significant differences (p < 0.05) in Cd removal efficiency for the GASS powder concentration from 0.05 to 1.00 g/L. Additionally, there were also significant differences in the Cd removal efficiency between the treatments (with GASS additions) and the controls (without GASS additions) (p < 0.01). Results showed that the GASS additions in the solutions led to a decrease in Cd concentration greatly. This occurred because the surface area and available active sites for Cd sorption increased with GASS powder concentration [28,29]. Due to the excessive active sites on the surface of GASS powder, the final Cd removal efficiency was similar for treatments of 2, 3, 5, and 10 g/L. The concentration of 2 g/L was selected as the suitable amount of GASS powder for further study.

3.2. Effect of initial pH on Cd removal and final solution pH

Changes of Cd removal efficiency and solution pH by GASS powder at initial pH from 1.5 to 5.5 were shown in Fig. 3(A). The solution pH is one of the important factors in metal removal process. At 60 min, final solution pH exceeded 7.0 for initial pH 2.5 and 1.5 treatments and exceeded 8.0 for initial pH 3.50, 4.50, and 5.50 treatments. There were significant differences in Cd removal efficiency between all treatments and the control ($p < 0.01$). The Cd removal efficiency of GASS powder was significantly affected by initial pH ranged from 1.5 to 3.5. With increasing pH, the Cd removal efficiency increased and reached a maximum with initial pH ranged from 3.5 to 5.5. Furthermore, as the initial solution pH decreased, the residual Cd concentrations in the solution increased (Fig. 3(B)). As a result, the Cd removal capacity of GASS powder at pH 3.5–5.5 was significantly higher than at pH 2.5 and 1.5. Results showed that the initial solution pH greatly influenced the Cd removal capacity of GASS. This occurred because the pH change affects the degree of ionization of the sorbate and the surface property of the sorbent [30]. With low pH, the abundant H^+ in the solution has a great effect on the direction of reversible ion exchange equilibrium [15]. With high pH, the reason for high Cd removal efficiency was possibly related to the compound effect of Cd ion removal capacity of GASS and the decrease of solubility of Cd by forming chemical complexes in solution. Our study showed that the pH values of 3.5–5.5 were an optimal range for Cd removal with GASS material.

3.3. Effect of contact time on Cd removal and final solution pH

The effect of contact time on Cd removal efficiency of GASS powder is shown in Fig. 4(A). When contact time ranged from 2.00 to 40 min, the solution pH increased steadily until it exceeded 8.0. The Cd removal efficiency of the treatments increased quickly with the contact time extended from 2 to 40 min, and exceeded 90% after 10 min. After 40 min, no significant differences were found in Cd removal efficiency among treatments ($p > 0.05$). For each contact time, the other treatments were highly significantly different as compared to the control ($p < 0.01$). No significant improvement on Cd removal of GASS was observed and the removal efficiency remained above 97% after 40 min. When the contact time was from 2 to 40 min, the Cd removal capacity of GASS increased significantly (Fig. 4(B)). The increase in Cd removal capacity of GASS powder began to slow down after 40 min. These results indicated that Cd removal by GASS powder was a fast reaction process, and occurred primarily at the initial stage. Similar phenomenon on metal removal was reported previously including fungal biomass, eggshell waste, *os sepiae* [12,15,31]. At the later stage, no appreciable increase was observed possibly due to saturation of the surface sites of GASS powder available for Cd sorption.

3.4. Effect of temperature on Cd removal, final solution pH, and thermodynamic parameters

The effects of temperature on Cd removal efficiency and final solution pH by GASS powder were shown in Fig. 5(A). Results showed that temperature influenced the metal removal efficiency through its effect on the reactivity of binding sites on the surface of the tested materials or on the exothermic metal adsorptions under some conditions [12,32]. Our results demonstrated that when the temperature was in the range from 10 to 50℃, the Cd removal efficiency of GASS powder was above 95% without statistically significant difference ($p > 0.05$). All the final solution pH exceeded 8.0. However, as compared with the control, all treatments decreased the Cd concentrations effectively. Our study further revealed that the Cd removal by GASS powder was not greatly influenced when the temperature ranged from 10 to 50℃ (Fig. 5(B)). At this range, the residual Cd concentrations were all less than 4 mg/L except for the treatment at 10℃.

Thermodynamic parameters including ΔG (Gibbs free energy change), ΔH (enthalpy change), and ΔS (entropy change) for Cd adsorption by GASS powder were also used to calculate temperature-dependent adsorption isotherms based on Eqs. (6)–(8) (Table 2). Our results showed that the values of ΔG at all temperatures increased from –13.4650 to –5.5265 kJ/mol. The negative values of ΔG at different temperatures showed that the Cd removal by GASS powder was a spontaneous process. The degree of spontaneity of the reaction improved with increasing temperature, showing the removal process of Cd by GASS powder becomes favorable at higher temperatures. The positive values of ΔH indicated that the Cd removal by GASS powder was an endothermic process. Generally, the heat of chemical adsorption value was between 5.0 and 100 kcal/mol (20.9–418.4 kJ/mol), which are frequently used as the comparable values for classifying the adsorption processes. The ΔH value (50.5738 kJ/mol) for the removal process of Cd by GASS powder was between 20.9 and 418.4 kJ/mol. Therefore, Cd removal by GASS powder can be thought as chemical reaction [19], suggesting that chemisorption was the predominant mechanism. The positive values of ΔS revealed the increases in randomness at the solid–liquid interface [33].

