# Polyethylenimine Facilitated Ethyl Cellulose for Hexavalent Chromium Removal with a Wide pH Range

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**ABSTRACT:** Ethyl cellulose (EC) composites modified with 20.0 wt % polyethylenimine (PEI) (PEI/ECs) demonstrated effective hexavalent chromium, [Cr(VI)], removal from solutions with a wide pH range. For example, 4.0 mg/L Cr(VI) solution with a pH below 3.0 was completely purified by 3.0 g/L PEI/ECs within 5 min, much faster than the as-received EC (2 h) and activated carbon (several hours). These PEI/ECs adsorbents has overcome the low pH limitation of Cr(VI) removal; for example, 4.0 mg/L Cr(VI) solution with a pH of 11.0 was completely purified within 15 min. These adsorbents followed chemical adsorption as revealed from the pseudo-second-order kinetic study. These PEI/ECs following the isotherm Langmuir model have a maximum adsorption capacity of 36.8 mg/g, much higher than pure EC (12 mg/g), tetrabutylammonium-modified celluloses (16.67 mg/g), and magnetic carbon (16 mg/g). The reduction of Cr(VI) to Cr(III) by the oxidation of amine groups and hydroxyl groups of PEI/ECs was verified as the main mechanism for the Cr(VI) removal.

**KEYWORDS:** Cr(VI) removal, polyethylenimine (PEI), ethyl cellulose (EC), adsorption, kinetics, redox reaction
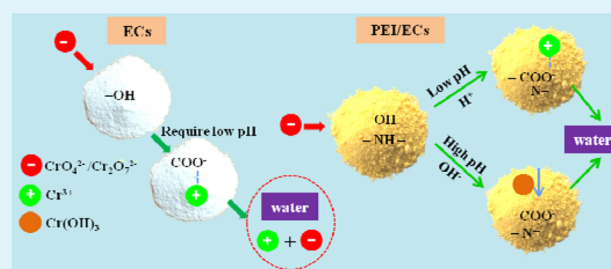
## INTRODUCTION

Among the commonly existing Cr(VI) and Cr(III) in surface and ground water arising from the wide usage of chromium in electroplating, printing, pigments, and other industries,[1] the former has been recognized as a serious environmental problem due to its toxicity to living organisms and potential carcinogenicity to humans.[2,3] Among the reported technologies, including the electrochemical precipitation,[4] ion exchange,[5] membrane separation,[6] photocatalysis,[7,8] and adsorption[3,9] to remove Cr(VI), adsorption is widely used due to its easy operation and great removal performance.[10−12] Adsorbents such as iron,[13] zero-valence aluminum (ZVAl),[2] polymers,[10,14,15] and biomass[16,17] have demonstrated high efficiency in removing Cr(VI). Recently, sustainable biocompatible cellulose with excellent mechanical and chemical properties[16,17] and abundant hydroxyl groups can not only act as electron donors for Cr(VI) reduction to Cr(III) but also provide active sites for Cr(III) adsorption or precipitation.[16,17] However, low adsorption capacity, slow removal rate, and limited solubility in common solvents arising from its intra- and inter-molecular hydrogen-bond network induced highly crystalline structure challenge its applications. Another challenge for Cr(VI) removal is the low pH suitability. Many adsorbents, including

polymers, cellulose, and magnetic carbon are efficient for Cr(VI) removal from acidic solutions usually with pH lower than 3, while they have a decreased efficiency in neutral or basic solutions.[14,17,18] Cellulose normally can only serve as a support for polymers rather than provide active sites for removing the pollutants.

Chemical modification is able to solve the aforementioned challenges by improving the physicochemical properties. For example, cellulose derivatives from the conversion of hydroxyl groups to ethyl acetate or other groups have a good solubility in traditional solvents and have been employed as the substrates to adsorbents for effectively removing Cr(VI).[19] Further enhancement was achieved by introducing exotic chemicals. For example, ethyl cellulose (EC) modified with polyaniline (PANI) by a homogeneous mixing method[19,20] has demonstrated great Cr(VI) removal with both amine groups of PANI and hydroxyl groups of cellulose participating in the Cr(VI) reduction. Cellulose grafted with amine groups of PANI,[19] cysteine,[21] triethylenetetramine,[22] and dimethylamine[23] were
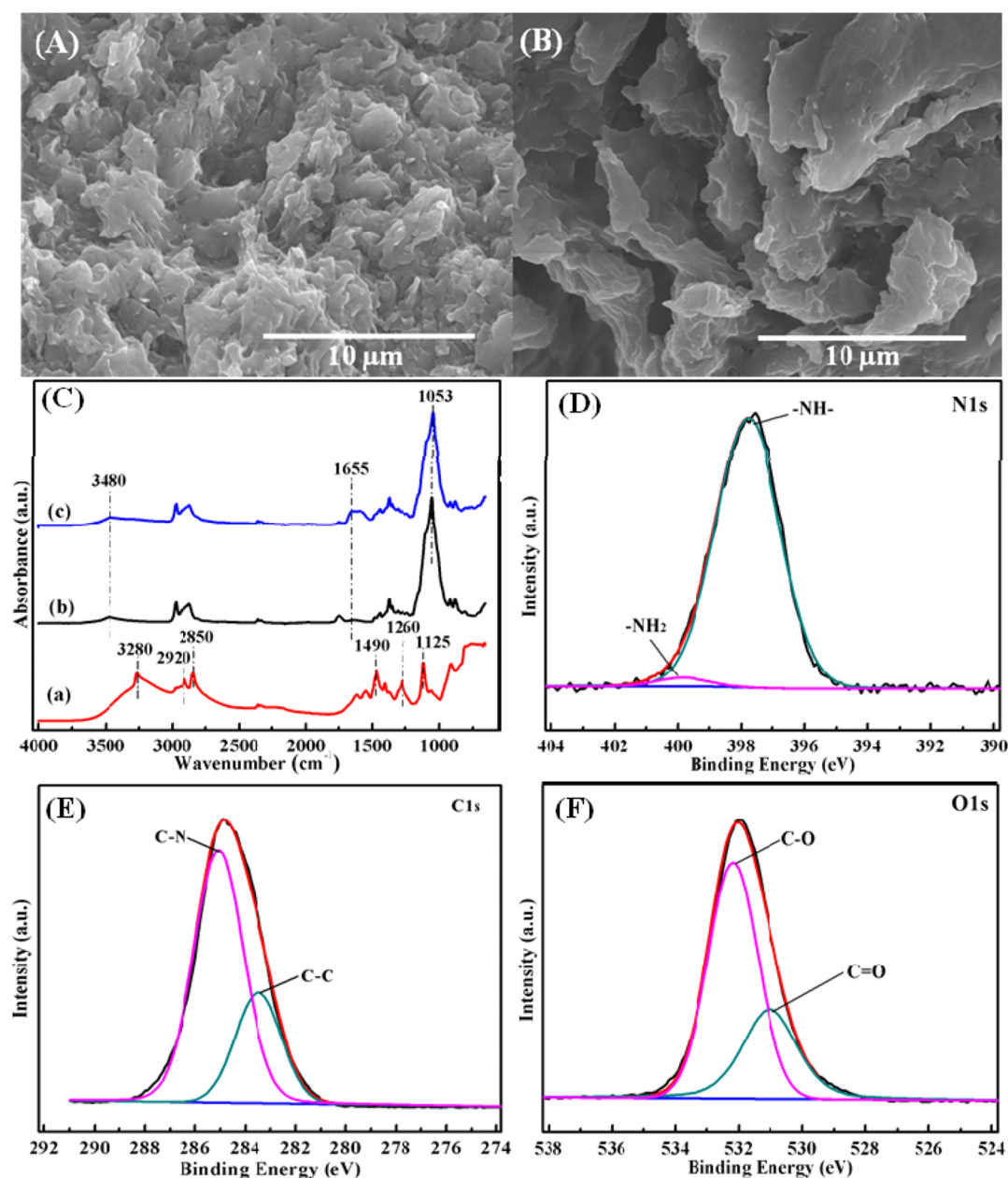
**Figure 1.** SEM images of (A) EC and (B) synthesized PEI/ECs; (C) FT-IR spectra of (a) PEI, (b) EC, and (c) PEI/ECs, and (D) N 1s, (E) C 1s, and (F) O 1s XPS spectra of the PEI/ECs.

