Efficient Removal of Cr(VI) from Aqueous Solution on the Hierarchical Porous N-Doped Carbon Derived from Soft Wood

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Efficient removal of Cr(VI) is one of challenges in wastewater treatment and remediation. The hierarchical porous N-doped carbon derived from renewable soft wood is facilely fabricated by a solvo-hydrothermal method and utilized to remove Cr(VI) efficiently. The as-obtained N-doped carbon exhibits hierarchical porous structure and large specific surface area of 324.2 cm$^2$/g. The fabricated N-doped porous carbon can rapidly and efficiently adsorb Cr(VI) in 1 h and the adsorption process follows the pseudo-second-order model. The high adsorption capacity of 182.8 mg/g based on Langmuir model, and it is competitive with other carbon materials reported to date. Besides, the hierarchical porous carbon is easy to be recycled and the adsorption performance maintains stable over five runs.

Keywords: soft wood, porous N-doped carbon, Cr(VI) removal, high adsorption

Introduction

Chromium (Cr) is commonly utilized in the industrial production process, tanning, painting, and dyeing. Widespread use often associates with heavy environmental issues, especially in the soil and surface water. As well known, chromium (Cr) has two forms both existing in the aqueous solution, trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). The latter Cr(VI) exhibits 500 times toxicity of Cr(III), which can cause serious damage on liver and kidney and deformity to living creatures. To control the emission of Cr(VI), Chinese government formulated the discharge limit of 0.05 mg/L for wastewater. Thus, it is emergent and challenging to remove Cr(VI) efficiently.

So far, different techniques have been employed such as ion exchange, membrane separation, reductive deposition method, adsorption, and electrocoagulation process. Recent years, adsorption method has drawn much attention for its easy operation, wide availability, and high efficiency. Carbon material, especially derived from the low-cost, easily available and renewable biomass such as rice husk, sugarcane bagasse and pineapple-peel, offers potential advantages over traditional adsorption materials in eco-friendly property, large adsorption capacity and stability. It can even be a good substitution of commercial activated carbon with high adsorption capacity.

Soft wood is mainly derived from gymnosperm trees such as pines and spruces, which is the source of about 80% of the world’s production of timber. Soft wood is mainly composed of lignin that is made from numerous polymeric aromatic hydrocarbon. Due to ligand effect of aromatic ring, the double bond from the side chain, the oxygen functionalities, and the bonding of lignin polymer can happen over many different sites, leading to difficult catalytic degradation. These attractive properties make soft wood as an ideal candidate to synthesize the carbon material. To the best of our knowledge, there is only few studies on soft wood for the removal of heavy metals such as Cu$^{2+}$, Zn$^{2+}$ and Pb$^{2+}$, but the facile synthesis of N-doped carbon derived from soft wood and further utilized for the removal of Cr(VI) in wastewater is not reported. Herein, the hierarchical porous N-doped carbon fabricated from the renewable biomass soft wood was achieved by a modified solvo-hydrothermal method. This new route involves the direct interaction of soft wood precursor, urea and ammonia water, resulting in a more homogeneous and easy control process. The as-made porous N-doped carbon with large surface area can remove Cr(VI) in solution efficiently and rapidly, which is a promising candidate for the removal of other heavy metals from wastewater.

Experimental

Reagents

Potassium dichromate (K$_2$Cr$_2$O$_7$, 99.8%) and sodium hydroxide (NaOH, 97%) were purchased from Macklin (Shanghai, China). Lignin was obtained from CTI (Shanghai, China), and urea was obtained from Alfa Aesar. Nitric acid was purchased from Guangzhou Chemical Regent Factory. Aqueous ammonia was obtained from Sinopharm Chemical Regent. All chemicals in this study were of analytical grade and used without any pretreatment.

Material synthesis

The typical synthesis of adsorbent preparation was performed as follows: 1.0 g soft wood (mashed through 200 mesh) and 2.0 g urea were firstly dissolved in 20 mL of aqueous ammonia (3.8%, w/w) and stirred for 6 h at 25 °C. Then the mixture was transferred into a 100 mL autoclave with Teflon container.
The hydrothermal treatment was performed at 120 °C for 6 h. After that, the obtained gel was washed by pure water and further dried under N₂ environment at 120 °C for 6 h. Finally, the residue was heated in a quartz tube reactor under pure N₂ conditions at 350 °C for 2 h with the heating rate of 5 °C/min.

