Transformation of polyvinyl chloride (PVC) into a versatile and efficient adsorbent of Cu(II) cations and Cr(VI) anions through hydrothermal treatment and sulfonation

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Abstract

The reuse of waste polyvinyl chloride (PVC) has drawn much attention as it can reduce plastic waste and associated pollution, and provide valuable raw materials and products. In this study, sulfonated PVC-derived hydrochar (HS-PVC) was synthesized by two-stage hydrothermal treatment (HT) and sulfonation, and shown to be a versatile adsorbent. The reoval of Cu(II) cations and Cr(VI) anions using HS-PVC reached 81.2 ± 1.6% and 60.3 ± 3.8%, respectively. The first stage of HT was crucial for the dichlorination of PVC and the formation of an aromatic structure. This stage guaranteed the introduction of -SO_3H onto PVC-derived hydrochar through subsequent sulfonation. HT intensities (i.e., temperature and time) and sulfonation intensity strongly determined the adsorption capacity of HS-PVC. Competitive adsorption between Cu(II) and Cr(VI) onto HS-PVC was demonstrated by binary and preloading adsorption. The proposed Cu(II) cations adsorption mechanism was electrostatic adsorption, while Cr(VI) were possibly complexed by the phenolic -OH and reduced to Cr(III) cations by C=C groups in HS-PVC. In addition, HS-PVC derived from PVC waste pipes performed better than PVC powder for Cu(II) and Cr(VI) removal (> 90%). This study provides an efficient method for recycling waste PVC and production of efficient adsorbents.

Keywords: Polyvinyl chloride; Hydrothermal treatment; Sulfonation; Adsorption; Cu(II) cations and Cr(VI) anions

1. Introduction

Polyvinyl chloride (PVC) is irreplaceable in the infrastructure of modern society (Cui et al., 2021). However, large quantities of plastic waste continuously enter aquatic and terrestrial ecosystems, leading to ubiquitous pollution worldwide (Kawecki and Nowack 2019, Miao et al., 2020). For example, the accumulated PVC waste in China will exceed 500 million tons by the end of 2050, posing a daunting challenge for the safe and effective disposal of this halogenated waste (Liu et al., 2020).

Mechanical recycling (25.5%), incineration (9.3%), and landfill disposal (36.0%) are currently the main solutions for solving the problem of PVC waste (Yu et al., 2016, Ye et al., 2017, Liu et al., 2020). However, mechanical recycling is still rudimentary and only suitable for source-separated PVC waste. Incineration and landfill disposal of PVC waste normally release hazardous compounds, such as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Furthermore, the land requirements of landfills must be considered (Wiedinmyer et al., 2014). Thus, reliable alternative methods to treat PVC waste safely and efficiently in an environmentally sound and high value-added way are worth pursuing (Lau et al., 2020). Such an approach is in line with the European Union’s strategy for plastics in a circular economy (Matthews et al., 2021).

Hydrothermal treatment (HT), conducted at relatively low temperatures of 160 to 300°C, can pretreat PVC waste for dehydrochlorination (Ma et al., 2019, Ning et al., 2020), permitting subsequent pyrolysis to produce chars and liquid hydrocarbons with a low Cl content, such as alkene and polyene (Poerschmann et al., 2015, Jiang et al., 2021). However, cost- and energy-intensive conditions, such as noble metal catalysts and high temperature (500℃), are typically adopted for lighter oil production by catalytic pyrolysis of plastic (Kunwar et al., 2016, Maity et al., 2020). On the other hand, PVC waste can be converted into coal-alternative fuels by HT processes amended with cellulose (Shen et al., 2017), pinewood sawdust (Huang et al., 2019), and corncob (Lu et al., 2020). Yet, another important recycling method has been undervalued and ignored, i.e., the potential transformation of PVC-derived hydrochar (H-PVC) into an effective adsorbent for the removal of contaminants, such as heavy metals.