reported to be effective in Cr(VI) reduction and adsorption. PANI-modified magnetite[14] and cellulose[19] composites have demonstrated fast Cr(VI) removal and high removal capacities in acidic solutions but have decreased performances with increased solution pH value. Polyethylenimine (PEI), composed of plenty of amine groups on the linear type macromolecular chains,[24−26] makes it excellent for Cr(VI) reduction. Moreover, it has a high zero potential point with pH up to 10, allowing PEI to be positively charged in neutral and basic solutions.[27,28] However, the high solubility of PEI in water challenges its recycling for heavy metal removals. Recently, insoluble polymers,[29] biomass,[10,30] and magnetic particles[31] have been used to immobilize PEI to prevent its leaching during adsorption, and the reported techniques include a surface-coating method.[32,33] The PEI modified composites have demonstrated great nitrate[32] and phosphate removal.[33]

However, the PEI-cellulose composites for Cr(VI) removal have not been reported, and their potential for treating polluted water with wide pH values was not explored. In this study, PEI/ECs prepared by a homogeneous mixing method were studied for the first time for Cr(VI) removal. The Cr(VI) removal performances were explored by adsorption batch assays. The Cr(VI) removal from solutions with wide pH values ranging from 1.0 to 11.0 was evaluated together with the effects of treatment time and Cr(VI) concentration. Meanwhile, the removal kinetics and isothermal behaviors were studied to disclose the removal rate and maximum removal capability of the hybrid adsorbent. The Cr(VI) removal mechanisms over a wide pH range were determined to reveal the Cr(VI) removal of the novel adsorbent.

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## ■ MATERIALS AND METHOD

**Synthesis of PEI/ECs.** Polyethylenimine (1.0 g, PEI, MW: 10 000 g/mol, Linear, Sigma-Aldrich) was dissolved in 50 mL ethanol (99.5%, Fisher Scientific) to obtain a 20.0 g/L PEI solution. Ethyl cellulose (4.0 g, EC, with 48−49.5% ethoxy content, Sigma-Aldrich) in 400 mL ethanol was sonicated and mechanically stirred at 300 rpm for 1 h. The PEI solution was then added into the EC solution drop by drop and was continuously stirred for another 1 h to obtain a homogeneous mixture. The well-mixed solution was heated at 50 °C. The EC composites with a 20.0 wt % PEI loading were obtained when ethanol was completely evaporated. The PEI/ECs were washed five times by using deionized water and then dried in a vacuum oven at 50 °C overnight.

**Cr(VI) Removal.** 4.0 g/L Cr(VI) stock solution was prepared using potassium dichromate ($K_2Cr_2O_7$, 99%, Alfa Aesar Company). The effect of initial pH on the Cr(VI) removal was investigated with an initial pH value of 1.0, 2.0, 3.0, 5.0, 7.0, 9.0, and 11.0, which was adjusted by NaOH (1.0 mol/L) and $H_2SO_4$ (1.0 mol/L) with a pH meter (Vernier Lab Quest with pH-BTA sensor). The PEI/ECs (60.0 mg) were added into 20.0 mL Cr(VI) solutions (4.0 mg/L). The pH values and Cr(VI) concentrations in the solutions were measured at controlled time intervals. For comparison, the as-received EC (60.0 mg) was also used to treat 20.0 mL Cr(VI) solution at pH 1.0 with an initial Cr(VI) concentration of 4.0 mg/L for 60 min. The effect of initial Cr(VI) concentration on the Cr(VI) removal was studied by using PEI/ECs (60.0 mg) to treat Cr(VI) solutions (20.0 mL, pH = 1.0) with Cr(VI) concentration varying from 2.0 to 200.0 mg L$^{-1}$ for 30 min. For kinetic studies, the PEI/ECs (60 mg) were carried out to treat 20.0 mL Cr(VI) solution with 20.0 mg/L Cr(VI) at a pH of 1.0, 7.0, and 11.0, respectively. The Cr(VI) concentration was determined by the colorimetric method.[3] For the measurement of total Cr concentration, the solution was first oxidized by ammonium persulfate [APS, $(NH_4)_2S_2O_8$, 98%, Sigma-Aldrich] in an acidic condition at 100 °C. The total Cr concentration was determined by the same procedures as the Cr(VI) measurement. APS was added into the desorption solution for the oxidation of Cr(III) to Cr(VI), and therefore the measured Cr(VI) concentration was the total Cr concentration. The Cr(III) concentration was calculated from the difference between the total Cr and Cr(VI) concentration. All the Cr(VI) removal tests were all conducted at room temperature by using the obtained standard fitting equation: $A = 9.7232 \times 10^{-4}C$, where $C$ is the concentration of Cr(VI) and $A$ is the absorbance at 540 nm obtained from the UV−vis test.