3.5. Effect of initial Cd concentration on Cd removal, final solution pH, and Cd removal capacity of GASS

The initial Cd concentration had a great effect on Cd removal efficiency and solution pH (Fig. 6). The solution pH levels for all of the treatments exceeded

Table 2
Thermodynamic parameters for the removal of Cd by GASS

Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol/K)
283	−5.5265	50.5738	0.1977
293	−6.9045		
303	−9.9157		
313	−10.8249		
323	−13.4650		

7.0. With the initial Cd concentration increased from 5 to 100 mg/L, the removal efficiency had no significant differences ($p > 0.05$) and they all remained at nearly 100%. On the other hand, the GASS addition to the solutions significantly impact the Cd concentrations based on statistical comparison between the control and treatments ($p < 0.01$). When the initial Cd concentration increased from 150 to 500 mg/L, the removal efficiency of Cd decreased below 40% at last. Meanwhile, there were significant differences in Cd removal efficiency among treatments with different concentrations ($p < 0.05$), indicating that the increase in initial Cd concentrations was disadvantage to the GASS powder adsorption. This phenomenon was possibly related to the ratio of Cd ions to adsorptive sites on GASS powder surface. It has been reviewed that surface groups or substances such as acetamido, alcoholic, and carbonyl in agricultural waste materials were closely related to metal uptake process and greatly influenced the metal removal efficiency [34]. At the beginning, the ratio of the amount of Cd ions to active sites on the surface of GASS powder was very low with the concentrations ranged from 5 to 100 mg/L, suggesting that the Cd removal process was primarily related to active sites on the surface of GASS powder. However, with the initial Cd concentration increased, the ratio of the initial amount of Cd ions to active sites on the surface area of GASS powder subsequently increased. As a result, the Cd removal efficiency gradually decreased due to the reduction in surface sorption sites of GASS powder. Results showed that the Cd removal efficiency was closely related to the initial Cd concentration. This phenomenon was also reported in other metal removal experiments with different biomass materials [12,35].

The Cd removal capacity was analyzed by observing the change in amount of Cd removal per unit of GASS powder dry weight as a function of the residual Cd concentration in solutions (Fig. 7). The amount of Cd removal increased rapidly when the residual Cd concentration is less than 50 mg/L. After the increase in residual Cd concentration from 45.0 to 315.5 mg/L, the removal capacity of GASS powder remained around a constant value, showing saturation of the active sites for Cd ions in the GASS powder. The metal uptake capacity is an important factor for metal removal application using different materials, and is highly related to the performance for metal removal of a tested material.

A linear regression analysis was conducted using $1/Q$ or $\lg Q$ (y axis) versus $1/C_r$ or $\log C_r$ (x axis) according to Langmuir and Freundlich isotherms, where Q was the Cd removal capacity and C_r was the residual metal concentration in solution at equilibrium. Based on data obtained (Table 3), slope $1/ab$ and intercept $1/b$ of Langmuir equation were calculated. Parameters of n and K in the Freundlich equation were also derived from the experimental results. The correlation coefficient value calculated according to Langmuir model ($R^2 = 0.9776$) was significantly higher than that of Freundlich model ($R^2 = 0.8368$). According to the direct correlations of residual concentrations vs. GASS powder capacity described in Fig. 7, it was clear that the equilibrium adsorption of Cd by GASS powder was a better fit for the Langmuir model. As a result, the Cd removal capacity under current experimental conditions was determined as 81.301 mg/g.

As different experimental conditions were used to obtain the Cd removal capacity, it was hard to compare them directly. Here, some reported materials originated from carbon and carbonates were compared with GASS powder. For example, carbonate hydroxylapatite derived from eggshell waste showed its capacity as 111.0 mg/g [15], which was higher than that of GASS powder. The capacity of carbon nanotubes sheets on Cd was 75.84 mg/g, being slightly lower than that of GASS powder [22]. However, GASS powder used in this experiment was raw material, which suggested that it was possible to improve the Cd removal capacity through pretreating with chemical agents. Furthermore, as a raw material which was always cheap and easy to utilize in practice, GASS showed an excellent ability to abstract the Cd from aqueous solutions.

Table 3
Langmuir and Freundlich isotherm and correlation coefficients for Cd removal by GASS

Isotherm type	Linear regression equation	Correlation coefficient (R^2)	Adsorption constant	Isotherm equation
Langmuir	$y = 0.0219\,x + 0.0123$	0.9776	$a = 0.562$, $b = 81.301$	$Q = \frac{81.301\,C_r}{1.78 + C_r}$
Freundlich	$y = 0.355\,x + 1.2474$	0.8368	$n = 2.817$, $K = 17.677$	$Q = 17.677\,C_r^{\frac{1}{2.817}}$

3.6. Solution pH change with GASS addition

As observed in Figs. 2–6, the final solution pH in treatments at 60 min exceeded 7.0. The addition of GASS powder led to the enhancement of solution pH. The pH changes at times from 0 to 60 min with different amounts of GASS powder were determined (Fig. 8). The pH changes for the treatments with initial GASS amount ranged from 0.05 to 10.0 g/L all increased at 2 min, and then, decreased gradually until it reached a peak as compared with the control (0 g/L). Furthermore, the pH changes showed that higher GASS powder addition led to the sharp fluctuations of solution pH, especially at 2 min. As a typical invasive gastropod, GAS always accumulates much more $CaCO_3$ in shells during its growth. Interestingly, as the solution pH does not exceed 7.0 with the addition of pure $CaCO_3$, it was implied that some basic groups other than CO_3^{2-}, e.g. hydroxyl, carbonyl, and acetamido were released from the GASS during the sorption process. The quantity of basic groups may be related to the amount of the GASS powder because the pH change obviously increased as the amount of addition in the solution increased at different times.

