The novel PEI-modified biochars and their application for the efficient elimination of Cr(VI) from aqueous solutions

Zhimin Lv, Shimin Yang, Yan Liu, Jin Zhou, Lingbao Xing and Lei Chen

ABSTRACT

In this study, the polyethyleneimine (PEI) was grafted onto the biochars from chestnut shells and nori via the cross-linking reaction. Scanning electron microscopy, transmission electron microscopy and Fourier transferred infrared spectroscopy analysis indicated that the PEI was successfully grafted on the surface of biochars. The PEI modified and pristine biochars were used as adsorbents to remove Cr(VI) from aqueous solutions as a function of pH, ionic strength, contact time and initial concentrations of Cr(VI) through batch technique. The strongly pH-dependent and ionic strength-independent of Cr(VI) sorption indicated that the sorption was mainly dominated by electrostatic interaction and inner-sphere surface complexation. The maximum sorption capacities of PEI modified chestnut shell and nori biochars were 141.42 and 222.84 mg/g, respectively, which were significantly higher than those of pristine biochars. The PEI grafted onto the biochars significantly enhanced Cr(VI) sorption capacity because PEI, which contains volumes of amine/imine groups, provided an excellent platform for Cr(VI) ions removal. In addition, the sorption–desorption experimental results indicated that the PEI modified biochars possessed a stable and recyclable performance. All these results manifested that the PEI modified biochars could be applied as environmentally friendly and efficient adsorbents for the removal of Cr(VI) from wastewater.

INTRODUCTION

Nowadays, a large amount of heavy metal ions, which have been produced in the industrial processes of steel manufacturing, mining, leather tannery, electroplating, metallurgy and textile, are widely present in the soil and groundwater systems (Zhu et al. 2017). They have become a threat to human health and the environment because they are poisonous, nonbiodegradable, and persistent (Wen et al. 2016). Among them, chromium is a significant metal widely used in various industries. Being a poisonous substance, Cr(VI) not only causes cancer and other detrimental diseases in human beings, but also poses an environmental hazard (Cheng et al. 2016). Some kinds of Cr(VI) compounds can lead to biological mutation, cancer and malformation in biological systems (Bhattacharya et al. 2008; Wen et al. 2017). The level of Cr(VI) allowed in drinking water, surface water and industrial effluents has been set at 50, 100 and 250 μg/L by the World Health Organization (WHO), respectively. As a consequence, it is very important to develop an efficient way to remove Cr(VI) before it is discharged into the ecological system.

Many methods of removing Cr(VI) from sewage water include film separating, chemical precipitation, ion exchange and oxidation/reduction (Zhang et al. 2015; Ren et al. 2016; Long et al. 2017; Nag et al. 2017). These approaches suffer from weaknesses such as high-energy requirements, low efficiency, low selectivity, high operational cost and secondary waste pollution. Compared with other methods, the sorption technique is simple to operate, flexible to design and efficient to eliminate the contaminants (Singha & Das 2011). Different adsorbents, including sulfonated graphene oxide composite, amidoxime/graphene oxide composites, and iron sulfide particles, have been used to eliminate pollutants from aqueous solutions (Li et al. 2017). The carbonaceous materials which is deemed to be the potential absorbents have been widely used in efficient elimination of contaminants because of their high stability, low cost, easy availability, large specific surface area and micropore volumes (Chandra et al. 2010; Liu et al. 2017). Biochar can be used as a means of removing...
heavy metals from wastewater. For example, the biochar produced from switchgrass was used as an adsorbent for the removal of mercury from wastewater (Ding et al. 2016). Biochar of pine needles show a very great sorption capacity for Organic Contaminants (Chen et al. 2008). Peanut hulls biochar is a new type of highly efficient absorbent for Cr(VI) removal (Han et al. 2016). The chestnut shells are a residue of various food industries. In China, the annual production of chestnut shells is huge. Most of the residue is burned directly without any treatment. This kind of material possesses a great sorption capacity for cadmium ions and phenol from aqueous solutions, but there is inadequate bibliography about Cr(VI) sorption (Cobas et al. 2016). In addition, there are an enormous amount of nori in the oceans which cover over two-thirds of Earth’s surface. However, there are rarely studies about nori for heavy metals’ elimination. For these reasons, this study assesses the sorption capacity of chestnut shells and nori biochar for Cr(VI). Nevertheless, the sorption capacity of pristine biochar was limited due to the lack of surface functional groups that served as active sites metal ion binding (Liu et al. 2016a 2016b). The polyethyleneimine (PEI) contains many amino groups on the linear macromolecular chains, which can chelate metal cations and bonds metal anions by electrostatic attraction. However, PEI is a kind of water soluble liquid, thus it must be grafted onto the biochar for its maneuverability as an adsorbent (Pang et al. 2011).