Unfortunately, the adsorption capacity of organic compounds by H-PVC is very low, primarily because surface-related adsorption prevails over hydrophobic partitioning (Poerschmann et al., 2015). Several studies showed that the adsorption of hydrochar derived from natural biomass sources was enhanced by introducing functional groups, such as −OH, −COOH, and $-NH_2$, which could trap heavy metal ions from aqueous solutions (Azzaz et al., 2020, Yang et al., 2021). Sulfonation is an attractive modifications method for various carbon materials due to the unique surface chemistry and low production costs. Large amounts of oxygen functionalities, such as −OH, −COOH, and lactones, along with $-SO_3H$ groups, are introduced into the surface of the carbon materials, improving their hydrophilic/oxyphilic properties after sulfonation. Sulfonated carbon materials have been widely applied in the catalysis of esterifications, acetalization, etherifications, and transesterifications (Konwar et al., 2019). However, sulfonated PVC-derived hydrochar (HS-PVC) has rarely been reported, albeit potentially being a cost-effective adsorbent for heavy metals.

The novelty of the present work is the development of two-stage HT and sulfonation to synthesize PVC-derived adsorbents for the removal of both Cu(II) cations and Cr(VI) anions. A systematic investigation was conducted to discern the mechanisms underlying functional group modifications of PVC through different strategies and treatment intensities. The adsorption mechanisms of Cu(II) and Cr(VI) were clarified to understand the adsorption behavior onto HS-PVC. The performance of HS-PVC to adsorb Cu(II) and Cr(VI) from natural water was evaluated. PVC waste pipes were used to synthesize HS-PVC and test its applications. Furthermore, the versatility of HS-PVC for the adsorption of low concentrations of Cu(II) and Cr(VI) (20 mg/L) and other metals, i.e., Mn(II), Cd(II), Ni(II), and Co(II) was investigated. This study provides a practical approach for the sustainable reuse of waste PVC as an efficient adsorbent to remove heavy metal cations and anions.

2. Materials and methods

2.1. Preparation of PVC-derived adsorbents

Raw PVC powder (sieved through a 100 mesh) was purchased from a plastic chemical company (Guangdong, China). Hydrothermal batch reactions were conducted by loading 10 g of Raw PVC with 40 mL distilled water in 100-mL airtight stainless-steel tubular reactors with internal polyphenylene containers. The reactors were heated to 250 ℃ for 6 h in a homothermic oven (DHG-9013A, China). The reactors were then cooled to room temperature in a water bath to prepare the H-PVC. Ten grams of Raw PVC was sulfonated in flasks (250 ml) with concentrated sulfuric acid (98%) at a sulfonation intensity of 1:10 (g/mL) in a shaking bath (70 °C and 110 rpm for 12 h) to produce the sulfonated PVC (S-PVC). Unless otherwise specified, sulfonation intensity refers to the ratio of adsorbent mass to the volume of sulfuric acid in this paper. Specifically, a relatively low temperature of sulfonation (70 °C) was chosen according to the literature (Xiao and Hill 2020). The HS-PVC was synthesized by sulfonation of H-PVC with the same process as described for S-PVC. The S-PVC and HS-PVC were washed three times with distilled water to eliminate the unreacted sulfuric acid. The Raw PVC, H-PVC, S-PVC, and HS-PVC were dried in a homothermic oven at 105 °C for 24 h. The dried PVC-derived adsorbents were then ground and sieved through a 100 mesh (147 um) before adsorption of Cu(II) and Cr(VI).

2.2. PVC-derived adsorbents for highly efficient removal of Cu(II) and Cr(VI)

2.2.1. Cu(II) and Cr(VI) removal using Raw PVC, H-PVC, S-PVC, and HS-PVC

A stock solution of 500 mg Cu(II)/L (7.87 mM) was prepared by dissolving 1965 mg of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) in 1 L of ultrapure water. A stock solution of 250 mg Cr(VI)/L (4.81 mM) was prepared by dissolving 770 mg of potassium dichromate ($K_2Cr_2O_7$) in 1 L of ultrapure water. Batch experiments of Cu(II) and Cr(VI) removal were performed by adding 10 g/L of Raw PVC, H-PVC, S-PVC, and HS-PVC to flasks (250 mL) in a water bath shaker (25 °C and 100 rpm) for 12 h. All samples were withdrawn from the flasks and filtered through membrane filters with a pore size of 0.22 μm for subsequent Cu(II) and Cr(VI) determination.