3.7. SEM and EDX analysis of GASS

To gain further insight into the Cd removal mechanisms, the ultrastructure of GASS powder was analyzed by SEM (Fig. 9). The SEM results indicated that GASS powder before treated was composed of different sizes of particles, and these particles were mainly in the shape of slim flake, irregular lump, and similar bulk (Fig. 9(A)). The surface in flake-shaped structure may provide a good chemical interface for binding metal ions [11]. After being used, the surface of GASS powder became significantly rougher, and many small

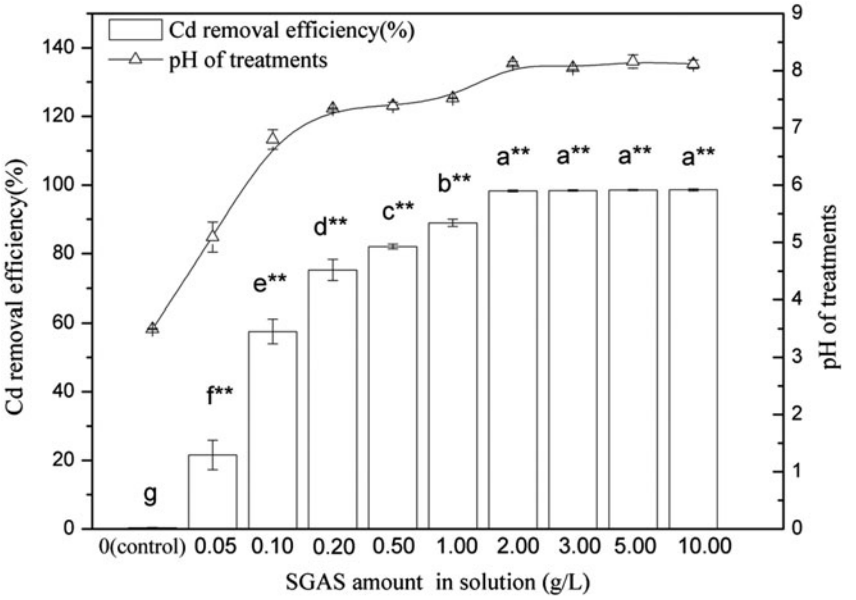

Fig. 2. Effects of GASS amount on Cd removal efficiency and final solution pH. The experiment was conducted at 30°C in a solution with pH 3.5 and Cd = mg/L for 60 min with the agitation rate of 200 rpm. The error bars represented standard errors of the mean. The symbol "**" represented the significance between the control and treatments. The symbol "a–g" represented the significance level among treatments.

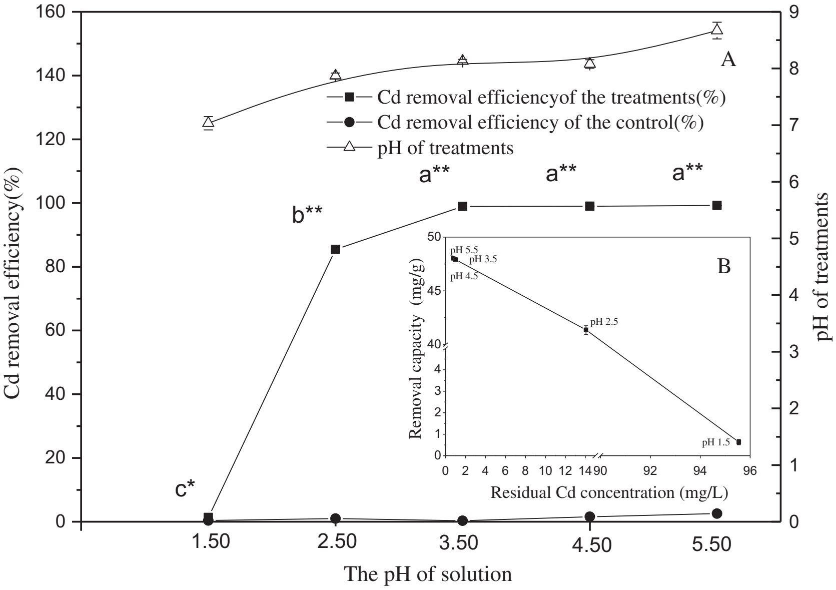

Fig. 3. Change of Cd removal from solutions by GASS at different initial pHs: (A) effects of initial pH on Cd removal efficiency and final solution pH; (B) change of Cd removal capacity with residual Cd concentrations increasing in solution. The experiment was conducted at 30˚C and GASS (2 g/L) with Cd = 100 mg/L for 60 min with the agitation rate of 200 rpm. The error bars represented standard errors of the mean. The symbol "**" or "*" represented the significance between the control and treatments. The symbol "a–c" represented the significance level among treatments.

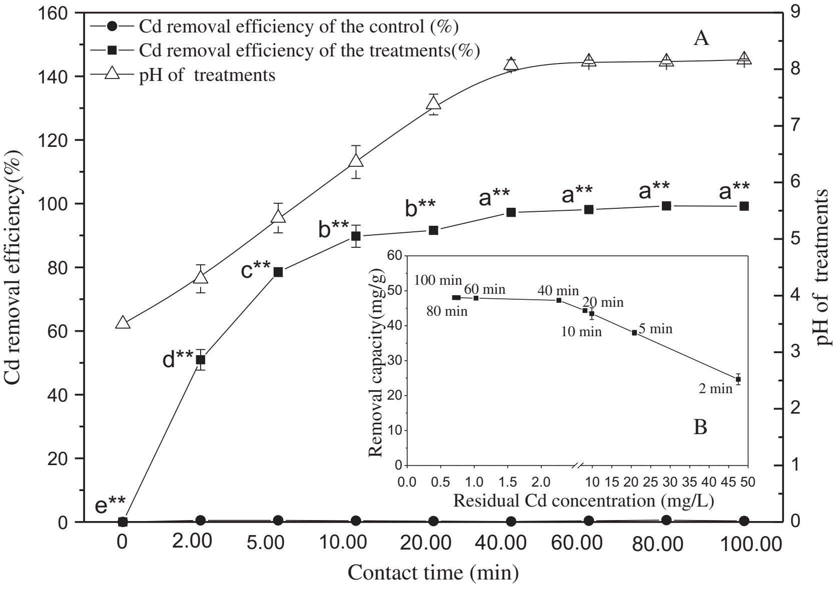

Fig. 4. Change of Cd removal from solutions by GASS at different contact times: (A) effects of contact time on Cd removal efficiency and final solution pH; (B) change of Cd removal capacity with residual Cd concentrations increasing in solution. The experiment was conducted at 30˚C and GASS (2 g/L) in a solution with pH 3.5 and Cd = 100 mg/L with the agitation rate of 200 rpm. The error bars represented standard errors of the mean. The symbol "**" represented the significance between the control and treatments. The symbol "a–e" represented the significance level among treatments.