In this work, PEI-chestnut-biochar and PEI-nori-biochar composites were synthesized and characterized by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). PEI modified biochars were used to remove Cr(VI) from aqueous solution. The interaction mechanisms between PEI modified biochars and Cr(VI) were discussed. The results demonstrated that PEI modified biochars were promising adsorbents for Cr(VI) removal.

**MATERIALS AND METHODS**

**Materials**

Potassium dichromate (K2Cr2O7), 1, 5-diphenylcarbohydra-
dize and PEI were purchased from Shanghai Macklin Biochemical Co., Ltd, China. Nitric acid, glutaraldehyde, anhydrous ethanol, potassium hydroxide and methyl alcohol were obtained from Yantai Chemical Reagent Co., Ltd, China. All chemicals were used as received without any further purification.

**Adsorbent preparation**

Chestnut shells and nori were obtained from the farms in Zibo City and Tsingtao City, Shandong Province, China. The biochar precursors were oven-dried at 100 °C and then the samples were pyrolyzed at 800 °C for 2 h under a flow of N2 condition in a horizontal tube furnace. In the end, the biochar materials were washed with 3 mol/L potassium hydroxide (KOH) to wipe off the impurities and then rinsed with deionized water until the pH value was 6.8–7.3 (Zhou et al. 2017).

The synthetic method for modified biochars was carried out according to previous reports (Zhao et al. 2016; Tong et al. 2011). In brief, 3 g of pristine biochars were added to 0.1 L 10% (w/v) PEI/methanol solution in a 250 mL conical flask, and agitated at 140 rpm and 30 °C for 24 h. The doping solution was immediately transferred into a conical flask containing 200 mL 25% (w/v) glutaraldehyde for cross-linking. The mixture was agitated at 160 rpm and 30 °C for 30 min. The biomass was sieved and then rinsed with deionized water to get rid of any excess solvents, followed by drying overnight at 60 °C. The PEI modified biochars were defined as PEI-chestnut-biochar and PEI-nori-biochar.

**Characterization**

SEM and TEM images were recorded with a JEOL JSM-6330F microscope and a JEOL-2010 microscope, respectively. FT-IR spectrum was recorded by using a Perkin–Elmer Spectrum 100 spectrometer over a range of 500–4,000 cm⁻¹ using potassium bromide (KBr) as a diluent. The phase ingredient and crystal structure of the fabricated samples were determined by the Philips XPert Pro Super XRD analysis, equipped with a Cu Ka source (k = 1.542 Å) of 5–60° with a step size of 0.02°.

**Sorption experiments**

The sorption experiments were conducted in batch mode by using a constant temperature water bath oscillator. The Cr(VI) stock solution (1.0 g/L) was prepared with K2Cr2O7. The preparation of solution with various concentrations were obtained by dilution of the stock solution. The sorption experiments were carried out by using 2 mL Cr(VI) solutions with concentrations of 5–100 mg/L and a varying amount of NaNO3 solutions in the polyethylene
tubes. The pH was adjusted within the range of 1–12 using different concentrations of HNO₃ and NaOH solution. After that, the centrifuge tubes were shaken at 180 rpm for 24 h, and the suspension was centrifuged at 8,000 rpm for 15 min (Wu et al. 2017). The concentration of Cr(VI) was followed by the colorimetric method using 1,5-diphenylcarbazide as chromogenic reaction agent at the wavelength of 540 nm. All experiments were carried out in triplicate. In order to avoid causing irreversible ecological damage, we all solidify the used adsorbents in cement and then dispose of them in a hazardous waste landfill.