The Cr(VI) removal percentage (R %) is calculated using eq 1:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

where $C_0$ and $C_e$ (mg/L) are the Cr(VI) concentrations in solution before and after treatment, respectively. The removal capacity (Q, mg/g) is quantified by eq 2:

$$Q = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where $V$ (L) represents the volume of Cr(VI) solution and $m$ (g) is the mass of the used PEI/ECs.

**Characterization.** The morphology of PEI/ECs was examined by a Hitachi S4300 scanning electron microscopy (SEM). All the samples were sputter-coated with a thin layer of gold (about 5 nm) to ensure good conductivity. The functional groups were characterized by Fourier transform infrared spectroscopy (FT-IR, a Bruker Inc. Vector 22 coupled with an ATR accessory) in the range from 600 to 4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$. The X-ray photoelectron spectroscopy (XPS) measurements were performed in the Kratos AXIS 165 XPS/AES instrument using a monochromatic Al Kα radiation to monitor the elemental compositions. The N 1s, C 1s, O 1s, and Cr 2p peaks were deconvoluted into the components consisting of a Gaussian/Lorentzian line shape function (Gaussian = 80%, Lorentzian = 20%) on a linear background. The hydrophilicity of as-received EC and PEI/EC was determined by contact angle measurements with a contact angle analyzer (Future Digital Scientific Corp.).

## ■ RESULTS AND DISCUSSION

**Characterizations of PEI/ECs.** Figure 1 shows the morphologies of EC and the PEI/ECs. The pristine EC exhibits a small flake structure and rough surface. The PEI/ECs (Figure 1B) show larger flakes and much smoother surface, suggesting that PEI has been distributed homogeneously on the EC. Figure 1C,a shows the FT-IR spectrum of PEI. A broad and strong band ranging from 3000 to 3500 cm$^{-1}$ is assigned to the overlapping of −NH− and −OH stretching, while the peaks at 2920 and 2850 cm$^{-1}$ correspond to the C−H stretching vibration of −CH$_2$ and −CH groups in the PEI chains.[24] The peak at 1625 cm$^{-1}$ corresponds to the N−H vibration in PEI.[34] After it was mixed with EC (Figure 1C,c), these characteristic peaks at 3280 and 1125 cm$^{-1}$ disappeared and the peaks at 1490 and 1260 cm$^{-1}$ become weaker while other characteristic peaks at 2920, 2850, 1625, and 1563 cm$^{-1}$ are shifted to larger wavenumbers. Compared to the spectrum of EC (Figure 1Cb), a little increased intensity at 3480 cm$^{-1}$ is observed for the synthesized PEI/ECs, indicating that the −OH groups participated in the reaction between PEI and EC. It is consistent with the results of PEI-coated aerobic granule sludge by cross-linking between the −OH group and the −NH− group.[10,30] The N 1s peak (Figure 1D) was deconvoluted to two major components with binding energy peaks at 397.8 and 399.9 eV, which are assigned to secondary (−NH−) and primary (−NH$_2$) amine groups, respectively.[35,36] The abundant amine groups show that PEI/ECs can act as electron donors for the Cr(VI) reduction. As shown in Figure 1E, the C 1s peak was deconvoluted to two major components with the binding energy peaks at 283.5 and 285.1 eV, corresponding to the C−C and C−N, respectively.[35,36] The O 1s spectrum (Figure 1F) can be fitted to two peaks with the binding energies at 531.1 and 532.2 eV, which are assigned to C=O and C−O groups, respectively.[35,37] These have demonstrated that EC has been successfully modified with PEI by cross-linking −NH− groups of PEI with −OH groups of EC, which prevents the leakage of soluble PEI to aqueous solution when being used as the adsorbent for Cr(VI) removal.

The wettability behavior of EC before and after being modified with PEI was determined by the contact angle with water. The as-received EC has a contact angle of 113.1° (Figure 2A), demonstrating the hydrophobic property of EC. It is different from the cellulose fibers with a superhydrophilic characteristic due to the high density of hydroxyl groups.[38] For the EC used in this study, ~48% hydroxyl groups have been converted into ethyl groups, leading to an obviously decreased hydrophilicity.[38] After being modified with 20.0 wt % PEI
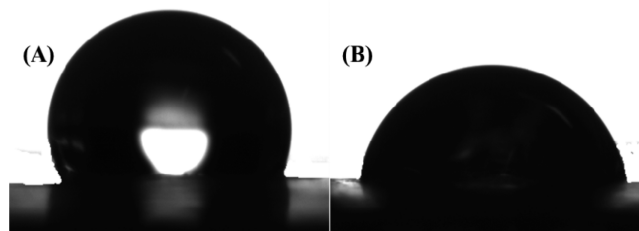