The removal efficiencies of Cu(II) and Cr(VI) were calculated as:

$$\text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where C_0 (mg/L) and C_t (mg/L) were the concentrations of Cu(II) and Cr(VI) at the start of the experiment and time t (h). Unless otherwise specified, all calculations of Cu(II) and Cr(VI) removal efficiencies by PVC-derived adsorbents followed this equation. The concentrations of Cu(II) and Cr(VI) were determined by inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific iCAP Q, USA).

2.2.2. Cu(II) and Cr(VI) removal using HS-PVC under different intensities of HT temperature, HT time, and sulfonation and correlation analyses

HS-PVC was synthesized under different intensities of HT (temperature and time) and sulfonation as follows: HT temperatures from 220 °C to 260 °C (in 10 °C intervals, HT time of 6 h and sulfonation intensity of 1:10), HTC times from 2 h to 6 h (in 1 h intervals, HT temperature of 250 ℃, and sulfonation intensity of 1:10), and sulfonation intensities from 1:1 to 1:10 (in 1:10 intervals, HT temperature of 250 ℃, and HT time of 6 h). 10 g/L HS-PVC fabricated with different HT intensities and sulfonation were used for Cu(II) and Cr(VI) removal at 25 °C and 100 rpm. To investigate the individual effects of the intensities of HT temperature, HT time, and sulfonation on Cu(II) and Cr(VI) removal, enhancements of Cu(II) and Cr(VI) removal were calculated by comparing the lowest value with the highest one (250 °C vs. 220°C, 6 h vs. 2 h, and 1:10 vs. 1:1, respectively).

2.2.3. Adsorption kinetics and isotherms of Cu(II) and Cr(VI) removal using HS-PVC

The adsorption kinetics of Cu(II) and Cr(VI) removal were studied based on the removal efficiencies of HS-PVC as described in Section 2.2.1. Adsorption isotherm experiments were carried out with different initial concentrations of Cu(II) (i.e., 100, 200, 300, 400, 500, 600, and 800 mg/L) and Cr(VI) (50, 100, 150, 200, 250, and 300 mg/L) at three different temperatures (25, 35, and 45 °C) using 10 g/L HS-PVC under optimum operational conditions (250°C, 6 h, and a sulfonation intensity of 1:10).

Pseudo-first-order (PFO) and pseudo-second-order (PSO) models were used to evaluate Cu(II) and Cr(VI) removal kinetics of HS-PVC, and their linearized equations are given in *Eqs.* (2) and (3), respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 \mathrm{t} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_1 and k_2 are the rate constants of PFO and PSO, respectively, and q_e and q_t (mg/g) are the amounts of adsorbed Cu(II) and Cr(VI) (mg/g) at equilibrium and at time t, respectively. Values of k_1, k_2, and q_e were calculated based on the Levenberg-Marquardt method at the 95% confidence level.

To predict the adsorption capacity of the adsorbents, two widely used isotherms (i.e., Langmuir and Freundlich) were selected among several models. *Eqs*. (4) and (5) express the Langmuir isotherm and the Freundlich isotherm, respectively.

$$q_e = \frac{b q_m C_e}{1 + b C_e} \quad (4)$$

$$q_e = K_F C_e^{1/n} \quad (5)$$

where q_m (mg/g) is the maximum adsorption capacity of the adsorbent and b (L/mg) is the Langmuir constant related to the adsorption energy. K_F (mg/g) is the Freundlich adsorption isotherm constant related to the extent of adsorption and n is the heterogeneity factor of the Freundlich model. Values of b, q_m, K_F, and n were also calculated based on the

Levenberg-Marquardt method at the 95% confidence level.