The uptake of adsorbents can be calculated by the following equation:

\[
q_e = \frac{(C_0 - C_e) \cdot V}{m}
\]

where \(q_e\) is the sorption capability of Cr(VI) (mg/g); \(C_0\) and \(C_e\) (mg/L) are the initial and equilibrium concentrations of Cr(VI), respectively; \(m\) (g) is the amount of adsorbent; and \(V\) (L) is the volume of the solution.

**RESULTS AND DISCUSSION**

**Characterization**

SEM images of the PEI-chestnut-biochar and PEI-nori-biochar before and after Cr(VI) sorption are shown in Figure 1. The pristine-chestnut-biochar and pristine-nori-biochar (Figure 1(a) and 1(e)) have rougher and more porous surfaces, whereas PEI-chestnut-biochar and PEI-nori-biochar (Figure 1(b) and 1(f)) have lots of cracks and channels of mesoporous. SEM image (Figure 1(c)) clearly shows that PEI-chestnut-biochar adsorbent surface is covered with a thin layer of Cr(VI) clusters. The cracks and channels of PEI-nori-biochar (Figure 1(g)) are filled with Cr(VI) clusters. The sorption of Cr(VI) on PEI modified biochar surfaces was confirmed by SEM-EDX analysis (Figure 1(d) and 1(h)); substantial amounts of Cr(VI) also appear in the EDX of the PEI-chestnut-biochar and PEI-nori-biochar, indicating Cr(VI) is successfully adsorbed on the biochar surface.

Figure 2 shows the TEM images of pristine and PEI modified biochars which display the existence of many isolated carbon sheets. The surface of pristine-chestnut-biochar and pristine-nori-biochar (Figure 2(a) and 2(c)) without PEI are smooth, whereas the PEI-chestnut-biochar and PEI-nori-biochar (Figure 2(b) and 2(d)) exhibits rougher and thicker sheet morphology. The increase of the thickness results from the PEI deposition on both sides of the pristine biochar sheets. These results suggest that PEI has successfully modified biochar.

The XRD profiles of the pristine and PEI modified biochars are shown in Figure 3(a). The band is observed at \(\approx 24^\circ\), which accords with graphite (002) band. The (002) band is ascribed to the stacking of the graphitc basal planes (Gao et al. 2016). The (002) peak indicates that the biochars have a greatly disordered structure in the XRD pattern, which contains aliphatic side chains and amorphous carbon. In theory, the (002) peak should be symmetric; nevertheless, the obvious asymmetry of this peak is attributed to the existence of the \(\gamma\) band, which is associated with the packing of saturated structures (Lu et al. 2002).

To characterize the functional groups of the pristine and PEI modified biochars, the FT-IR analysis was carried out and the FT-IR spectra were shown in Figure 3(b). The peaks at around 1,585 and 3,430 cm\(^{-1}\) are attributed to N-H and -OH stretching vibration, respectively. The peak around 2,929 cm\(^{-1}\) is attributed to C-H stretching vibration, and the peak at 670 cm\(^{-1}\) (aromatic, C-H out of plane bending) is found in all biochars (Ma et al. 2014). In comparison with the spectrum of pristine biochars, the spectra of PEI-chestnut-biochar and PEI-nori-biochar appear blue and shifting. The peaks of PEI-chestnut-biochar at 3395.2 and 1546.5 cm\(^{-1}\) shift to 3405.3 and 1552.4 cm\(^{-1}\), respectively. The peaks of PEI-nori-biochar at 3432.4 and 1585.5 cm\(^{-1}\) also changed into 3441.1 and 1594.7 cm\(^{-1}\), respectively. PEI grafted onto the pristine-chestnut-biochar and pristine-nori-biochar probably cause the changes of electron clouds environment for the N atoms (Babel & Kurian 2005; Zhao et al. 2016), which indicates that PEI has been successfully modified onto the pristine biochars.