**Figure 2.** Images of contact angle of (A) EC and (B) the synthesized PEI/ECs with deionized water.
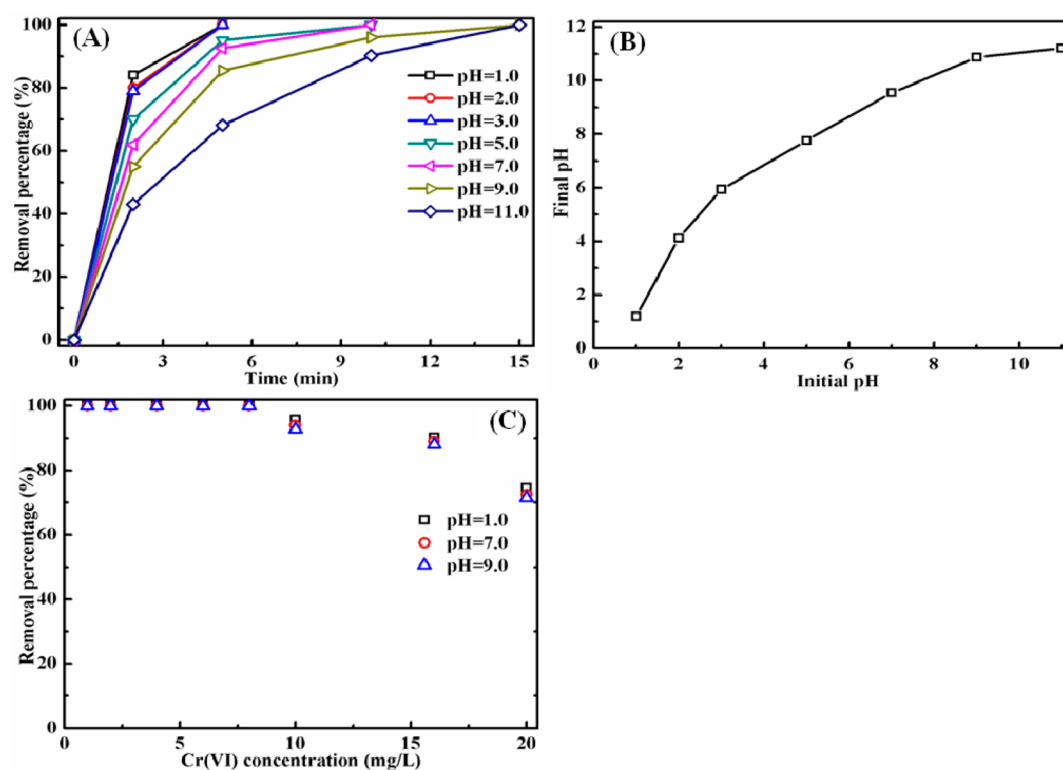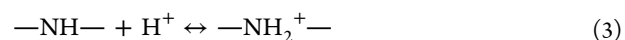
**Figure 3.** (A) pH value effect on the Cr(VI) removal. Cr(VI): 4.0 mg/L; volume: 20 mL; PEI/ECs dosage: 60 mg; (B) pH value change in solutions with different initial pH values; and (C) initial Cr(VI) concentration effect on the Cr(VI) removal by PEI/ECs (volume: 20 mL, PEI/EC dosage: 60 mg, pH: 3.0, time: 15 min).

(Figure 2B), the contact angle of the PEI/EC is decreased to 84.7°, demonstrating a hydrophilic behavior. The improved hydrophilicity of PEI/ECs is attributed to the introduced amine groups on the PEI chains. The enhanced hydrophilic behavior of the PEI/ECs may enhance the pollutants removal by accelerating the pollutant transfer from solution to the adsorbent surface.[39,40]

**Cr(VI) Removal Investigations.** The synthesized PEI/ECs have demonstrated great Cr(VI) removal with a wide initial pH range, Figure 3A. The Cr(VI) removal is highly pH dependent for the PEI/ECs, lower pH facilitates the Cr(VI) removal with a higher removal rate. For example, 4.0 mg/L Cr(VI) was completely removed from solutions with an initial pH below 3.0 by 3.0 g/L PEI/ECs within 5 min, while the removal rate was decreased obviously with increasing the pH value. The time for the total Cr(VI) removal by the PEI/ECs was much shorter than that of the pristine EC (>2 h), cellulose (1.5 h), and cellulose modified with silica (30 min),[41] methyltrioctylammonium chloride (30 min),[42] tetrabutylammonium iodide (30 min),[43] and glycidyl methacrylate (60 min).[22,23] It also performed better than other noncellulose adsorbents such as N-doped porous carbon (60 min)[44] and zero-valence magnesium (60 min)[45] and composites of chitosan beads-supported iron (several hours).[46]

Figure 3A shows that the Cr(VI) removal rate was decreased with increasing the initial pH of solution. It is worth noting that the 4.0 mg/L Cr(VI) solutions with initial pHs of 5.0 and 7.0 were completely purified by PEI/ECs within 10 min and within 15 min for the solution with an initial pH of 9.0 and 11.0. More importantly, more than 65% Cr(VI) was removed by PEI/ECs during the initial 5 min for all the solutions. It indicates that the PEI/ECs can totally remove Cr(VI) not only from acidic solutions but also from neutral and basic solutions. The PEI/ECs have demonstrated as effective adsorbents for Cr(VI) removal with a wide pH range. Although a little longer time was required for complete Cr(VI) removal from solutions with higher pH, the time (15 min) was still much shorter than that by many other adsorbents.[41−44] Pure EC was also used for Cr(VI) removal as a comparison in this study, only ~20% Cr(VI) was removed from the solutions with an initial pH of 1.0 within 15 min. The PEI/ECs, significantly different from many other adsorbents,[10−12] show much better Cr(VI) removal from basic solutions. The difference is mainly associated with the functional groups on the adsorbents surface. Carboxyl, the most functional group on the traditional adsorbents surface, is negatively charged at a pH above 5.[47,48] The electrostatic repulsion between the negatively charged adsorbents and negatively charged Cr(VI) ions prevents them from approaching the functional groups on the adsorbent surface. However, amine groups of PEI can be protonated even when the pH is above 10,[27] thus allowing the adsorption to occur by the electrostatic attraction at high pH. The increased pH indicates that the H+ was consumed during the Cr(VI) removal (Figure 3B), which might be related to the protonation of amine groups as eq 3.[10]

