RESEARCH ARTICLE



Enhanced adsorption of hexavalent chromium by a biochar derived from ramie biomass (*Boehmeria nivea* (L.) Gaud.) modified with β-cyclodextrin/poly(L-glutamic acid)

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Abstract This paper explored biochar modification to enhance biochar's ability to adsorb hexavalent chromium from aqueous solution. The ramie stem biomass was pyrolyzed and then treated by β -cyclodextrin/poly(L-glutamic acid) which contained plentiful functional groups. The pristine and modified biochar were characterized by FTIR, X-ray photoelectron spectroscopy, specific surface area, and zeta potential measurement. Results indicated that the β -cyclodextrin/poly(L-glutamic acid) was successfully bound to the biochar surface. Batch experiments were conducted to investigate the kinetics, isotherm, thermodynamics, and adsorption/desorption of Cr(VI). Adsorption capacities of CGA-biochar were significantly higher than that of the untreated biochar, and its maximum adsorption capacity could reach up to 197.21 mg/g at

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pH 2.0. Results also illustrated that sorption performance depended on initial solution pH; in addition, acidic condition was beneficial to the Cr(VI) uptake. Furthermore, the Cr(VI) uptake was significantly affected by the ion strength and cation species. This study demonstrated that CGA-biochar could be a potential adsorbent for Cr(VI) pollution control.

Keywords Ramie biomass \cdot Biochar \cdot Adsorption \cdot Hexavalent chromium $\cdot \beta$ -Cyclodextrin \cdot Poly(L-glutamic acid)

Introduction

Biochar, as a solid by-product of pyrolyzing organic matter, has been paid much research attention recently because of its potential applications in various fields. When applied in contaminated soils, biochar may not only sequestrate CO₂ via storing carbon in a more recalcitrant form but also enhance fertility and resilience of soil through increasing nutrient and water holding capacity (Tan et al. 2015a, b, 2016). In recent years, many researches have exhibited that biochar can serve as a potential environmental adsorbent to eliminate a variety of contaminants from soil and water systems (Huang et al. 2008; Tang et al. 2008; Betts et al. 2013; Suguihiro et al. 2013; Mohan et al. 2014). Moreover, due to the relatively cost affordable and a multitude of feedstock materials such as municipal solid and agricultural and forestry wastes, biochar is becoming one of the remediation agent alternatives for various pollutant control such as organic pollutants, heavy metals, and even nutrients (Tang et al. 2008; Devi and Saroha 2014; Ma et al. 2014; Trazzi et al. 2016).

However, the performance of biochar in adsorptive removal of contaminations would be influenced by several factors such as kinds of feedstock, production methods, and processing conditions (Invang et al. 2010; Beesley et al. 2011; Chen et al. 2014). Generally, most of the pristine biochars, which were prepared directly from organic matter without pretreatments or posttreatments, had relatively low heavy metal adsorption ability (Zhou et al. 2013). Therefore, lots of modification/activation approaches including functionalization and surface oxidization have been used to enhance the performance of biochar in removal contaminations (Zhang et al. 2012; Yakout 2015). Through these methods, the surface adsorption sites (especially the surface functional groups), which mainly controlled the adsorption of heavy metal ions on biochar, might be increased. For instance, Qian et al. found that the HNO₃/H₂SO₄ oxidization increased the carboxylic functional groups on biochar surfaces and the Al³⁺ adsorption capacity was significantly greater on oxidized biochar than primary biochar (Qian and Chen 2014). In addition, Ma et al. (2014) utilized polyethylenimine (PEI) to modify biochar for eliminating Cr(VI) from water solution, and the maximum adsorption ability was significantly enhanced compared with pristine biochar. Chen et al. (2014) reported that the surficial oxygen-containing groups of biochar played a crucial role in the properties and were related to the capacity of biochar particles to disperse into aqueous resulting in affecting the adsorption performance.