Figure 3(c) and 3(d) show the N\(_2\) adsorption/desorption isotherms of the various adsorbents. The N\(_2\) adsorption isotherm shows a type-I isotherm with a H4 type porous structure from IUPAC, which indicates the existence of microporous materials. The Brunauer–Emmett–Teller (BET) surface area of the pristine biochars and PEI modified biochars are displayed in Table S1 (available with the online version of this paper). The BET surface area of the PEI modified biochars samples sharply decreased, which could be attributed to the pristine biochars being successfully modified by PEI, which may block the pores of the pristine biochars.

**Effect of contact time on Cr(VI) sorption**

Figure 4(a) shows the sorption kinetics of Cr(VI) on the pristine and PEI modified biochars as a function of contact time.
in aqueous solutions. The sorption rate is very fast for different adsorbents at the initial 100 min, then the equilibrium is observed within 350 min. In the initial reaction period, the sorption rate is very fast because the sorption appears on the outer-sphere surfaces of various adsorbents and the initial high concentration of Cr(VI). With the reaction time extending, the sorption rate is very slow due to the sorption occurring on the inner-sphere surface and decreasing Cr(VI) concentration. From Figure 4(a), it can also be seen that Cr(VI) sorption kinetics become slow after PEI modification onto biochars. The pore volume sizes of PEI modified biochars become smaller, which hinder the
diffusion of Cr(VI) from the outer-sphere surface to the inner-sphere surface (Hu et al. 2014; Zhao et al. 2015). A reaction time of 24 h was chosen to achieve the complete sorption equilibrium. The sorption kinetic was simulated by using the pseudo-first-order and pseudo-second-order models (Shang et al. 2016). Their equations can be expressed
as follows:

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  

(2)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]  

(3)

where \(q_t\) (mg/g) and \(q_e\) (mg/g) are the amount of Cr(VI) adsorbed at time \(t\) and at equilibrium time, respectively. \(k_1\) (min) and \(k_2\) (g/(mg min)) are the rate constants of the pseudo-first-order equation and pseudo-second-order equation, respectively.

The fitting results of pseudo-first-order and pseudo-second-order are shown in Figure 4(b). The calculated kinetic parameters are collected in Table 1. From the above results, the kinetic data were better fitted by the pseudo-second-order model. In addition, the Weber–Morris model is widely used to study the diffusion mechanism of adsorbate and estimate whether the intraparticle diffusion is the rate-limiting factor (Bhattacharya et al. 2008).

\[
q_t = k_{pi} t^{1/2} + C_i
\]  

(4)

Equation (4) is used to describe the diffusion model. \(k_{pi}\) is the Weber–Morris rate constant and \(C_i\) is proportional to the boundary layer. By plotting \(q_t\) versus \(t^{1/2}\) (Figure 4(c)), the values of \(k_{pi}\) and \(C_i\) were obtained, and they are shown in Table 2. As observed from Figure 4(c), the linear drawing of PEI-nori-biochar can be divided into two processes. The rate of the first process is rapid due to the initial high Cr(VI) concentration and the number of sorption sites of adsorbent. As the reaction progressed, the sorption rates became very slow, in which the process occurs by intraparticle diffusion. The linear drawing of PEI-chestnut-biochar can be divided into three processes. The first process is an instantaneous sorption stage, deriving from the diffusion of Cr(VI) from the solution to the external surface of PEI-chestnut-biochar. The second process is closely related to the rate-limiting step, indicating that the second region is an intraparticle diffusion process through the pores of adsorbent. The third process manifests that the rate of the intraparticle diffusion is very low because the decrease of Cr(VI) concentration and sorption sites are close to saturation. Furthermore, the linear drawing of PEI-nori-biochar and PEI-chestnut-biochar do not pass the origin, which means that intraparticle diffusion is not the sole step of the rate-limiting reaction. As mentioned above, the reduced slopes were observed with the increase of sorption time, manifesting decreased diffusion rates which might be ascribed to the slowly blocking pores by Cr(VI) onto PEI modified biochar.