2.2.4. Competitive adsorption of Cu(II) and Cr(VI) onto HS-PVC in binary solution and preloading adsorption

Binary adsorption of Cu(II) and Cr(VI) was carried out by adding 10 g/L of HS-PVC to a binary solution with 500 mg Cu(II)/L and 250 mg Cr(VI)/L in the same solution to investigate the competitive adsorption between Cu(II) and Cr(VI). A separation factor was utilized to investigate the adsorption selectivity in the binary solution, defined as:

$$\alpha_2^1 = \frac{q_{e1} \times C_{e2}}{C_{e1} \times q_{e2}} \qquad (6)$$

where q_{e1} (mmol/g) and C_{e1} (mmol/L) were the equilibrium adsorption capacity and equilibrium concentration toward constituent 1, and q_{e2} (mmol/g) and C_{e2} (mmol/L) were the equilibrium adsorption capacity and equilibrium concentration toward constituent 2, respectively.

Preloading adsorption tests for Cr(VI) were performed by incubating 2.5 g HS-PVC in 250 mg/L Cr(VI) solution for 12 h. Then, the HS-PVC preloaded with Cr(VI) was used for the adsorption of Cu(II) for 12 h, as described in Section 2.2.1. The preloading adsorption tests for Cu(II) were performed under the same experimental conditions as those for Cr(VI). The removal efficiencies of Cu(II) and Cr(VI) were calculated to evaluate the competitive adsorption between Cu(II) and Cr(VI) onto the HS-PVC.

2.2.5. Effect of K(I) on Cr(VI) removal

The cations K(I) was present in the experimental Cr(VI) solutions prepared from $K_2Cr_2O_7$. To assess the impact of K(I) on the adsorption of Cr(VI) by HS-PVC, $HClO_4$ (36.62

mL, calculated as described in Text S1) was added to precipitate K(I) (*Ksp* of $KClO_4$ 1.5×10^{-2}) in the Cr(VI) solution (total volume 100 mL). Then, HS-PVC (10 g/L) was added to the treated Cr(VI) solution for adsorption for 12 h. Finally, the removal efficiency of Cr(VI) was calculated to evaluate the impact of K(I) on the adsorption of Cr(VI) using HS-PVC.

2.2.6. Low concentration Cu(II) and Cr(VI) removal using HS-PVC

The concentrations of Cu(II) and Cr(VI) in industrial applications, such as electroplating, leather tanning, and alloy manufacturing, range from 20 to 600 mg/L. Thus, 10 g/L of HS-PVC was added to 20 mg/L Cu(II) and Cr(VI) solutions to evaluate its adsorption performance for low concentrations of these heavy metals. The adsorption procedure was the same as in Section 2.2.1.

2.2.7. Cu(II) and Cr(VI) removal in natural water

To test the potential interference of natural water regarding Cu(II) and Cr(VI) adsorption on HS-PVC, natural water (untreated surface water) was sampled from the Jingyue Lake in Donghua University, Shanghai, China. This water was used to prepare Cu(II) (500 mg/L) and Cr(VI) (250 mg/L) solutions. 10 g/L of HS-PVC was added to these Cu(II) and Cr(VI) solutions and incubated for 12 h at 25°C and 100 rpm.

2.2.8. Cu(II) and Cr(VI) removal using HS-PVC derived from PVC waste pipes

To test the applications of HS-PVC in Cu(II) and Cr(VI) removal, real PVC waste pipes were used to prepare HS-PVC (real waste PVC). First, the PVC waste pipes were fragmented with a crusher and then washed with tap water. Subsequently, 10 g/L of the pretreated HS-PVC from pipes was added to Cu(II) (500 mg/L) and Cr(VI) (250 mg/L) solutions for 12 h adsorption (at 25°C and 100 rpm).