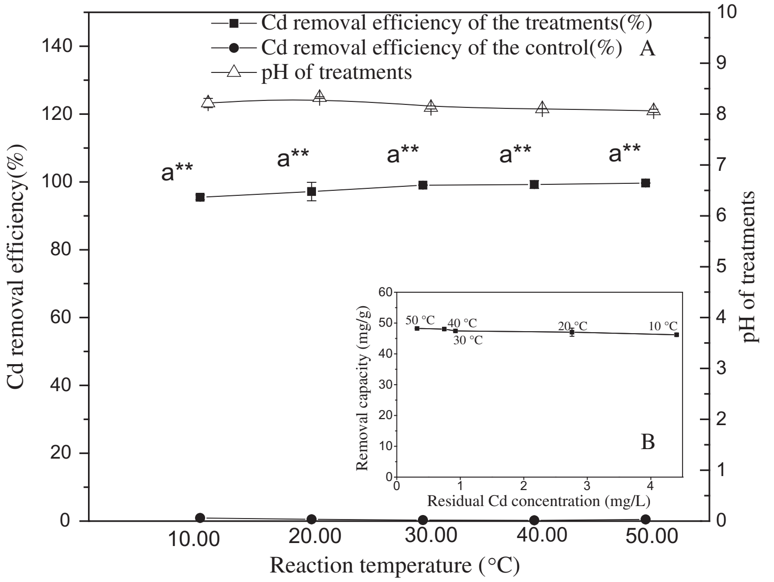

Fig. 5. Change of Cd removal from solutions by GASS at different temperatures: (A) effects of reaction temperature on Cd removal efficiency and final solution pH; (B) change of Cd removal capacity with residual Cd concentrations increasing in solution. The experiment was conducted in a solution of pH 3.5 and GASS (2 g/L) with Cd = 100 mg/L for 60 min with the agitation rate of 200 rpm. The error bars represented standard errors of the mean. The symbol "**" represented the significance between the control and treatments. The symbol "a" represented the significance level (not significant) among treatments.

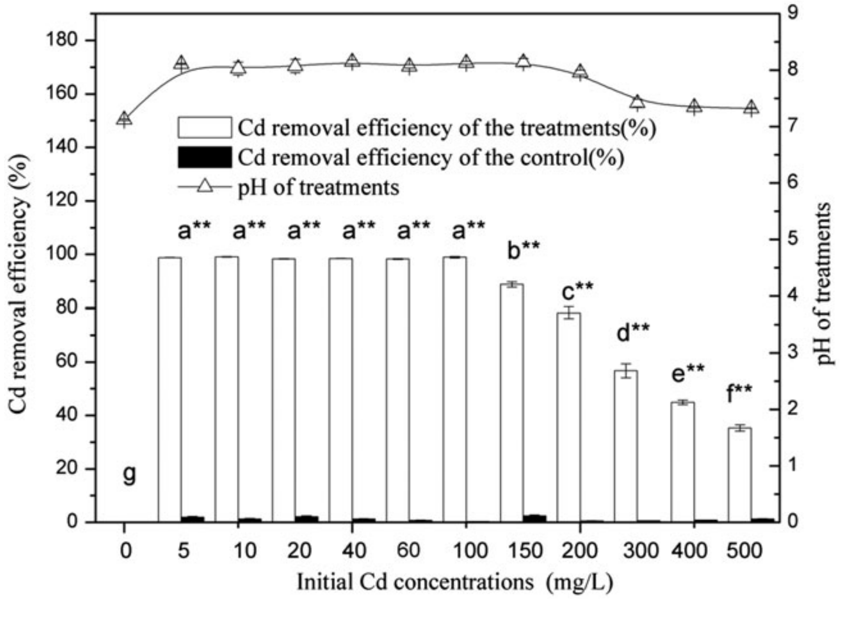

Fig. 6. Effects of initial metal concentration on Cd removal efficiency of GASS and final solution pH. The experiment was conducted at 30℃ in solution of pH 3.5 and GASS (2 g/L) for 60 min with the agitation rate of 200 rpm. The error bars represented standard errors of the mean. The symbol "**" represented the significance between the control and treatments. The symbol "a–g" represented the significance level among treatments.

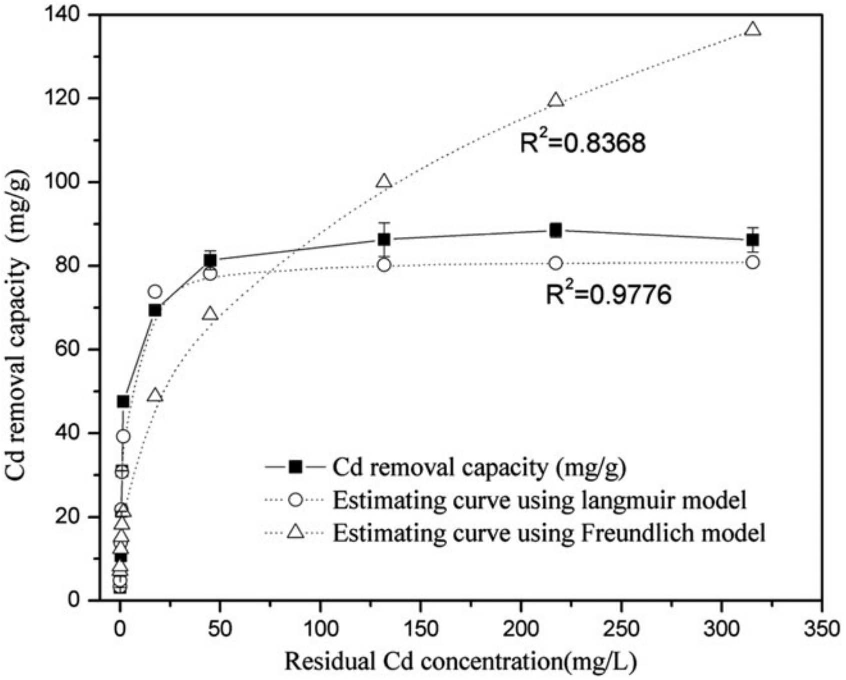

Fig. 7. The changes of Cd removal capacity of golden apple snail shell (GASS) as a function of residual Cd concentration. The R^2 represents the square of correlation coefficient of the fitting equilibrium isotherms on Cd removal by GASS material (Langmuir model: R^2 = 0.9776; Freundlich model: R^2 = 0.8368); Removal experiment was conducted at 30℃ in solution with pH 3.5 and GASS (2 g/L) for 60 min with the agitation rate of 200 rpm. The error bars represent standard errors of the mean.