![Figure 4](https://iwaponline.com/wst/article-pdf/77/8/2045/214734/wst077082045.pdf)

**Figure 4** Effect of contact time (a), linear pseudo-second-order kinetic (b), and plot of intraparticle diffusion model (c) of Cr(VI) sorption onto the pristine and PEI-modified biochars, \(T = 298\) K, \(C_0 = 20\) mg/L, pH = 3.0 ± 0.1, \(m/V = 0.15\) g/L.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
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<tr>
<td></td>
<td>(q_e) (mg/g)</td>
<td>(k_1 \times 10^{-2}) (min(^{-1}))</td>
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<tr>
<td>Pristine-chestnut-biochar</td>
<td>69.25</td>
<td>3.31</td>
</tr>
<tr>
<td>Pristine-nori-biochar</td>
<td>70.21</td>
<td>5.02</td>
</tr>
<tr>
<td>PEI-chestnut-biochar</td>
<td>89.24</td>
<td>2.31</td>
</tr>
<tr>
<td>PEI-nori-biochar</td>
<td>118.96</td>
<td>3.43</td>
</tr>
</tbody>
</table>
Effect of pH and ionic strength

Figure 5(a) and 5(b) show the sorption of Cr(VI) on PEI-chestnut-biochar and PEI-nori-biochar as a function of pH in 0.1, 0.01 and 0.001 M NaNO₃ solutions. The maximum performance is obtained at pH < 3.0, the sorption of Cr(VI) on adsorbents quickly drops with the increase of pH from 4.0 to 9.0 and, at last, maintains a low sorption capacity at pH > 9.0. The result is dependent on the species of Cr(VI) and the surface properties of PEI modified biochars at different pH values. Figure 5(c) shows the relative species distribution of Cr(VI) ions simulated by Visual MINTEQ ver. 3.1; the HCrO₄⁻/CrO₄²⁻ predominates at pH 2.0–6.0, while CrO₄²⁻ is the main species at pH > 7.0 (Cheng et al. 2019). From Figure 5(d), one can see that the zeta potentials of the PEI-chestnut-biochar and PEI-nori-biochar are measured as a function of pH and the point of zero charge (pHₚzpc) values of PEI-chestnut-biochar and PEI-nori-biochar composites were 6.0 and 6.8, respectively.

The removal of Cr(VI) can be through surface complexation and electrostatic attraction.

\[-\text{NH}_2^+ + \text{HCrO}_4^- = \text{NH}_3^+ \ldots \text{HCrO}_4^-\] (5)

At pH < pHₚzpc, the PEI modified adsorbents are protonated by the volumes of H⁺ causing the transformation of -NH₂ into -NH₃⁺ (Chen et al. 2015). The PEI-chestnut-biochar and PEI-nori-biochar have a great sorption capacity due to the strong positive-negative charge attraction between PEI-modified adsorbents and Cr(VI) species (Li et al. 2018).