Material characterization

The scanning electron microscope (SEM, ZEISSL Gemini 500, 10 kV) was used to study the morphology. The textural information of the carbon materials was further investigated by transmission electron microscopy (TEM, JEOL-2010, 200 kV). X-ray diffraction (XRD, Rigaku, D-MAX 2200 VPC, Cu Kα radiation, 26 mA, 40 kV, 2θ of 9°—90°, scanning speed of 10°/min) was used to analyze the crystal phase. X-ray photoelectron spectroscopy (XPS, Al-Kα source, K-Alpha+) was used to investigate the chemical states of surface. Micromeritics ASAP 2020 instrument was used to perform N₂ BET tests at 77 K, and materials were firstly activated for 3 h at 200 °C under vacuum.

Batch adsorption experiments

Batch adsorption experiments were performed to investigate the performance of adsorbent by adding 20 mg adsorbent to the 50 mL glass conical flask containing 25 mL solution with 80 mg/L Cr(VI). The glass conical flasks were stirred at 200 rpm, 30 °C for 12 h. Then the liquid containing Cr(VI) was separated by 0.22 μm membrane filters. The residual adsorbent was dried at 80 °C and washed slowly by the deionized water. The effect of initial pH (from 1.0 to 8.0), contact time (from 10 to 180 min), initial concentration of Cr(VI) (from 10 to 200 mg/L) were investigated. The cycling stability of the adsorbent was also performed by testing the adsorption performance after several cycles of adsorption and desorption.

Eqs. (1) and (2) were used to calculate the qₑ (the amount of adsorbed Cr(VI) per unit weight of adsorbent, mg/g) and desorption rate Q (%), respectively:

\[
q_e = \frac{C_0 - C_1}{W} \times V
\]

\[
Q = \frac{C_1 \times V}{q_e \times W} \times 100\%
\]

where \(C_0\) and \(C_1\) are the original concentration of Cr(VI) and the left concentration at time \(t\) (mg/L), \(W\) represents the amount of adsorbent used (g), \(V\) is the solution volume (mL), \(C_1\) is the equilibrium concentration of Cr(VI) in the desorption solution (mg/L), and \(V_1\) is the volume of desorption solution (mL).

Results and Discussion

Powder X-ray diffraction (XRD) pattern was initially used to study the phase structure of the as-made carbon material. As shown in Figure 1a, XRD pattern of the synthesized material exhibits two broad peaks corresponded to (002) at 22.8° and (100) at 42.9°, indicating the successful synthesis of carbon material. The \(d_{002}\) (interlayer spacing) of 3.93 nm and \(D\) (crystalline size) of 1.59 nm were calculated by Bragg’s law and Scherrer equation, respectively. XPS survey (Figure S1) of the as-made carbon material shows C, N and O peaks, where they should be. It confirmed that N doped successfully in the process. The C 1s spectrum (Figure 1b) could be deconvoluted into four peaks at 284.8, 285.7, 287.9 and 289.2 eV, showing the presence of C-C, C-N, C=O and COO groups.\(^\text{[18]}\) N 1s spectrum (Figure 1c) is fitted by two peaks at 398.7 and 400.4 eV, which corresponds to pyridinic N and pyrrolic N.\(^\text{[25]}\) Previous work has demonstrated these two nitrogen species were beneficial for enhancing the adsorption of heavy metals.\(^\text{[13]}\) Nitrogen (N\(_\text{d}\)) adsorption-desorption was studied to calculate the pore volume and surface area of the as-obtained N-doped carbon. The N\(_\text{d}\) adsorption-desorption isotherm is presented in Figure 1d. The pore volume and specific surface area were of 0.896 cm\(^2\)/g and 324.2 cm\(^2\)/g, respectively. The isotherm exhibited the type-IV shape, and the pore size is ~40.2 nm. The appearance of hysteresis loop (H\(_4\) type) in the \(P/P_0\) range of 0.55—0.95, indicating the existence of hierarchical porous structure.\(^\text{[34]}\)

![Figure 1](image1.png)

**Figure 1** (a) XRD pattern, (b) C 1s spectrum, (c) N 1s spectrum, (d) N\(_\text{d}\) adsorption-desorption isotherm (Inset is the pore size distribution).

The morphology of the as-obtained carbon was further studied by SEM. The surface in SEM images (Figures 2a and 2b) exhibits rough and porous structure, which is formed by numerous thin layers. TEM images (Figures 2c and 2d) further documents a number of thin layers are produced and the porous structure is clearly presented in thin layers.