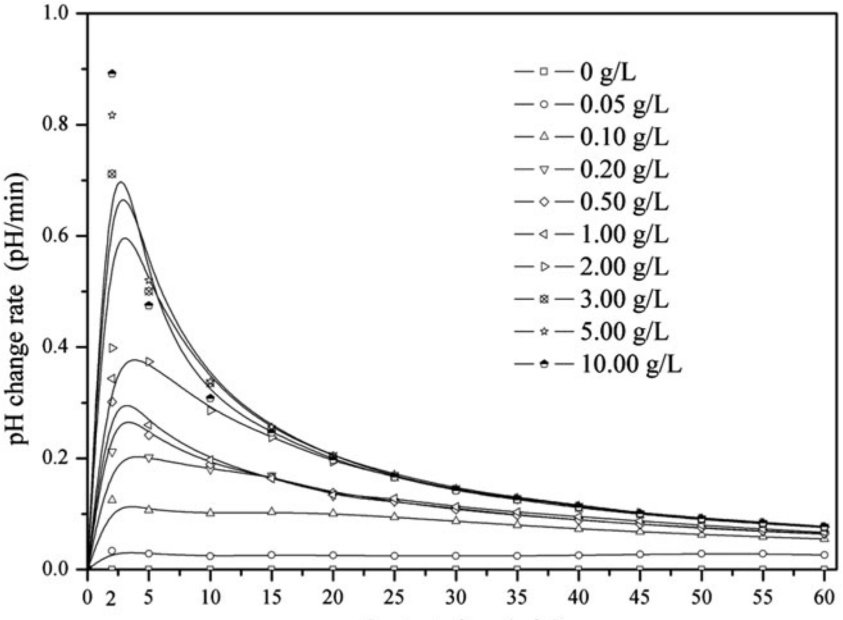

Fig. 8. The pH changes rate of the solution with different GASS amounts at various times. The experimental conditions were 30℃ in a 100 mg/L Cd solution (pH 3.5) with the agitation rate of 200 rpm for 60 min. The error bars represented standard errors of the mean.

particles appeared to be adhered on it (Fig. 9(B)). Also, the SEM results of GASS powder after being used showed that small particles in lumps existing in GASS before gradually diminished to some extent. It would be possible that the small particles were more active in Cd removal than the large particles. Previous studies discovered that shells of mollusks mainly contained elements of Ca, C, O, and Si [35,36]. Our EDX results confirmed that compositions of GASS powder were consistent with other mollusks (Fig. 9(C)). After GASS powder was used to remove Cd in solution, the Cd peaks were detected in material (Fig. 9(D)). It was evident that Cd was adsorbed or precipitated on the surface of GASS powder. As a result, it was more likely that small particles appeared on the surface of GASS powder after being used was related to Cd adsorption or precipitation.

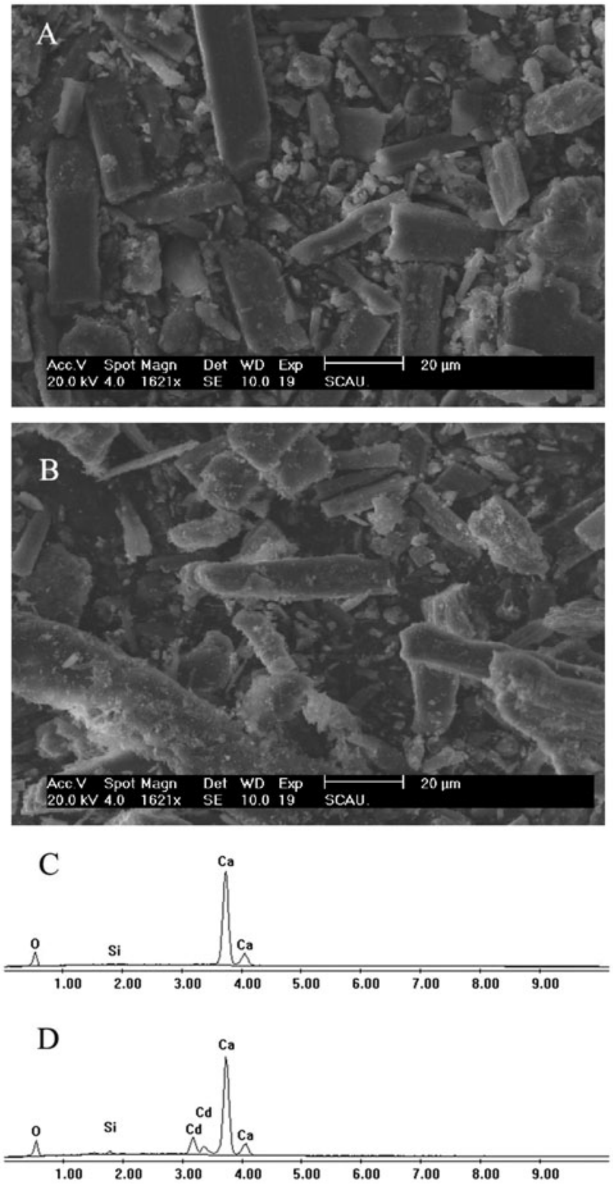

Fig. 9. SEM photomicrograph and spectra revealing elements of GASS before treatment (A, C) and after treatment (B, D). Note that the carbon peaks were not detected because of limitation of instrument. Removal experiment was conducted at 30℃ in solution with pH 3.5 containing GASS (2 g/L) and 100 mg/L Cd for 60 min with the agitation rate of 200 rpm.