### Table 2 | Intraparticle diffusion model parameters for removal of Cr(VI) by various adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Intra-particle-diffusion model</th>
<th></th>
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<tr>
<td></td>
<td>(K_{p1})</td>
<td>(C_1)</td>
<td>(R^2)</td>
<td>(K_{p2})</td>
<td>(C_2)</td>
<td>(R^2)</td>
<td>(K_{p3})</td>
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<tr>
<td>PEI-chestnut-biochar</td>
<td>6.07</td>
<td>29.76</td>
<td>0.990</td>
<td>2.27</td>
<td>51.91</td>
<td>0.989</td>
<td>0.47</td>
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<tr>
<td>PEI-nori-biochar</td>
<td>3.14</td>
<td>52.87</td>
<td>0.996</td>
<td>0.31</td>
<td>102.98</td>
<td>0.844</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5 | Effect of pH on Cr(VI) removal using PEI-nori-biochar (a) or PEI-chestnut-biochar (b), m/v = 0.15 g/L, \(C_0 = 20\) mg/L, \(T = 298\) K. The relative species distribution of Cr(VI) ions simulated by Visual MINTEQ ver. 3.1 (c), \(C_0 = 20\) mg/L, \(T = 298\) K. Zeta potential curves of PEI-nori-biochar and PEI-chestnut-biochar (d), m/v = 0.05 g/L, \(T = 298\) K.
When pH > pH_{zpc}, the surface of the adsorbents is deprotonated and electronegative. As a result, the sorption capacity of PEI-chestnut-biochar and PEI-nori-biochar decreases abruptly due to the electrostatic repulsion. With the pH value increasing, the deprotonation of nitrogen atoms cause the competition between Cr(IV) species and OH\(^-\)/C\(_0\) onto active sites of adsorbents surface (Kera et al. 2016).

The effect of ionic strength on Cr(VI) sorption is shown in Figure 5(a) and 5(b). The effect of ionic strength is fairly negligible to the sorption capacity of Cr(VI) on PEI modified biochars within the wide range of pH. Generally speaking, outer-sphere surface complexation was impressionable to the effect of ionic strength than inner-sphere surface complexation (Umoren et al. 2016a). A weak effect of ionic strength on Cr(VI) sorption onto PEI-chestnut-biochar and PEI-nori-biochar is obtained, indicating that the inner-surface complexation and electrostatic interaction are the dominant mechanism for the removal of Cr(VI).

**Effect of adsorbent dosage**

The dosage of biochar addition is an important factor to influence the sorption capacity of PEI modified biochars. The effect of adsorbents dosage is shown in Figure 6. The removal efficiency of the PEI-chestnut-biochar and PEI-nori-biochar composites increases with the increase of the adsorbent dosage. It can be interpreted as increased adsorbents surface area and availability of more active sites of adsorbents with a higher adsorbent dosage (Liu et al. 2016a, 2016b). Moreover, the distribution coefficient (K\(_d\)) decreases with the increase of the adsorbent dosage. At a low adsorbent dosage, there are volumes of Cr(VI) in the aqueous solutions to take up the sorption sites and the surface of adsorbents was highly saturated (Chen et al. 2015), causing a high K\(_d\) value. The \(\log K_d\) value of PEI-nori-biochar is higher than that of PEI-chestnut-biochar, indicating that PEI-nori-biochar possessed a significantly greater affinity for Cr(VI) than PEI-chestnut-biochar.

**Sorption isotherms**

In order to better understand the connection between the volume of adsorbed composites and contaminative composites in the wastewater, the sorption isotherms of Cr(VI) on PEI-chestnut-biochar and PEI-nori-biochar composites are shown in Figure 7. The sorption of Cr(VI) increased as Cr(VI) concentrations increased, because a higher Cr(VI) concentration has a higher sorption driving force, causing the increase of the collision probability between Cr(VI) and countless active sites of various adsorbents. The sorption of Cr(VI) on PEI-chestnut-biochar and PEI-nori-biochar increases with the increase of temperature, indicating that a high temperature is favorable for Cr(VI) sorption.