2.3. Characterizations of PVC-derived adsorbents

2.3.1. Characterizations of Raw PVC, H-PVC, S-PVC, and HS-PVC

The surface properties of Raw PVC, H-PVC, S-PVC, and HS-PVC were characterized by scanning electron microscopy (SEM) (HITACHI, S-4800, Japan) and contact angle measurements (θ) (Kino, SL200KS, USA). The specific surface area and pore distribution of Raw PVC, H-PVC, S-PVC, and HS-PVC were determined by the Brunauer−Emmett−Teller (BET) (Quantachrome, Autosorb-iQ, USA) method and mercury intrusion porosimetry (MIP) (Micromeritics, Auto pore lv, USA), respectively. Particle size distributions were calculated based on the SEM images (Table S1). The elemental composition of Raw PVC, H-PVC, S-PVC, and HS-PVC was analyzed by elemental analysis (Elementar, EL III, Germany) and energy dispersive spectroscopic (EDS) (IE 300 X, England) element mapping. The variation of functional groups of Raw PVC, H-PVC, S-PVC, and HS-PVC was characterized by Fourier transform infrared (FTIR) spectroscopy (Thermo Fisher, NEX US-670, USA). The thermostability of Raw PVC and HS-PVC was evaluated by thermogravimetric analysis (TGA, TA, Netzsch, Germany).

2.3.2. Characterizations of HS-PVC before and after adsorption of Cu(II) and Cr(VI)

The electric potentials of HS-PVC, HS-PVC after adsorption of Cu(II) (HS-PVC-Cu), and HS-PVC after adsorption of Cr(VI) (HS-PVC-Cr) were determined by zeta potential measurements (Brook Haven, 90 PALS, USA). In addition, the functional groups of HS-PVC and HS-PVC-Cr were analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo

Scientific, K-Alpha, USA), FTIR, solid-state ^{13}C nuclear magnetic resonance spectroscopy (NMR) (Agilent, 600M, USA), and Raman spectroscopy (Thermo Fisher, DXR, USA). The C1s XPS spectra were separated and characterized by C=C (284.8 eV), C-C (285.1 eV), C-O (286.1 eV), and C=O groups (288.7 eV). The regions of functional groups derived from the solid-state ^{13}C NMR spectra were divided into Carboxylic (220-161), Aromatic (161-113), Anomeric (113-93), Carbohydrate (93-44), and Alkyl (44-0) (Wang et al., 2016, Li et al., 2019).

2.4. Statistical analysis

All adsorption experiments were run in triplicate, and the results were expressed as mean values ± standard deviation. The triplicate PVC-derived adsorbents were pooled to minimize the potential variation before its characterizations (SEM, MIP, elemental analysis, FTIR, TGA, XPS, solid-state ^{13}C NMR, and Raman spectroscopy). Analyses of variance (ANOVA) were used to test for differences between treatments, and $p<0.05$ was considered statistically significant.

3. Results and discussion

3.1. Highly efficient Cu(II) cations and Cr(VI) anions removal using HS-PVC

Regarding Cu(II) removal, HS-PVC was significantly more efficient (81.2 ± 1.6%) compared to Raw PVC (28.5 ± 1.7%) and PVC solely pretreated by either HT (14.5 ± 3.2%) or sulfonation (20.6 ± 4.8%) within 12 h (Fig. 1A). In addition, HS-PVC was also highly efficient in removing Cr(VI) (60.3 ± 3.8%) compared to Raw PVC (6.1 ± 1.3%) and PVC solely pretreated by either HT (14.0 ± 4.6%) or sulfonation (7.0 ± 4.8%) within 12 h (Fig. 1B). The adsorption of Cu(II) reached equilibrium within 30 min while the adsorption efficiency of Cr(VI) was only 49.3 ± 1.0% at 30 min and then slowly increased to equilibrium within 3 h (Fig. S1). This suggested different adsorption mechanisms for Cu(II) and Cr(VI) onto HS-PVC. Biomass-derived hydrochar was also widely employed in the adsorption of metal cations, such as Cu(II), Zn(II), and Pb(II) (Deng et al., 2020, Kazak and Tor 2020, Song et al., 2020) or metal anions, such as Cr(VI) ($Cr_2O_7^{2-}$) (Li et al., 2020). Cu(II) and Cr(VI) could be simultaneously removed by hydrochar derived from chitosan with Fe_2O_3 modifications. However, the main adsorption mechanisms were chelation adsorption of Cu(II) and electrostatic adsorption-coupled Cr(VI) reduction due to the specific dual-core Fe_2O_3@C structure (Wang et al., 2017). The present study firstly provided a metal-free modification of hydrochar derived from waste PVC for simultaneous Cu(II) cations and Cr(VI) anions removal.