Poly(L-glutamic acid) (PLGA), as a synthetic poly amino acid, is biodegradable and possess abundant functional groups which can be incorporated in other matters through further chemically modification (Melancon et al. 2010). Since PLGA is a biocompatible polymeride, it has been applied to fabricate scaffolds for drug delivery and tissue engineering applications and as biodegradable magnetic resonance imaging (MRI) contrast reagents (Melancon et al. 2010; Yan et al. 2014a, b). Besides, this natural biopolymer has been used as an adsorbent for heavy metal adsorption due to containing multiple functional groups (Bhattacharyya et al. 1998; Inbaraj et al. 2009). β-Cyclodextrin (β-CD), as a doughnut-shaped cyclic oligosaccharide, is a cyclic oligosaccharide containing seven glucopyranose units (Crini et al. 2007). It has the capability of forming inclusion complexes with heavy metal ions in its hydrophobic cavity via hostguest interactions and has been widely used as a heavy metals adsorbent (Badruddoza et al. 2011, 2013; Wang and Chen 2014). Nevertheless, up to now, little or no attention has been paid to the use of β -CD/PLGA (CGA) hybrid to modify the surfaces of biochar for promoting its adsorption ability to heavy metals. The β -CD/PLGA-modified biochar (CGA-biochar) will be attracting considerable attention as both β-CD/PLGA and biochar are economically affordable and environment-friendly, and CGA-biochar will possess combinative advantages of the relatively large surface area of biochar and abundant surface functional groups of β -CD/ PLGA composite.

In this work, ramie (Boehmeria nivea (L.) Gaud.) stem was chosen as the feedback material for biochar production. Ramie was usually used in textile, which was widely planted in Asian countries. Especially in China, the production of ramie fiber could reach up to 500,000 t per year, which occupied 96-97% of world output (Liu et al. 2016). Therefore, massive stem waste, which was generated after bark stripping, could be recycled as the raw biomass feedstock for biochar production. After biochar was obtained through pyrolyzing ramie stem biomass, the biochar was modified by β-CD/PLGA hybrid and applied for the Cr(VI) uptake. Influences of initial pH value, modification, initial concentration, and background electrolyte cations on the Cr(VI) uptake by CGA-biochar from aqueous solution were examined. Finally, the analysis on desorption and repeated use of CGA-biochar was also performed.

Materials and methods

Chemicals

β-Cyclodextrin (98%) and poly(L-glutamic acid) (98%) used without further purification were purchased from Beijing Solarbio Science & Technology Co. Ltd. and Shanghai Ekear Biotechnology Co. Ltd., respectively. K₂Cr₂O₇, 1-ethyl-3-(3-dimethyl)aminopropyl carbodiimide (EDC), ethylenediamine, and *N*-hydroxyl succinimide (NHS) were analytical grade and provided by Tianjin Hengxin Chemical Preparation Co., Ltd. All solutions were diluted preparation via using Milli-Q water (18.25 MΩ/cm).

Preparation of modified biochar

Fresh feedback material used for biochar production in this research was ramie stem biomass (lignin content about 13.41% as characterized by Angelini and Tavarini (2013)), and it was collected from the farm in Changsha, Hunan Province, China. Firstly, ramie stem biomass was washed with Milli-Q water and dried under vacuum at 60 °C. After that, a lab-scale tubular reactor (SK-G08123K, China) was used to pyrolyzing pretreated biomass in N2 environment at 450 °C for 2 h according to Huang et al. (2016). Then, the samples were washed, dried at 80 °C, and sieved through a 150-mesh screen. The β-CD/PLGA hybrid was synthesized as illustrated by the previously reported method (Du et al. 2014), and the detailed information was provided in the Supplementary material. After that, the modification of biochar by β-CD/PLGA hybrid was performed as the following: 2 g biochar was added into Milli-Q water and ultrasonicated for 2 h at room temperature. Subsequently, for the purpose of activating the functional groups of biochar, the mixture of 50 mL EDC (0.1 M) and NHS (0.1 M) was poured into the dispersion to activate the functional groups of biochar. After adjusting the pH to 7.0, the mixed solution was continuously stirred for 2.5 h. Afterwards, 4 g β -CD/PLGA composites and 10 mL ethylenediamine were added into above solution with ultrasonicating 10 min. Then, the mixed solution was continuously stirred at 60 °C for 2 h. After filtration, the obtained precipitates were rinsed with 2% (*w*/*v*) NaOH and Milli-Q water repetitively until pH value was neuter. Then, modified biochar was collected by filtration and oven-dried under vacuum at 65 °C for 1 day. The obtained novel biochar was named as CGA-biochar. The preparing process of CGA-biochar is depicted in Fig. 1.