The Langmuir and Freundlich (Shao et al. 2012) isotherms models were used to simulate Cr(VI) sorption behavior of PEI-chestnut-biochar and PEI-nori-biochar. Their equations can be expressed as follows:

\[
q_e = \frac{q_{\text{max}} L C_e}{1 + L C_e} \quad (6)
\]

\[
q_e = K_f C_e^{1/n} \quad (7)
\]

where \(C_e\) (mg/L) is the equilibrium concentration, \(L\) is the sorption isotherm model constant, and \(q_{\text{max}}\) (mg/g) refers to maximum sorption capacity. \(K_f\) is related to sorption and \(n\) is the dimensionless unit on behalf of the surface heterogeneity.

Table 3 shows the equilibrium data of Cr(VI) sorption which were carried out to match the Langmuir and Freundlich isotherm models. The Freundlich model \((R^2 = 0.989-0.996)\) displays better correlation than the Langmuir model \((R^2 = 0.756-0.936)\), which indicates that PEI-chestnut-biochar and PEI-nori-biochar for Cr(VI) sorption are multilayer and heterogeneous sorption because the heterogeneous distribution of active sites on the modified adsorbents' surface (Karamanis & Assimakopoulos 2007). The sorption intensities \(n\) between 3.33 and 6.32 for PEI-chestnut-biochar and PEI-nori-biochar at three different temperatures, indicate it is favorable to the sorption (Brown et al. 2000; Yang et al. 2011). The sorption
capacity of PEI-nori-biochar and PEI-chestnut-biochar is remarkably higher than that of pristine biochars and the sorption capacity of four materials is in the order of PEI-nori-biochar > PEI-chestnut-biochar > pristine-nori-biochar > pristine-chestnut-biochar. The decrease of surface area and pore volume of PEI modified biochar after being modified by PEI; however, PEI provided the surface functional groups and enhanced the surface active sites for Cr(IV) removal, which confirm that the adsorption mechanism can be mainly attributed to the surface functional groups. From Table S2 (available with the online version of this paper), Cr(VI) sorption capacities of PEI-nori-biochar and PEI-chestnut-biochar are higher than the other adsorbents reported in previous literature. The PEI-chestnut-biochar and PEI-nori-biochar exhibited a significant sorption capacity.

It is well known that Cr(VI) can be eliminated by bio-sorbent materials via reduction mechanisms. The XPS spectroscopy technique was carried out to evaluate the interaction mechanism between biochar and Cr(VI). As shown in Figure S1A (Figure S1 is available online), PEI-nori-biochar exhibits the significant signals of Cr 2p peaks after removal, indicating amounts of Cr(VI) adsorbed onto the PEI-nori-biochar. The binding energies at 578.1 and 576.3 eV could be corresponded to Cr(VI) and Cr(III) (Zhu et al. 2017), respectively (Figure S1B). Moreover, it manifests that the portion of Cr(VI) has been reduced to Cr(III) on the surface of PEI-nori-biochar. The electrons needed for chemical reduction of Cr(VI) may come from the electron donor groups (e.g. amino) of the PEI-nori-biochar.

**Sorption thermodynamics**

Appropriate assessment of thermodynamics can evaluate whether the sorption process is spontaneous or not. The thermodynamics parameters include Gibbs free energy ($\Delta G^0$), enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$). The thermodynamics equations can be represented as

$$\Delta G^0 = -RT \ln K_f$$

$$\Delta H^0 = \Delta C_p \Delta T$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

where $R$ is the gas constant, $T$ is the temperature in Kelvin, $K_f$ is the equilibrium constant, and $\Delta C_p$ is the change in heat capacity.

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<th>Adsorbent</th>
<th>Langmuir</th>
<th>Freundlich</th>
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<td>$T$ (K)</td>
<td>$L$ (L/mg)</td>
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<tr>
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<td></td>
<td>318</td>
<td>0.442</td>
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Table 4 | Thermodynamic parameters for Cr(VI) sorption of PEI-chestnut-biochar and PEI-nori-biochar