The adsorption capacity of hydrochar was highly dependent on the functional groups formed during HT (Tong et al., 2021). However, the structure and component of PVC ($[-CH_2-CHCl-]n$) were simpler compared to natural biomass, suggesting fewer functional groups anchored in H-PVC than in natural biomass. This may explain why H-PVC is of little significance for the adsorption of Cu(II) and Cr(VI) (Fig. 1), which was in line with poor adsorption in wastewater remediation (Poerschmann et al., 2015). Sulfonation was also an efficient modification of adsorbents derived from tea waste and cellulose for Cu(II) or Cr(VI) removal (Dong et al., 2016, Ahsan et al., 2018). However, the adsorption of Cu(II) and Cr(VI) using S-PVC was still low in this study. This paper showed a possible synergistic effect of HT and sulfonation in the modifications of the methodology to produce a highly efficient adsorbent.

3.2. Characterization during the fabrications of HS-PVC from Raw PVC in combination with HT and sulfonation

The microstructure of the PVC-derived adsorbents was characterized by SEM (Fig. 2A to 2D). A rough surface and non-porous structures were observed in Raw PVC (Fig. 2A). After HT treatment, the surface of H-PVC became smoother with an internal porous structure (Fig. 2B) mainly due to dehydrochlorination, aromatization, and depolymerization reactions during HT (Ning et al., 2020). There was no apparent difference between Raw PVC and S-PVC in the SEM images (Fig. 2A and 2C), indicating that sulfonation possessed a marginal impact on the surface structure. In contrast, the HS-PVC was fragmented with an internal porous structure due to HT and sulfonation (Fig. 2D), which was consistent with a significant decrease of particle size in HS-PVC compared to the Raw PVC (Fig. 3A and Table S2). In addition, the hydrophobicity and hydrophilicity of adsorbents may influence the performance of the adsorption process (Adam et al., 2020). The hydrophobicity of S-PVC was similar to that of Raw PVC (Fig. 2E and 2G). However, the hydrophobicity was higher after HT (Fig. 2E and 2F), resulting in hydrophobic partitioning as described in the literature (Poerschmann et al., 2015), which was consistent with the low adsorption efficiency of Cu(II) and Cr(VI) by H-PVC (Fig. 1). Furthermore, the hydrophilicity of HS-PVC was significantly higher than that of H-PVC (Fig. 2F and 2H), indicating that sulfonation improved the hydrophilicity of

HS-PVC, which is a prerequisite for the adsorption of Cu(II) and Cr(VI).

The BET surface areas of Raw PVC (2.59 m^2/g), H-PVC (4.95 m^2/g), S-PVC (2.01 m^2/g), and HS-PVC (0.59 m^2/g) (Table S3) were relatively low compared to those of biomass-derived hydrochar (118 m^2/g) in the literature (Sheng et al., 2019). According to the analysis of MIP (Fig. S2), the pore size in HS-PVC was mainly in the mesoporous (2-50 nm) and microporous (>50 nm) regions (Erdem et al., 2020, Rueda-Marquez et al., 2021). The results revealed that the Cu(II) and Cr(VI) adsorption mostly occurred in the mesoporous and microporous regions of the HS-PVC.

Elemental analysis (Fig. 3B) showed that the Cl/C molar ratio (0.5) of Raw PVC was similar to the stoichiometric value of ($[-CH_2-CHCl-]_n$). However, the molar ratio of Cl/C on the surface of Raw PVC (0.85 ± 0.37) was higher than 0.5 according to EDS element mapping (Fig. 3C), suggesting that most of the -Cl functional groups were on the surface of Raw PVC. The Cl/C ratio of H-PVC significantly decreased (Fig. 3B and 3C) compared to the Raw PVC after pretreatment by HT due to the dehydrochlorination (Poerschmann et al., 2015). The elemental composition of the entire Raw PVC and S-PVC was similar (Fig. 3B), but surface Cl was lower, and surface O slightly higher in S-PVC than in Raw PVC (Fig. 3C). This indicated that sole sulfonation only impacted the chemical composition on the surface of Raw PVC (Fig. 3C), causing no obvious chemical modifications to the entire Raw PVC (Fig. 3B). Additionally, the O/C and S/C ratios of HS-PVC increased, resulting in an O/S ratio of 3.04 (elemental analysis in Fig. 3B) or 3.16 (EDS element mapping in Fig. 3C). Thus, it could be hypothesized that the introduction of S-containing functional groups such as $-SO_3H$