Characterizations

The functional groups on pristine biochar and modified biochar were examined through a Fourier transform infrared spectrum (FTIR) (Nicolet 5700 Spectrometer, USA) with the KBr pellet technique in the wavenumber ranging from 400 to 4000 cm^{-1} . Surface element compositions of biochar before and after modification examined by X-ray photoelectron spectroscopy (XPS) (Thermo Fisher, USA). Elemental composition of adsorbents was performed in an elemental analyzer (Vario EL III, Elementar, Germany). The BET specific surface area of biochar or CGA-biochar was investigated via using a thermal analysis instrument (Quantachrome, USA). Zeta potential was analyzed with a zeta potential meter (Zetasizer Nano-ZS90, Malvern). The speciation of Cr(VI) in aqueous solution (100 mg/L) as a function of pH was provided through using the program visual MINTEQ.

Batch sorption experiments and analyses

The sorption performance of CGA-biochar was investigated by batch experiments. Generally, 100 mg biochar was added into Cr(VI) solution (50 mL) in a Erlenmeyer flask.



Fig. 1 Schematic depiction of the preparing process. a Synthesis of β-CD/PLGA hybrid. b Synthesis of CGA-biochar

After that, the mixed solution was placed in a constant temperature water bath shaker at 160 rpm for shaking 24 h. Then, the reaction solutions were filtered via 0.56-um membrane filters, and the residual concentrations of Cr(VI) were analyzed through using an UV spectrophotometer at a wavelength of 540 nm using the 1.5diphenylcarbazide method (Qu et al. 2014). The total chromium was investigated by an atomic adsorption spectrophotometer (TAS-990F, Beijing Persee, China) (Fu et al. 2017). The initial solution pH value was adjusted via diluting NaOH or HCl solution (both 0.1 M). To investigate effect of the modification on sorption kinetic, sorption kinetic research was conducted at 100 mg/L initial Cr(VI) concentration at 298 K, pH 2.0. Influence of initial Cr(VI) concentration on the Cr(VI) uptake by CGA-biochar was investigated at three different initial Cr(VI) concentrations (20, 100, and 600 mg/L). Sorption isotherm investigation was conducted through varying the initial Cr(VI) concentration from 20 to 800 mg/L under three different temperatures (298, 318, and 338 K). For investigating the effect of background electrolyte cations, various cations, including Na⁺, K⁺, Ca²⁺, and Mg²⁺ (in the chloride form), were added to the reaction solution ranging from 0.001 to 1 M.

To evaluate the reusability of the CGA-biochar, adsorptiondesorption experiments were performed. The CGA-biochar (100 mg) which has been used to eliminate 100 mg/L Cr(VI) was added into 0.5 mol/L NaOH solution (50 mL) and shaken at 160 rpm for 24 h. After filtration, biochar was separated and rinsed to neutral by Milli-Q water and dried at 60 °C under vacuum. After that, the desorbed biochar was added into Cr(VI) solution (100 mg/L, 50 mL) in a flask again and also placed in a water bath shaker at 160 rpm for shaking



Fig. 2 FTIR spectrum of $\beta\text{-CD/PLGA},$ pristine biochar, and CGA-biochar

24 h. Meanwhile, six successive adsorption-desorption processes were performed.

The amount of adsorbed Cr(VI) at equilibrium $(q_e, mg/g)$ was measured via the following equation:

$$q_e = \frac{V(C_o - C_e)}{W} \tag{1}$$

where C_o and C_e (mg/L) are the initial Cr(VI) concentration and equilibrium total chromium concentration, respectively, V (mL) stands for the volume of initial solutions, and W (mg) represents the mass of CGA-biochar.