$$—NH— + H^+ \leftrightarrow —NH_2^+— \tag{3}$$

The effect of initial Cr(VI) concentration on the Cr(VI) removal by PEI/ECs was investigated (Figure 3C). 3.0 g/L PEI/ECs can completely remove 8.0 mg/L Cr(VI) within 5 min at pH 1.0. The Cr(VI) removal percentage is observed to decrease with increasing the initial Cr(VI) concentration. The decreased Cr(VI) removal percentage is mainly due to the limited available active sites and the loss of PEI active sites
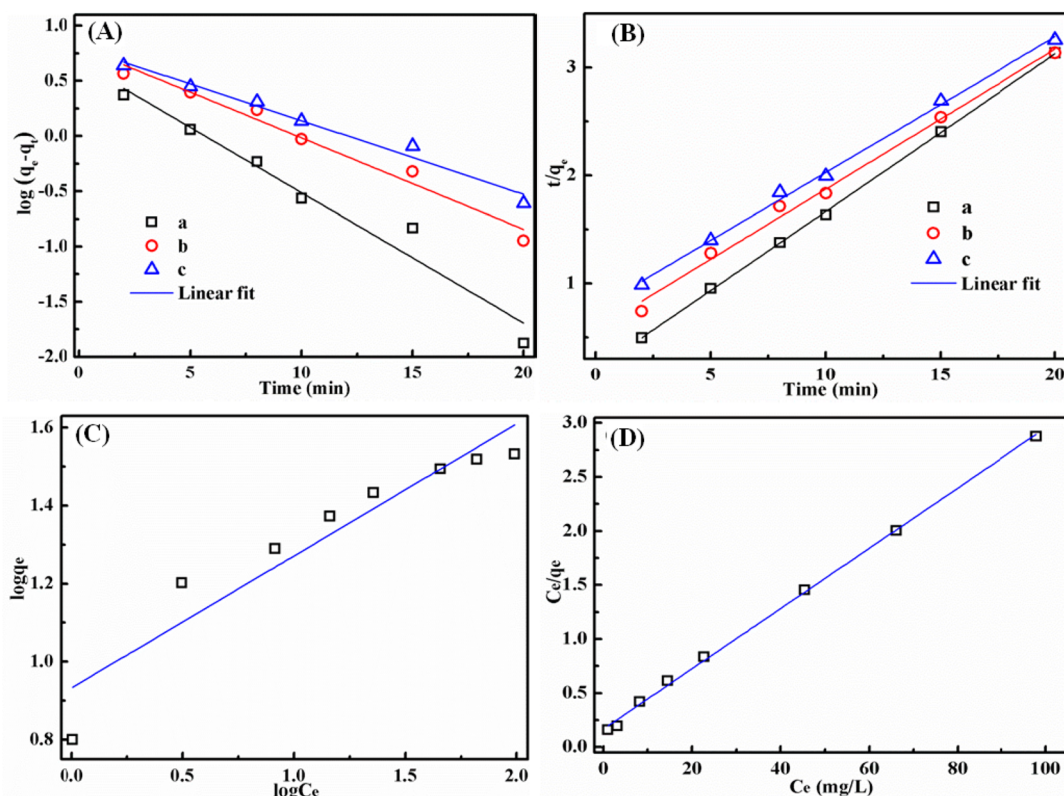
**Figure 4.** Cr(VI) adsorption kinetic by PEI/ECs fitted by (A) pseudo-first-order and (B) pseudo-second-order models at a pH of (a) 1.0, (b) 7.0, and (c) 9.0; Cr(VI) adsorption isotherm by PEI/ECs fitted by the (C) Langmuir and (D) Freundlich models.

caused by its overoxidation with high Cr(VI) concentrations. However, more than 80% Cr(VI) was removed by the PEI/ECs within 5 min, even though the initial Cr(VI) concentration was up to 20.0 mg/L. Figure 3C shows that the same Cr(VI) removal percentage as that at pH 1.0 was also achieved at pHs 7.0 and 11.0 with a little longer time (15 min). Generally, the PEI/ECs have a good Cr(VI) removal from all the acidic, neutral, and basic solutions, indicating that the PEI/ECs might have a wide practical application for the remediation of Cr(VI) contamination.

**Adsorption Kinetic and Isotherm.** It was observed that the Cr(VI) adsorption rate by PEI/ECs was rapid during the initial reaction stage and then gradually decreased (Figure 3A). Two models (i.e., pseudo-first-order and pseudo-second-order models) were employed to evaluate the Cr(VI) removal kinetics by PEI/ECs (Figure 4). The adsorption process was found to fit better with a pseudo-second-order model with a correlation more than 0.99 (Figure 4B), indicating a chemical adsorption controlled adsorption rate.[19] It is consistent with the results based on FT-IR (Figure 5A) and XPS (Figure 5, panels B−E), showing the reduction of Cr(VI) to Cr(III) by PEI/ECs.

Two isotherm models (i.e., Langmuir[3,19] and Freundlich)[3,19] were used to fit the Cr(VI) removal process by PEI/ECs. Adsorption isotherms describe the interaction between Cr(VI) and PEI/ECs and thus are critical for optimizing the application of the adsorbent. Two isotherm models (i.e., Langmuir and Freundlich) were used to fit the Cr(VI) removal process by PEI/ECs in this study. The Langmuir isotherm applicable for monomolecular layer adsorption has been applied to obtain a maximum adsorption capacity and is described as eq 4:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \tag{4}$$

where $C_e$ is the equilibrium concentration (mg/L) of Cr(VI), $q_e$ is the Cr(VI) amount adsorbed at equilibrium (mg/g), $q_{max}$ is the adsorption capacity of PEI/ECs (mg/g), and $b$ is a constant (L/mg).

The Freundlich isotherm, describing the adsorption on a homogeneous surface through a multilayer adsorption mechanism, is an empirical model that considers heterogeneous adsorptive energies on the surface of absorbent and is described by eq 5;

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \tag{5}$$

where $q_e$ is the amount of Cr(VI) adsorbed on the surface of PEI/ECs at equilibrium, $C_e$ is the equilibrium concentration, and $k_f$ and $n$ are constants of the Freundlich model.