![Figure 2](image2.png)

**Figure 2** SEM (a, b) and TEM (c, d) images of the hierarchical porous N-doped carbon.

We initially performed the comparison test among N-doped carbon derived from soft wood, carbon derived from soft wood and commercial activated carbon. As shown in Figure S2, it is clear to note that the N-doped carbon exhibited the best ad-
The higher pH value on oneorbent could effect after protonation, resulting in electronic donor groups on the adsorbent could effectively reduce Cr(VI) to Cr(III).

As shown in Figure 3b, the adsorption capacity increases quickly in the first 10 min, then it decreases and finally reaches the equilibrium of 45 mg/g in 1 h. At the beginning, adsorption sites of fresh carbon were active to adsorb Cr(VI) with a high speed. With time prolonging, the active sites were covered and the adsorbent finally saturated. The effect of initial concentration was also investigated as shown in Figure 3c. The adsorption capacity improved with a relatively steady speed with initial concentration increased (10 to 80 mg/L). A maximum of ~91 mg/g was produced. To evaluate the stability of adsorption capacity, 2.0 mol/L Na$_2$CO$_3$ aqueous solution was used to desorb the Cr(VI) and reused the sorbent to treat 80 mg/L Cr(VI) solution up to five times. In Figure 3d, $q/t$ is the ratio of adsorption capacity after t times of regeneration to initial adsorption capacity. Obviously, the sorbent capacity has slight decrease comparing to the first adsorption, indicating that the sorbent can maintained a high activity and stability after the regeneration.

In this study, the adsorption kinetics of this adsorption process was studied using pseudo-first-order and pseudo-second-order models, which are described in Eqs. (3) and (4), respectively.

$$q_t = q_e (1 - e^{-kt})$$  

$$q_t = \frac{k_2 q_e t}{1 + k_2 q_e t}$$

where $q_t$ (mg/g) and $q_e$ (mg/g) represent the amount of adsorbed Cr(VI) at time $t$ and at equilibrium; $k_1$ (min$^{-1}$), $k_2$ (g·mg$^{-1}$·min$^{-1}$) and $e$ represent constants. The plots and calculated values of parameters are shown in Figure 4 and Table S1, respectively. The correlation coefficient ($R^2 = 0.996$) of pseudo-second-order model (Figure 4b) was greater than pseudo-first-order model (Figure 4a), and the theoretical $q_e$ (45.29 mg/g) and experimental adsorption capacity (45 mg/g) were in good agreement. These revealed that pseudo-second-order model was better fit to describe the whole process, which means that the chemical adsorption was dominated the whole process. Freundlich and Langmuir model were applied to understand comprehensively the interaction between Cr(VI) and adsorbent, which are described in Eqs. (5) and (6):

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n}$$

$$q_e = \frac{q_m C_e}{1 + b C_e}$$

$q_e$ (mg/g) is the equilibrium adsorption capacity, $C_e$ (mg/L) is the equilibrium concentration of Cr(VI), $K_F$ and $n$ represent constants, $q_m$ (mg/g) is the theoretical maximum adsorption capacity, and $b$ is a coefficient in Langmuir model equation. The plots and values are shown in Figure 5 and Table S2, respectively. According to the fitting results in Table S2, the Langmuir model is better fit with a relatively high $R^2$ of 0.969, indicating that the monolayer adsorption, which means that the adsorption process only takes place at surface active sites, and one site is occupied by one Cr(VI). The maximum adsorption capacity was 182.8 mg/g. To benchmark our fabricated N-doped C, the adsorption capacities were compared in Table S3. It is clear to understand the interaction between Cr(VI) and adsorbent.
see the synthesized N-doped C was one of the best candidates to remove Cr(VI). Besides, the facile synthesis of N-doped C from renewable biomass made it more attractive.

Conclusions

Hierarchical porous N-doped carbon was successfully synthesized from the renewable soft wood biomass efficient for the removal of Cr(VI) from wastewater. The as-prepared N-doped carbon with large surface area of 324.2 cm$^2$/g could efficiently remove Cr(VI) in the aqueous solution at pH 2.0. Pseudo-second-order model catered for the adsorption process, and the adsorption capacity based on Langmuir model was 182.8 mg/g, which was much higher than most of the carbon materials reported previously. Besides, N-doped carbon can be reused for several times, which is promising to remove different heavy metals from wastewater.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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