Results and discussion

Characterization of the biochars

Changes in surface functional groups between pristine and modified biochar were reflected by the FTIR spectrum. Figure 2 exhibits the FTIR spectrum of pristine and modified biochar. The peaks of B-CD/PLGA spectrum at 1045 and 1440 cm⁻¹ were contributed to stretching vibration of C-O-C and -NHCO- stretching vibration on β-CD, respectively, indicating that the β-CD/PLGA was synthesized successfully. As shown in the spectra of pristine biochar, a predominant peak at 3430 cm^{-1} could be associated with -OH stretching vibration. Nevertheless, the functional groups in CGA-biochar were much more plentiful than those of primary biochar. For CGA-biochar, the peak of O-H stretching vibration was shifted to 3418 cm⁻¹ and enhanced significantly. The peak of -NHCO- stretching vibration was also observed at 1545 cm^{-1} , and the position and intensity were clearly changed. The weaker peak at 1040 cm⁻¹ attributing to the C-O-C stretch was also found. These results clearly demonstrated that the β-CD/PLGA was coated in the biochar successfully. Meanwhile, the surface element characterization of the primary and CGA-biochar was also analyzed. After modification, CGA-biochar exhibited a lower carbon content and a higher percentage of nitrogen and oxygen, indicating the presence of β -CD/PLGA on biochar surfaces (Table 1). Based on FTIR and XPS spectrum, β-CD/PLGA hybrid was successfully bound on the surface of biochar after the modification, which could offer more adsorption active sites for Cr(VI) ions.

The BET specific surface area (SSA) of pristine biochar $(9.63 \text{ m}^2/\text{g})$ and CGA-biochar $(60.34 \text{ m}^2/\text{g})$ were measured, and the results exhibited that CGA-biochar owned higher SSA compared with pristine biochar. Besides the SSA, the stability of adsorbent in the aqueous solution was another crucial factor influencing the adsorption performance. Therefore, the enhancement of adsorption capacity was necessary to increase its stability of adsorbent. According to Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Zhang et al. 2009), the

Table 1 Physiochemicalcharacteristics of biochar beforeand after modification

Samples	Elemental compositions examined by XPS (wt%)			Elemental compositions examined by elemental analyzer (wt%)			Surface area (m^2/g)	
	С	Ν	0	С	Н	0	N	
Pristine biochar	87.87	1.62	10.51	67.41	2.94	28.54	0.81	9.63
CGA-biochar	58.55	3.93	37.52	57.66	2.13	37.88	1.85	60.34

zeta potential (ZP) of the adsorbent suspension was closely correlated with the stability because of the electrostatic repulsion among the adsorbent particles (Schierz and Zänker 2009). Higher zeta potential (absolute value) indicated further mean distance among the adsorbent particles and thus resulted in better stability. As seen from Fig. 3, due to the high ZP of β -CD/PLGA, the ZP of CGA-biochar was higher than that of pristine biochar at pH 2.0, which indicated that CGAbiochar was more stable in aqueous solution compared with pristine biochar. This result demonstrated that β -CD/PLGA could promote the stability of biochar, which was favorable to enhance the adsorption capacity of biochar.

Effect of initial pH value

The solution pH value, which is related to the sorption mechanism, can significantly affect the adsorption performance, since it can lead to the change of surficial properties of adsorbent (i.e., the extent of dissociation of functional groups) and conversion of the chromium species (Bayramoğlu and Arıca 2005). As illustrated in Fig. S1, there were various anionic forms of Cr(VI) in the solution, including chromate CrO_4^{2-} at alkaline pH, dichromate $HCrO_4^{-}$, and CrO_4^{2-} at acidic pH. In