(O/S=3) into HS-PVC occurred. The absorption peaks of HS-PVC from the FTIR at 1030 cm^{-1} (O=S=O) and 1169 cm^{-1} (-SO_3H) verified this assumption (Fig. 3D) (Chen et al., 2019). The functional group -SO_3H was only detected in HS-PVC, indicating that the introduction of -SO_3H onto HS-PVC was attributed to the synergy effect of HT and sulfonation. In addition, the thermostability of HS-PVC was higher than that of Raw PVC according to the TGA patterns (Fig. S3), which was mainly due to aromatization during HT (Park et al., 2016). It has been reported that the presence of aromatic groups was essential for the sulfonation of petroleum coke by concentrated H_2SO_4 (Xiao and Hill 2020). In this study, HT was crucial to forming an aromatic structure (Fig. 3D) for the introduction of -SO_3H during sulfonation to fabricate HS-PVC for highly efficient Cu(II) and Cr(VI) removal. Moreover, the functional group C=C in HS-PVC (Fig. 3D) was crucial for removing Cr(VI), which was confirmed in the following section.

3.3. Correlations of Cu(II) and Cr(VI) removal with HT intensities and sulfonation

The adsorption properties of HS-PVC were highly dependent on HT temperature and time (see time curves in Fig. S4 and Fig. S5). The adsorption efficiencies of Cu(II) and Cr(VI) increased from 36.9 ± 3.0% and 46.0 ± 3.8% at 220 °C to 81.1 ± 2.1% and 61.7 ± 2.7% at 250 °C, but declined to 63.7 ± 3.2% and 57.2 ± 1.3% at 260 °C, respectively (Fig. 4A). In addition, the adsorption efficiencies of Cu(II) and Cr(VI) also increased from 56.5 ± 1.7% and 9.2 ± 1.1% at 2 h to 80.0 ± 2.8% and 58.5 ± 1.1% at 6 h, followed by declines to 54.5 ± 2.0% and 2.2 ± 1.2% at 8 h, respectively (Fig. 4B). Higher HT intensities benefited PVC dehydrochlorination (Zhang et al., 2020), providing more sites for subsequent SO_3H

introduction during sulfonation. It has been reported that proper HT intensities (HT temperature = 250 °C and HT time = 6 h in this study) benefited the formation of the aromatic structure (Ning et al., 2020). In contrast, higher HT intensities affected the stability of the carbon structure (Ning et al., 2020), which explained the declines in the adsorptions of Cu(II) and Cr(VI) onto HS-PVC at 260 °C (Fig. 4A) and 8 h (Fig. 4B).

The sulfonation intensity also affected the introduction of functional groups (Konwar et al., 2019), thus affecting the adsorptive performance of HS-PVC. The adsorption time curves of sulfonation intensity regarding Cu(II) and Cr(VI) removal by HS-PVC were shown in Fig. S6. With the increasing sulfonation intensity, the adsorption efficiencies of Cu(II) and Cr(VI) increased from 38.1 ± 3.2% and 28.4 ± 3.5% at the sulfonation intensity of 1:1 to 81.0 ± 1.3% and 59.6 ± 2.4% at the sulfonation intensity of 1:10 (Fig. 4C). The adsorption of Cu(II) and Cr(VI) was positively correlated with the increase in sulfonation intensity from 1:1 to 1:10.