The Cr(VI) solutions with initial concentrations ranging from 12.0 to 200 mg/L were treated by 3.0 g/L PEI/ECs at pH 3.0. In accordance with the correlation coefficient values, the Langmuir model was observed to fit better for the Cr(VI) adsorption isotherm (Figure 4C), indicating that the Cr(VI) adsorption by PEI/CEs was limited by monolayer coverage. This may be attributed by the homogeneous surface of PEI/ECs (Figure 1B). The maximum Cr(VI) removal capacity by the PEI/ECs calculated by the Langmuir model was 36.8 mg/g, much higher than that by pure EC (12 mg/g), cellulose (13.4 mg/g), cellulose-modified with silica (19.46 mg/g),[41] tetrabutylammonium iodide (16.67 mg/g),[43] and other adsorbents such as the N-doped carbon with magnetic particles (16 mg/g).[44] It performed as well as the cellulose grafted with 38 wt %
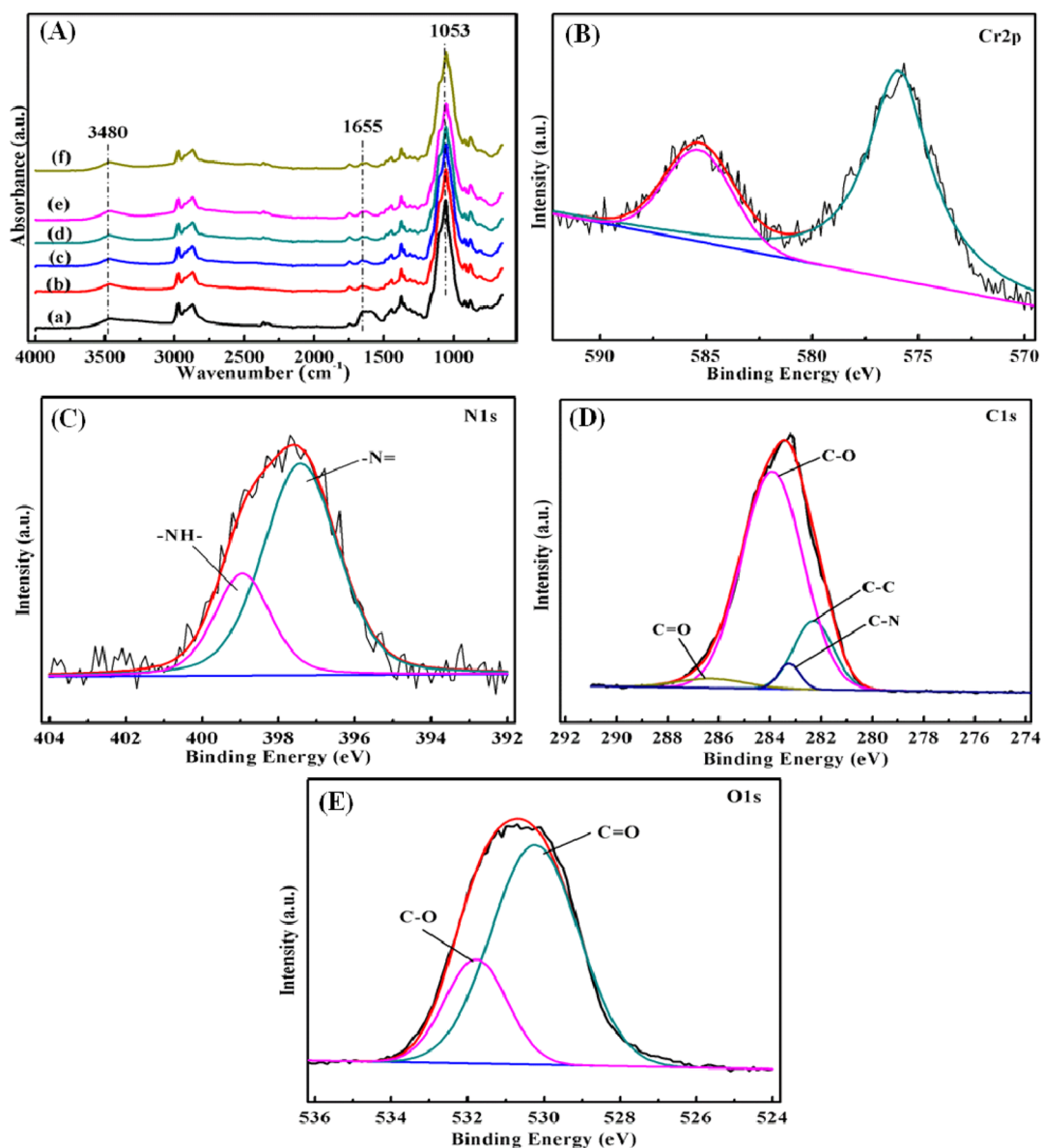
**Figure 5.** (A) FT-IR spectra of (a) PEI/ECs and PEI/ECs treated by (b) 4, (c) 20, (d) 80, (e) 160, and (f) 200 mg/L Cr(VI) at pH 2.0; (B) Cr 2p, (C) N 1s, (D) C 1s and (E) O 1s XPS spectra of PEI/ECs after treatment with 1000 mg/L Cr(VI) solution.

methyltrioctylammonium chloride with an adsorption capacity of 38.94 mg/g.[42]

**Cr(VI) Removal Mechanism.** Many processes such as the electrostatic attraction, redox reactions, and precipitation could get involved in the Cr(VI) removal. Herein the adsorbent hydrophilic property, electrostatic attraction, and redox reactions were considered for these novel PEI/ECs adsorbents. The enhanced hydrophilic behavior facilitates the Cr(VI) transfer between the wastewater and the adsorbent surface. The $HCrO_4^-$ and $H_2CrO_4$ are the dominant species at pH lower than 6.8, while only $CrO_4^{2-}$ is stable at pH above 6.8.[10] All the forms of Cr(VI) are negatively charged in the solution.[10] It can be inferred that the PEI/ECs can not only remove $HCrO_4^-$ and $H_2CrO_4$ but also remove $CrO_4^{2-}$ and $Cr_2O_7^{2-}$. The amine groups of PEI/ECs can be protonated and positively charged with pH below 10.[27,28] As shown in Figure 3B, protons were consumed during the Cr(VI) removal process, which might be related to the protonation of amine groups and the reduction of Cr(VI). For the negatively charged Cr(VI), the electrostatic

attraction plays an important role in allowing the ions to approach the positively charged surface of PEI/ECs.