Fig. 3 Zeta potentials of adsorbents at 30 °C. **a** CGA-biochar at pH 2.0. **b** Pristine biochar at pH 2.0. **c** β -CD/PLGA at pH 7.0. **d** CGA-biochar at pH 7.0. **e** Pristine biochar at pH 7.0

this work, the effect of different initial solution pH on the Cr(VI) uptake by CGA-biochar is illustrated in Fig. 4. Results exhibited that the sorption ability decreased gradually with increasing in initial solution pH from 2.0 to 10.0. Thus, it could be concluded that the Cr(VI) uptake by CGA-biochar was pH-dependent, and lower pH might be more beneficial to the removal of Cr(VI). One of the crucial reason might be that the pH affected the deprotonation or protonation of the adsorbent. When solution pH was decreased, a mass of protons could be facile to coordinate with functional groups on CGA-biochar surface. In particular, when pH was less than the pH_{pzc} of CGA-biochar (3.4), the positively charged CGAbiochar would easily attract the negatively charged species ions such as CrO_4^{2-} and $HCrO_4^{-}$. Hence, the better Cr(VI) adsorption capacity onto CGA-biochar was obtained at the lower pH. Especially at pH 2.0, the maximum adsorption amount (41.15 mg/g) appeared. In contrary, when pH increased, the deprotonation began and the functional groups on CGA-biochar surface gradually became into negative charge, which resulted in rejecting the chromium anions and significantly decreasing the Cr(VI) sorption capacity onto CGA-biochar.

In addition, it is well known that Cr(VI) was a strong oxidant and the oxidation ability of Cr(VI) was affected by its pH, reagent



Fig. 4 Effect of initial solution pH on Cr(VI) by CGA-biochar and zeta potential of CGA-biochar. The initial Cr(VI) concentration was 100 mg/L

structure, and nature of the reaction medium (Wei et al. 2013). Particularly in the lower pH environment, the Cr(VI) oxidizing ability would be promoted by the strong acid solution. Cr(VI) existing as oxo anions in aqueous solution, thus, was deemed to not only be adsorbed by CGA-biochar but also reduced to form Cr(III) through electron-donor groups. From Fig. 5, it indicated that Cr(III) appeared together with Cr(VI) in the equilibrium concentration. In addition, Cr(III) increased dramatically at the beginning and then decreased gradually with adsorption. These results indicated that Cr(VI) was reduced to Cr(III) when reacted with CGA-biochar, and part of Cr(III) might be retained at CGAbiochar and the other part might be released into solution. In order to further investigate reduction reaction, CGA-biochar was examined via XPS after adsorption. As seen from Fig. S2, the peaks at 577.3 and 576.0 eV could correlate to the Cr(VI) and Cr(III) (Huang et al. 2016), respectively, suggesting that both Cr(III) and Cr(VI) presented in CGA-biochar surface and after adsorption partial Cr(VI) were transformed to Cr(III). The electrons, which were required for Cr(VI) reduction, might be supplied by hydroxyl and amino (the electron-donor groups) of CGA-biochar. Moreover, the similar phenomenon was observed on the hexavalent chromium by polyethylenimine-modified biochar (Ma et al. 2014).

Adsorption kinetics

Figure 6a exhibits the influence of modification on the sorption kinetics of Cr(VI). After grafting β -CD/PLGA, the sorption ability of Cr(VI) onto CGA-biochar was considerably enhanced, which might attribute to more functional groups such as hydroxyl, carboxyl, and amine groups introduced on CGA-biochar surface. These functional groups might play a crucial role in the Cr(VI) uptake. Figure 6b exhibits the linear fitting for Cr(VI) adsorption onto biochars via simulating



Fig. 5 Time variation of Cr(III), Cr(VI), and total Cr concentration ($C_e = 100$ mg/L, pH = 2.0)

pseudo-second-order kinetic model. Meanwhile, the simulated results are provided in Table S1. The non-linear forms of pseudo-second-order kinetic model are presented as Eq. (2) (Jiang et al. 2016, 2017a):

$$\frac{t}{q_{\rm t}} = \frac{1}{k_2 q_{\rm e}^2} + \frac{t}{q_{\rm e}}$$
(2)

where q_t and q_e (mg/g) stand for the uptake amount at time t and equilibrium, respectively; k_2 (1/min) presents the rate constant of this model. According to simulated date, the pseudo-secondorder model well described the sorption process, which suggested a chemisorption process (Ghadim et al. 2013; Li et al. 2017a, b). Therefore, the rate-determining step of the Cr(VI) sorption process was chemisorption. The chemical action between polar functional groups on CGA-biochar and chromium ions might take place, including ion exchange and chelating reaction (Huang et al. 2016). k^2 of the pristine biochar and CGA-biochar are 0.077 and 0.071 1/min, respectively. Since diffusion is the rate-limiting step in the sorption process, it could suggest that β -CD/PLGA modification might plug the pore of CGA-biochar and then restricted the transmission of Cr(VI) to CGA-biochar (Ma et al. 2014). Therefore, after modification, k_2 was decreased. Nevertheless, compared with the sorption ability of the primary biochar and CGA-biochar, the change of k_2 was not remarkable, which indicated that modification was beneficial to the elimination of Cr(VI) via sorption.