3.8. Infrared absorbance spectra of GASS

In order to analyze the changes in functional groups of raw GASS powder and treated GASS in the Cd solution, tests for the infrared spectra of GASS were performed (Fig. 10). In general, the CO_3^{2-} group existed extensively in the mollusk. In the GASS materials, functional groups including the CO_3^{2-}, OH^-, OH, C–H, carbonyl groups, silicate, and water molecules were also detected at different wavenumbers according to references published in the technical literature [36–40]. A series of bands were observed in treated GASS powder (712.46, 699.47 cm^{-1}) and raw GASS (712.56, 699.60 cm^{-1}) were observed, and these bands were assigned to the v_1 (E) mode of CO_3^{2-}. The bands appeared at 862.09 cm^{-1} (Fig. 10(A)) and 861.60 cm^{-1} (Fig. 10(B)) were regarded as the v_2 (A_2) mode of CO_3^{2-}. The band situated at 1,032.60 cm^{-1} (Fig. 10(A)) and 1032.06 cm^{-1} (Fig. 10(B)) was assigned to the v_1 (A_1) mode of the CO_3^{2-}, which generally existed in aragonite. The bands situated at 1,473.87 cm^{-1} (Fig. 10(B)) and 1,474.62 cm^{-1} (Fig. 10(A)) were assigned to the v_3 (E) mode and v_1 (A_1) mode of CO_3^{2-}. The bands situated at 3,698.06 cm^{-1} (Fig. 10(A)) and 3698.17 cm^{-1} (Fig. 10(B)) reflected the presence of water molecules. The absorption bands around 3,422.69 cm^{-1} (Fig. 10(A)) and 3,424.25 cm^{-1} (Fig. 10(B)) were attributed to the adsorbed and structural water molecules resulting from the organic matter [37], which proved that organic matter indeed existed in GASS. Furthermore, the bands situated at 3,620.42 cm^{-1} (Fig. 10(A)) and at 3,620.48 cm^{-1} (Fig. 10(B)) were assigned to the OH^- group, which may function in Cd removal process. Meanwhile, bands around 2,521.43 cm^{-1} (Fig. 10(A)) and 2,521.21 cm^{-1} (Fig. 10(B)) were assigned to OH group of HCO_3^- [38]. It is also assigned that bands at around 1,788.66 cm^{-1} (Fig. 10(A)) and 1,789.25 cm^{-1} (Fig. 10(B)) were from carbonyl stretching of carbonate of aragonite or stretching of carbonyl of acidic proteins [38,39]. As described in the literature [39], the bands at around 2,919.21 cm^{-1} (Fig. 10(A)) and

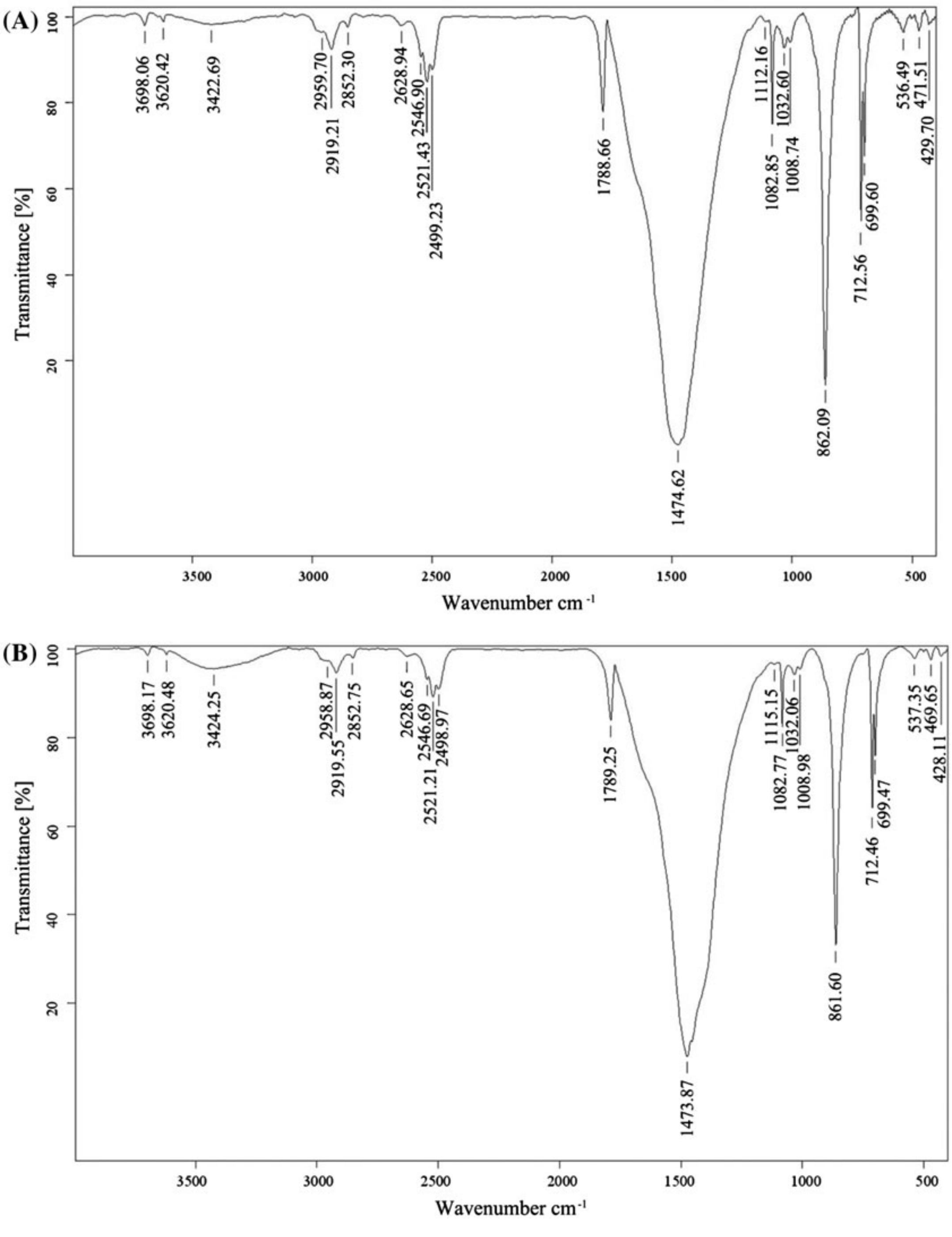

Fig. 10. Infrared absorbance spectra of GASS before (A) and after treatment (B) by FTIR. Experiment was conducted at 30℃ in solution with pH 3.5 containing GASS (2 g/L) and 100 mg/L Cd for 60 min with the agitation rate of 200 rpm.