The functional groups of the PEI/ECs after being treated with Cr(VI) were determined by FT-IR (Figure 5A). The intensity of peaks at 3480 and 1655 cm$^{-1}$ was decreased, indicating that the amine groups participated in the Cr(VI) removal process. Moreover, the decreased intensity at 1053 cm$^{-1}$ suggests that the −OH groups also act as active sites for the Cr(VI) reduction.[17] However, no changes were observed for the peaks at 2920 and 2850 cm$^{-1}$, corresponding to the −CH$_3$ asymmetric and symmetric stretching of methyl groups. It is consistent with the previous reports that the −OH acted as electron donors for the Cr(VI) reduction by its oxidation to carboxyl groups.[16,17] The results suggest that both the amine groups of PEI and the hydroxyl groups of EC participated in the Cr(VI) reduction reaction, promoting the superior performance of the PEI/ECs on Cr(VI) removal over the as-received EC.

Figure 5B shows the Cr 2p XPS spectrum of PEI/ECs treated by 1000 mg/L Cr(VI) at pH 3.0 for 15 min. As documented, the characteristic binding energy peaks at 577.0−580.0 and 586.0−588.0 eV correspond to Cr(III), and Cr(VI) contribute the peaks at 580.0−580.5 and 589.0−590.0 eV.[49] The binding energy peaks of Cr 2p spectra were observed to be located at 575.9 and 585.4 eV, indicating that the Cr adsorbed on the surface of PEI/ECs was in the form of Cr(III). No Cr(VI) was detected by Cr 2p XPS spectrum, indicating that the Cr(VI) adsorbed on the adsorbent was completely reduced to Cr(III). As shown in Figure 5C, the N 1s peak was deconvoluted to two major components with binding energy peaks at 397.4 and 398.9 eV, corresponding to imine and amine groups.[35,36] The proportion of amine groups was decreased in the PEI/ECs after being treated with Cr(VI), while the proportion of imine groups was increased significantly, indicating that the amine groups acted as electron donors for the Cr(VI) reduction. This result is consistent with the results based on FT-IR (Figure 5A). The peak of C 1s spectra of the Cr(VI)-adsorbed PEI/ECs (Figure 5D) was deconvoluted to four major components at 282.3, 283.3, 283.9, and 286.4 eV, corresponding to the C−C, C−N, C−O, and C=O, respectively.[35,36] Moreover, the portion of C−N was decreased, and the C=O group was observed in PEI/ECs after being treated with Cr(VI). However, the portion of the C=O was low, indicating that the amine groups in PEI play the most important role in the Cr(VI) reduction. The O 1s spectrum (Figure 5E) was fitted to two peaks. The new binding energies at 530.1 and 530.8 eV could be assigned to C−O and C=O groups,[35,37] suggesting that the hydroxyl group was oxidized to carboxyl group by Cr(VI).

The Cr(VI) and total Cr concentrations remained in the solutions after treatment were also measured in order to determine whether the Cr(III) reduced from Cr(VI) was also removed from solutions. No Cr(VI) was detected in all the solutions after treated with PEI/ECs, indicating that Cr(VI) was reduced to Cr(III). No Cr(III) was detected in the solution with an initial pH above 3.0 (data were not shown), while 232 and 110 ug/L of Cr(III) were measured in the solutions with an initial pH of 1.0 and 2.0, respectively.

For practical application, the recycling and regeneration of the adsorbent is indispensable. The Cr was desorbed from Cr(VI)-adsorbed PEI/ECs by 1.0 M HCl solution at room temperature. The regenerated PEI/ECs were used to treat 4.0 mg/L Cr(VI) solution (20 mL) for 20 min. The adsorption−desorption was conducted for 6 cycles, and the Cr(VI) removal efficiency was measured (Figure 6). The removal efficiency was 100% at the fifth cycle and was then slightly decreased to 96% at the sixth cycle. It indicates that the PEI/ECs are promising absorbents with a high Cr(VI) removal efficiency.

On the basis of the aforementioned analysis, the Cr(VI) removal mechanisms by the as-received ECs and PEI/ECSs were schematically shown in Figure. 7. For the as-received ECs, the Cr(VI) was reduced to Cr(III) by the oxidation of hydroxyl groups to carboxyl groups under the low pH conditions (Figure 7A). The Cr(III) reduced from Cr(VI) were adsorbed on the cellulose surface and were partially released to the solution in the form of Cr(III). However, the introduction of PEI significantly enhances the Cr(VI) removal from aqueous solution. As shown in Figure. 7B, the Cr(VI) was completely reduced to Cr(III) and was completely adsorbed on the adsorbent surface when the initial pH was above 3.0. This is related to the solution pH and the surface property of the
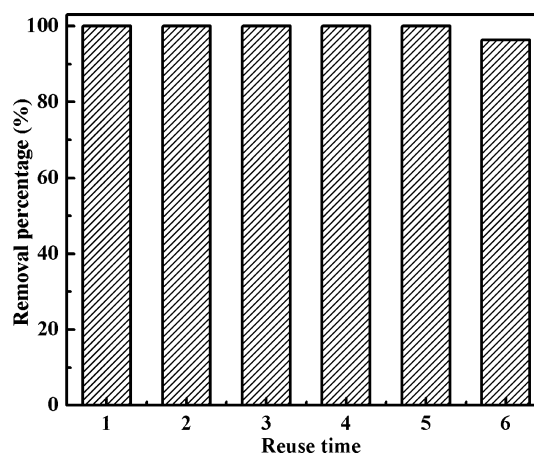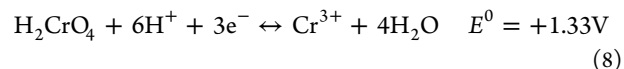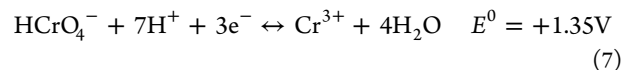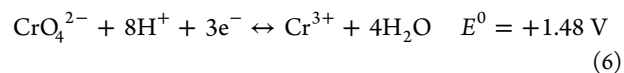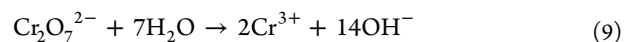