The influence of initial concentrations on removal of Cr(VI) by CGA-biochar was analyzed (Fig. 3), and the simulated data through utilizing pseudo-second-order kinetic model is also provided in Table S2. As exhibited in Fig. 6c, the Cr(VI) uptake by CGA-biochar increased with increase of initial concentrations. The high R^2 (correlation coefficient) and a little discrepancy between the calculated and experimental q_e values at different initial Cr(VI) concentrations both showed that the sorption process of Cr(VI) by CGA-biochar could be preferably fitted by the pseudo-second-order kinetic model. Moreover, k_2 value at 20 mg/L was 0.101 g/(mg min) and higher than those at 100 and 600 mg/L, indicating that Cr(VI) uptake by CGA-biochar at low Cr(VI) concentration could quickly reach the equilibrium.

Adsorption isotherm and thermodynamic parameters

To further describe the Cr(VI) sorption behavior of CGA-biochar, the isotherm data were investigated by using the Freundlich and Langmuir isotherm models (Fig. 7). These two isotherm models can be written as (Azarudeen et al. 2013; Jiang et al. 2017b)

$$q_{\rm e} = K_{\rm f} C_{\rm e}^{\rm N} \tag{3}$$

$$q_{\rm e} = \frac{K_{\rm L} q_{\rm m} C_{\rm e}}{1 + K_{\rm L} C_{\rm e}} \tag{4}$$



Fig. 6 a Adsorption kinetics of Cr(VI) onto pristine biochar and CGA-biochar and c the CGA-biochar with different initial Cr(VI) concentrations. b, d The linear fits of the adsorption kinetics by pseudo-second-order model. The initial Cr(VI) concentration was 100 mg/L, and pH was kept at 2.0



Fig. 7 Adsorption isotherms of Cr(VI) onto CGA-biochar. All adsorption isotherms were carried out at pH = 2.0

where C_e (mg/L) presents the equilibrium concentration of Cr(VI); q_e and q_m (mg/g) are the uptake amount at equilibrium and the maximum sorption capacity of the biochar, respectively. The K_f [(mg/g)/(mg/L)^N)] and K_L (L/g) stand for the Freundlich and Langmuir constants which are related to the relative sorption capacity of biochar, respectively; N is the energetic heterogeneity.

The isotherm parameters simulated from the above models are provided in Table 2. Based on the comparison of the values of R^2 (correlation coefficient) at three different temperature in Table 2, it could conclude that the Freundlich model better fitted the adsorption data than the Langmuir model on the basis of R^2 , suggesting that the sorption surface of CGAbiochar is energetically heterogeneous. It might be contributed to the additive functional groups coated on the biochar surface after modification, including hydroxyl and amino groups. Furthermore, the constant *N* of Freundlich model at three temperatures was 0.49, 0.40, and 0.41, respectively. These relative

 Table 2
 Freundlich and Langmuir isotherm parameters for adsorption of Cr(VI) onto CGA-biochar

<i>T</i> (K)		298	308	318
Freundlich	$K_{\rm f}$ (L/mg)	6.13	14.21	16.95
	N	0.49	0.40	0.41
	R^2	0.992	0.975	0.982
Langmuir	$q_{\rm m}$ (mg/g)	159.50	180.13	200.81
	$K_{\rm L}$ (L/mg)	0.006	0.012	0.016
	R^2	0.967	0.932	0.944

large value of N indicated that the interaction between CGAbiochar and Cr(VI) ions was strong.