2,919.55 cm^{-1} (Fig. 10(B)) were from stretching of C–H bonds of proteins, which may originate from the GAS metabolism. The bands of 1,112.16 and 471.51 cm^{-1} (Fig. 10(A)) in GASS before treatment and 1,115.15 and 469.65 cm^{-1} (Fig. 10(B)) after treatment possibly indicated the silicate in GASS material [40], which were consistent with the results of EDX analysis.

However, as for various bands, it was an interesting phenomenon that no significant shifts were observed between raw GASS and treated GASS. The possible reasons were: (1) the CO_3^{2-} attended the Cd removal reaction and formed new chemical compound with Cd, which precipitated on the surface of treated GASS material; (2) newly formed chemical compounds precipitated on the surface of GASS, which hindered the further reaction. So, some inner functional groups of GASS did not react in the solution; (3) since the pH changed quickly in Cd removal, metal hydroxide complex possibly formed on the surface of GASS. Thus, OH^- group still could be found in the treated GASS materials; and (4) some groups may be inactive in Cd removal reaction in the solution, such as C–H, carbonyl groups, silicate, and water molecules from organic matter. As a result, the groups such as CO_3^{2-}, OH^-, OH, C–H, carbonyl groups, silicate, and water molecules were extensively contained in GASS after treatment. In other words, they existed simultaneously in GASS before treatment and GASS after treated in the Cd solution.

3.9. XRD analysis of GASS and Cd removal

To investigate the mechanisms occurred during the Cd removal process when the GASS powder was added into the Cd solution, the XRD technique was employed to analyze the physical transformation of main phases of GASS before and after treatment (Fig. 11). Our XRD analysis for GASS powder with different powder diffraction files (PDFs) was consistent with previous studies, which reported that GASS was mainly composed of $CaCO_3$ in the crystal form of calcite and aragonite [36]. The XRD patterns of raw GASS were well matched with the pure crystal form of aragonite (PDF No. 41-1475) and calcite (PDF No. 05-0586). However, the pattern of GASS after reaction was changed to the crystal form of aragonite (PDF No. 41-1475), calcite (PDF No. 05-0586), otavite (PDF No. 42-1342), and $CdCO_3$ (PDF No. 52-1547). It was possible that that $CaCO_3$ in the form of calcite and aragonite in GASS both participated in the Cd removal process. Reference information (PDF No. 42-1342) showed that the synthetic otavite existed in the tested sample, which was also in agreement with current experiment results and indicated the formation of otavite during the Cd removal reaction. Calcite was the thermodynamically stable phase at room temperature and atmospheric pressure [41]. However, aragonite precipitates were a metastable form and kinetically favored [42]. Under current constant temperature conditions in experiment, it was possible that aragonite was more involved in otavite formation process.

Ion exchange may be a principal mechanism for the removal of Cd ions. It was likely that Cd ions reacted with $CaCO_3$ and replaced Ca^{2+} in crystals of calcite and aragonite. The chemical reaction was described as Eq. (9), which could be further divided into four parts (Eqs. (10)–(13)):

$$Cd^{2+} + CaCO_{3(s)} \leftrightarrow CdCO_{3(s)} + Ca^{2+} \tag{9}$$

$$CaCO_{3(s)} \leftrightarrow Ca^{2+} + CO_3^{2-} \tag{10}$$

$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^- \tag{11}$$

$$HCO_3^- + H^+ \leftrightarrow H_2O + CO_{2(g)} \tag{12}$$

$$CO_3^{2-} + Cd^{2+} \leftrightarrow CdCO_{3(s)} \tag{13}$$

As the solubility product constant (K_{sp}) of $CdCO_3$ in aquatic solution was nearly 1,000 times less than that of $CaCO_3$, the trend of $CaCO_3$ switching into $CdCO_3$ existed consistently. Also, at lower pH, the hydrogen ions accelerated such process by attacking $CaCO_3$ on the surface. It is noted that CO_3^{2-} was mainly provided in chemical dissolving reaction (Eq. (10)), which could be driven by CO_2 evolution from the solution (Eq. (12)). As a result, some of CO_3^{2-} were changed into CO_2 through the chemical reaction (Eqs. (11) and (12)), and other was consumed by Cd^{2+}. Furthermore, as H^+ and Cd^{2+} both reacted with the CO_3^{2-}, they were in competitive relationships in these reactions. The $CaCO_3$ was dissolved in the solution (Eq. (9)). In acidic solution, abundant H^+ has more chances to react with CO_3^{2-} (Eq. (11)). Therefore, CO_2 was formed and escaped from the solution (Eqs. (11) and (12)). When H^+ was depleted progressively, the reaction of Cd^{2+} with CO_3^{2-} was dominant in this process (Eq. (13)). As a result, the $CdCO_3$ was formed and precipitated on the surface of GASS as followed.