**Figure 6.** Cr(VI) removal efficiency of the regenerated PEI/ECs. Cr(VI): 4.0 mg/L; PEI/ECs: 60.0 mg; pH: 7.0; treating time: 20 min.

adsorbent after being treated with Cr(VI). For the Cr(III) species, the $Cr^{3+}$ is dominating when the pH is blow 4, the $Cr(OH)_2^+$ and $Cr(OH)^{2+}$ exist with the pH ranging from 4.0 to 8.5, and then the $Cr(OH)_3$ and $Cr(OH)_4^-$ are dominating with pH higher than 8.5.[24] The Cr(III) can be complexed with amide groups, leading to the Cr(III) deposition on the surface of the adsorbent. On the other hand, EC with abundant −OH groups (Figure 1B) acts as active sites for the adsorption and precipitation of positively charged Cr(III) ions. Moreover, the protons were consumed for the Cr(VI) reduction (Figure 3B), leading to the increased pH in the solution after being treated with PEI/ECs. Both the PEI/ECs and $Cr^{3+}$ were positively charged at low pH, leading to the release of $Cr^{3+}$ to the solution by electrostatic repulsion. Moreover, the increased pH values decreased the positive charges on the adsorbent surface to improve the Cr(III) adsorption on the adsorbent surface. The obviously increased pH after the Cr(VI) removal in the acidic solutions indicates the protons consumption during the Cr(VI) reduction process. Most protons were consumed during the initial 5 min. Theoretically, three electrons are required for the reduction of one Cr(VI) to Cr(III), eq 6−8.[50]

$$CrO_4^{2-} + 8H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \quad E^0 = +1.48 \text{ V} \tag{6}$$

$$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \quad E^0 = +1.35V \tag{7}$$

$$H_2CrO_4 + 6H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \quad E^0 = +1.33V \tag{8}$$

The increased pH value was also observed in the solutions with an initial pH ranging from 7.0 to 11.0. Different mechanisms are involved in the Cr(VI) removal from the neutral and basic solutions (Figure 7B). Cr(VI) was reduced to Cr(III) with the oxidation of amide and hydroxyl groups of PEI/ECs. The $Cr_2O_7^{2-}$ is the main form existing in the solutions with pHs above 6.8.[24] Stoichiometrically, the reduction of 1 mol $Cr_2O_7^{2-}$ results in a release of 2 mol $Cr^{3+}$ and 14 mol hydroxide ion (OH−) (eq 9). The $Cr^{3+}$ was precipitated under basic conditions. The complete precipitations of the released 2 mol $Cr^{3+}$ hydroxides (eq 10) can consume 6 mol OH−. Thus, the accumulations of the remaining OH− in the solution lead to an increased pH.
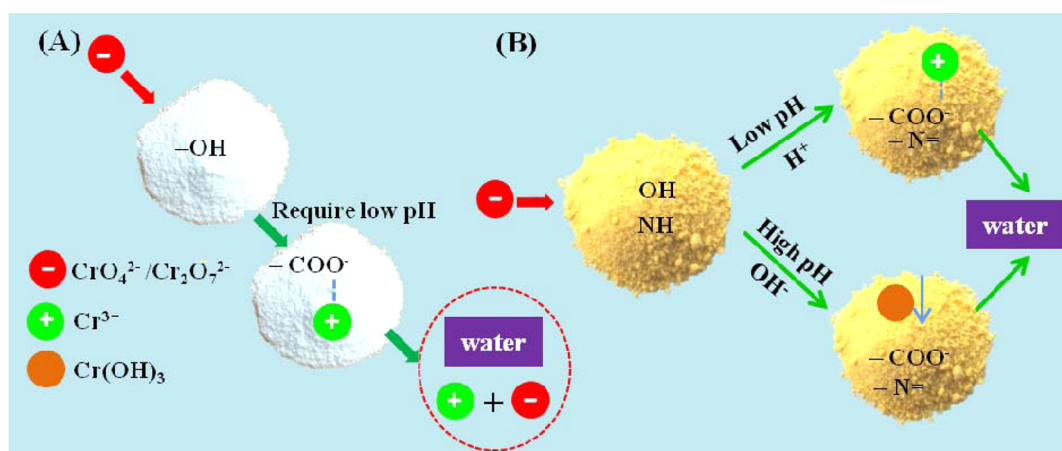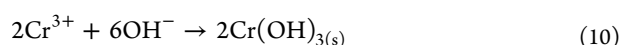
$$Cr_2O_7^{2-} + 7H_2O \rightarrow 2Cr^{3+} + 14OH^- \tag{9}$$

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**Figure 7.** Cr(VI) removal mechanism for the absorbent of (A) as-received EC and (B) PEI/ECs.

$$2Cr^{3+} + 6OH^- \rightarrow 2Cr(OH)_{3(s)} \tag{10}$$

## CONCLUSION

The synthesized PEI/ECs with a PEI loading of 20.0 wt % have demonstrated a significant removal rate and removal capacity for Cr(VI). The Cr(VI) removal by PEI/ECs is highly pH dependent and has a higher removal rate at lower pHs. For example, 4.0 mg/L Cr(VI) solution (20 mL) can be completely removed by 60 mg PEI/ECs within 5 min under the acidic conditions. Meanwhile, 4.0 mg/L Cr(VI) basic solutions can also be totally purified by 3.0 g/L PEI/ECs within 15 min. Fitting with pseudo-second-order kinetics indicates the chemical adsorption characteristics of Cr(VI) by the PEI/ECs. The PEI/ECs follow the Langmuir isotherm better with a calculated maximum adsorption capacity of 36.8 mg/g. The introduced PEI has improved the hydrophilicity of the adsorbent and enhanced the Cr(VI) reduction to Cr(III). Moreover, the protons have been consumed to give an obviously increased pH value during the Cr(VI) reduction, which improved the Cr(III) adsorption or precipitation on the surface of PEI/ECs. The possible mechanism has been proposed, considering the synergy between the PEI and EC substrate and compared with the pristine EC.

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### Notes
The authors declare no competing financial interest.

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