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>298 K lnKd</th>
<th>308 K lnKd</th>
<th>318 K lnKd</th>
<th>ΔH°(kJ mol⁻¹)</th>
<th>ΔS°(J mol⁻¹ K⁻¹)</th>
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<tbody>
<tr>
<td>PEI-chestnut-biochar</td>
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<td>3.57</td>
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<td>20.88</td>
</tr>
<tr>
<td>ΔG°(kJ mol⁻¹)</td>
<td>-6.22</td>
<td>-6.43</td>
<td>-6.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEI-nori-biochar</td>
<td>4.00</td>
<td>4.41</td>
<td>5.02</td>
<td>4.00</td>
<td>16.72</td>
</tr>
<tr>
<td>ΔG°(kJ mol⁻¹)</td>
<td>-4.98</td>
<td>-5.15</td>
<td>-5.31</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Zhou et al. 2016):

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0
\]

(8)

\[
\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]

(9)

where \( R \) (8.314 J/mol/K) is the universal gas constant and \( T \) (K) is the temperature; \( C_e \) (mg/L) is the equilibrium concentration, and \( q_e \) is the equilibrium sorption capacity.

As shown in Figure S2 (available online), \( \Delta H^0 \) and \( \Delta S^0 \) can be calculated by plotting \( \ln K_d \) versus \( 1/T \). Thermodynamic parameters for Cr(VI) sorption onto PEI-chestnut-biochar and PEI-nori-biochar are listed in Table 4. The values of \( \Delta H^0 \) for Cr(VI) on PEI-chestnut-biochar and PEI-nori-biochar samples are positive and increased with increasing temperature, indicating that the sorption process is endothermic. The dehydration of Cr(VI) from Cr(VI) aqueous complex ion needed energy, and this energy exceeded the exothermicity of Cr(VI) to adhere to the surface of adsorbents; that is why a high temperature is good for Cr(VI) sorption (Chen et al. 2009). The negative \( \Delta G^0 \) values indicated that the sorption process is spontaneous. The values of \( \Delta G^0 \) decreased with increasing temperature, suggesting that the sorption process is more favorable at a higher temperature. Therefore, the sorption of Cr(VI) on PEI-chestnut-biochar and PEI-nori-biochar is a spontaneous and endothermic process.

Desorption and recycle of adsorbents

The desorption and recycling of PEI-chestnut-biochar and PEI-nori-biochar is of crucial importance for heavy metal ion sorption from wastewater. Figure S3 (available online) shows sorption–desorption experimental results. The maximum recovery efficiency of 95% is achieved effectively by 1 M NaOH that is better than using deionized water. The PEI-chestnut-biochar and PEI-nori-biochar all showed high efficiency for the sorption of Cr(VI) from aqueous solutions after six sorption–desorption cycles, indicating that the modified adsorbents possessed a stable and recyclable performance for the removal of Cr(VI) from wastewater.

CONCLUSIONS

In this paper, the PEI-chestnut-biochar and PEI-nori-biochar were synthesized, and they displayed a fast removal rate and excellent sorption capacity under low Cr(VI) concentration. The sorption of Cr(VI) is independent of the pH of solution and independent on ionic strength, indicating that electrostatic attraction and the reduction of Cr(VI) to Cr(III) play primary roles in Cr(VI) removal onto PEI modified biochars. The sorption followed pseudo-second-order kinetics. The sorption isotherms could be well fitted by the Freundlich model. The thermodynamic data suggested that the sorption process was spontaneous and endothermic. The PEI grafted onto the biochars significantly enhanced Cr(VI) sorption capacity because PEI contains volumes of amine groups which can adsorb Cr(VI) ions. In addition, the PEI-nori-biochar and PEI-chestnut-biochar were a form of regeneration adsorbents. Thus, all the results showed that PEI-nori-biochar and PEI-chestnut-biochar were cost-effective and environmentally friendly adsorbents to remove Cr(VI) from wastewater.

REFERENCES


Zhang, R., Chen, C., Li, J. & Wang, X. 2015 Investigation of interaction between U(VI) and carbonaceous nanofibers by batch experiments and modeling study. *J. Colloid Interface Sci.* **460**, 237–246.


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