Moreover, it was also found that Cd removal process was related to pH change of the solution. The pH change was mainly due to the depletion of H^+ through Eqs. (11) and (12). Meanwhile, basic group OH^- have been confirmed in GASS materials, which was helpful to increase the solution pH through the reaction with H^+ and further accelerate the Cd precipitation. In the raw GASS powder and treated GASS, the CO_3^{2-} existed mainly in the form of $CaCO_3$ and the mixture of $CaCO_3$ and $CdCO_3$. At the same time, abundant and diverse organic groups were found in GASS materials. As a result, it was not strange that no significant difference was found in the function group changes in the Fourier transform infrared spectrometer (FTIR) analysis. In conclusion, the mechanism of Cd removal from the solution was closely related to the

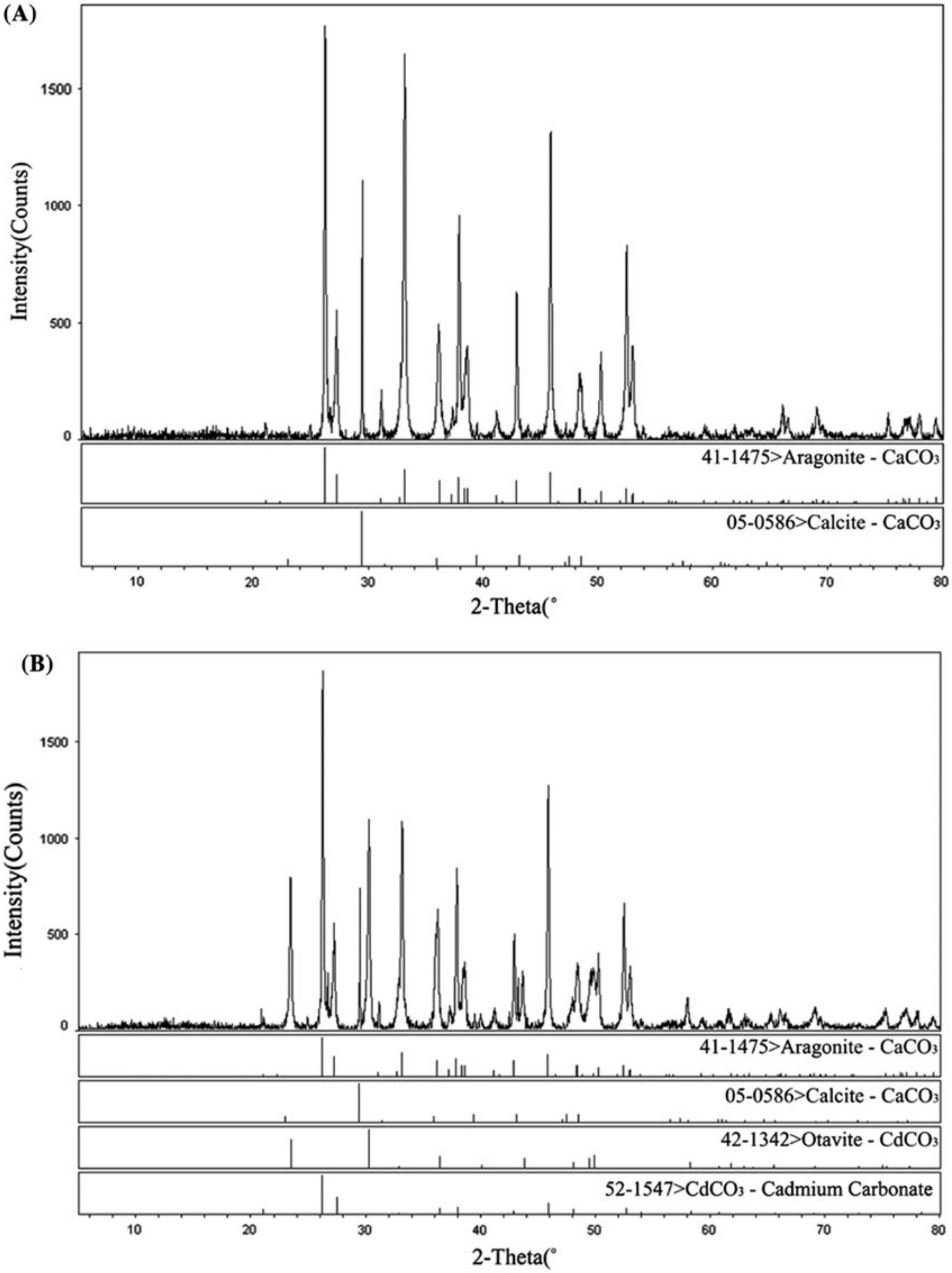

Fig. 11. Main phases of powder XRD patterns of GASS before (A) and after (B) the treatment by XRD. Removal experiment was conducted at 30°C in solution with pH 3.5 containing GASS (2 g/L) and 100 mg/L Cd for 60 min with the agitation rate of 200 rpm.

ion exchange, the micro-precipitation reaction, and pH change.

4. Conclusions

The amounts of GASS, initial Cd concentrations, initial pH, and contact time were all positively related to the Cd removal efficiency. The Cd removal/adsorption capacity was estimated to be 81.301 mg/g according to the Langmuir model. It was found that Cd was precipitated from the solution in different crystals of $CdCO_3$. The mechanism of Cd removal was mainly dominated by the ion exchange between Ca ion and Cd ion, also by the micro-precipitation between CO_3^{2-} and Cd ions and by the pH increase in the H^+ depletion process. This work indicated that GASS could be used as an effective biomaterial for the Cd removal. As the GAS was a harmful invasive gastropod and widely dispersed in South China, utilization of GASS will be helpful to improve the GAS control as compared to other waste seashells utilization. Meanwhile, the formation of otavite in this Cd removal experiment was very useful in control of GAS because it indicated that a potential economic benefit from the useful mineral otavite obtained. Therefore, a mature otavite recovery technique from treated GASS material should be studied, which would be another important future research.

Acknowledgment

This work is supported by the National Natural Science Foundation of China (Nos. U1131006, 30770403, and 30900187), Training Project for High-level Talents of Guangdong Regular Higher Education Institutions, Science and Technology Program of Guangdong province, China (No. 2015B090903077), the President Foundation of South China Agricultural University (No. 2009K029), and China Scholarship Council.

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