The thermodynamic parameters are estimated from the data in Fig. 7 and exhibited in Table 3. The ΔG° values were decreased with increase of temperature, indicating that the higher temperature was favorable to the Cr(VI) uptake by CGA-biochar. Besides, the positive value of ΔH° proved that the sorption process was endothermic, which could explain why the adsorption ability of Cr(VI) increased with increasing in temperature. The positive value of ΔS° proved during the sorption process the randomness at the adsorbate-adsorbent interface was increased.

Effect of background electrolyte cations

Alkali metals, including Na⁺, K⁺, Ca²⁺, and Mg²⁺, distribute ubiquitously in natural waters and wastewaters, and these metal ions may affect adsorption Cr(VI) on the adsorbent. Hence, it is rather important to analyze the effect of background electrolyte cations on sorption performance of CGA-biochar. As illustrated in Fig. 8, the uptake amount of Cr(VI) by CGA-biochar was reduced gradually with increasing in ionic strength in the range of 0 to 1 M. This observed phenomenon might be attributed to the hindrance of electrostatic interaction between the charges on CGA-biochar surface and Cr(VI) ions in the presence of cations and the competition between Cr(VI) and Cl⁻ for adsorption sites (Gan et al. 2015). Besides, divalent cations (Ca^{2+} and Mg^{2+}) resulted in a lower absorbed amount of Cr(VI) compared with monovalent cations (Na⁺ and K⁺) in the test concentration ranges. The possible reason might be that the electrostatic attraction of bivalent cations was more stronger than that of monovalent cations, which would produce stronger hindrance of

 Table 3
 Thermodynamic parameters of Cr(VI) adsorption onto CGAbiochar

T (K)	$\ln K^0$	ΔG^0 (kJ/mol)	ΔS^0 (J/K mol)	ΔH^0 (kJ/mol)
298	0.207	-0.513	142.627	-41.794
308	0.998	-2.556		
318	1.263	-3.338		



Fig. 8 Effect of background electrolyte cations on Cr(VI) by CGA-biochar. The initial Cr(VI) concentration was 100 mg/L, and pH was kept at 2.0

electrostatic interaction between the charges on CGA-biochar surface and Cr(VI) ions (Hu et al. 2014). Furthermore, it is reported that covalent nature of Mg^{2+} was stronger compared with that of Ca^{2+} (Kennedy et al. 2004), which might lead to higher direct hydration. Thus, Mg^{2+} might produce less hindrance of electrostatic interaction between the charges on CGA-biochar surface and Cr(VI) ions. Therefore, Mg^{2+} was less influential than Ca^{2+} on Cr(VI) uptake by CGA-biochar, while was more influential than Na⁺ and K⁺.

Desorption and reuse

To evaluate the reusability of CGA-biochar, regeneration experiments were conducted at six cycles. As observed from Fig. 9, the



Fig. 9 Adsorption capacity of Cr(VI) by CGA-biochar during six sorption/desorption cycles

sorption ability of Cr(VI) onto CGA-biochar reduced gradually with the increasing in cycles. Nevertheless, the sorption ability of Cr(VI) onto the recycled CGA-biochar could remain at 31.38 mg/g after six adsorption/desorption cycles. The decrease of the Cr(VI) adsorption ability might be attributed to the reduction of specific surface area and the loss of functional groups on CGA-biochar. However, it was still indicated that CGA-biochar could be regenerated successfully via using sodium hydroxide and could be utilized for several cycles without significantly decreasing sorption capacity. Thus, it could be concluded that CGA-biochar was a low-cost adsorbent and had a high potential application in Cr(VI) elimination.

Conclusions

A new biochar was successfully modified to eliminate Cr(VI) from water solution. Results indicated that the sorption performance of CGA-biochar was better than that of pristine biochar. The pseudo-second-order and Freundlich model well described the Cr(VI) sorption process of CGA-biochar. Moreover, the sorption ability remained higher at a low pH, and the ion strength and cation species had a significant influence on the adsorption performance. After several adsorptiondesorption cycles, the adsorbent had a good stability without significant decrease of the adsorption ability. In a word, CGAbiochar synthetized in this research had a promising application in Cr(VI) pollution control.

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