As summarized in Fig. 4D, the adsorption efficiency of Cu(II) increased by 117.4% while that of Cr(VI) only by 34.1%, when increasing the temperature from 220 °C to 250 °C. In contrast, the adsorption efficiency of Cu(II) improved only by 41.6%, while that of Cr(VI) increased by 534%, with HT time increasing from 2 to 8 h. These results indicated that the adsorption of Cu(II) was sensitive to HT temperature while the adsorption of Cr(VI) was rather sensitive to HT time. However, the impact of sulfonation intensity on the adsorption of Cu(II) (increasing 112.5% from 1:1 to 1:10) was similar to the adsorption of Cr(VI) (increasing 110.3% from 1:1 to 1:10).

3.4. Kinetics and isotherms of the adsorption of Cu(II) and Cr(VI) onto HS-PVC

Adsorption kinetics were essential to investigate the adsorption process (Song et al., 2020, Wang and Guo 2020). The adsorption of Cu(II) and Cr(VI) onto the HS-PVC (Fig. 5A and 5B) increased rapidly in the first 30 min and then decreased as the reaction approached equilibrium due to the saturation of active adsorbent sites. The values of q_e and rate constants (k_1 and k_2) obtained from the kinetic models (Fig. 5A and 5B) were shown in Table 1, along with the correlation coefficients (R^2). The R^2 value of the PSO model was higher than that of the PFO model for both Cu(II) and Cr(VI) adsorption. In addition, the q_e calculated by the PSO model was more consistent with the experimental value compared to that of the PFO model (Table 1). Hence, the adsorption process of Cu(II) and Cr(VI) onto HS-PVC could be well described by the PSO model, indicating that chemisorption might be the rate-limiting step. In addition, more active sites were reported with the PSO model compared to the PFO model (Wang and Guo 2020), which was crucial to the adsorption of Cu(II) and Cr(VI) onto HS-PVC.

Adsorption isotherms play a crucial role in investigating the chemical interactions between adsorbates and adsorbents (Yang et al., 2019, Wang and Guo 2020). The adsorption isotherms of the adsorption of Cu(II) and Cr(VI) onto HS-PVC at three different temperatures (25, 35, and 45°C) were shown in Fig. 5C-5F. During the adsorption of Cu(II), the R^2 values of the Langmuir model (0.94–0.96) were higher than those of the Freundlich model (0.82–0.89) at all tested temperatures (25, 35, and 45 °C) (Fig. 5C, 5D, and Table S4), indicating that the adsorption of Cu(II) by HS-PVC was a monolayer process. Similarly, the adsorption of Cr(VI) was also a monolayer process due to the higher R^2 values of the Langmuir model (0.94 at 25 ℃ and 0.95 at 35 ℃) compared to those of the Freundlich model (0.90 at 25 ℃ and 0.89 at 35 ℃) (Fig. 5E, 5F, and Table S4). However, the adsorption of Cr(VI) was fitted by the Langmuir and Freundlich model equally well according to R^2 values of 0.96 at 45℃. In addition, the values of K_F and q_m increased with the increasing temperature (Table S4), indicating an endothermic adsorption process (Xu et al., 2019).

3.5. Mechanisms for the adsorption of Cu(II) and Cr(VI) onto HS-PVC

The removal efficiency of Cu(II) decreased ($p<0.01$) by 19.9 % with the co-adsorption of Cr(VI), and that of Cr(VI) also significantly decreased ($p<0.01$) by 48.8% with the co-adsorption of Cu(II) (Fig. 6A). The selectivity of Cu(II) ($\alpha^{\mathrm{Cu(II)}}_{\mathrm{Cr(VI)}}= 4.11$) was higher than that of Cr(VI) ($\alpha^{\mathrm{Cu(II)}}_{\mathrm{Cr(VI)}}= 0.24$) in binary-component solution, indicating that Cu(II) can occupy adsorption sites more easily than Cr(VI). However, during the preloading test, the removal efficiency of Cu(II) decreased by 70.5% using Cr(VI) loaded HS-PVC, which was similar to the decrease in Cr(VI) removal (65.8%) using Cu(II) loaded HS-PVC (Fig. 6A). These results suggested that the Cu(II) and Cr(VI) adsorption might share similar adsorption sites on HS-PVC. The zeta potential, an important index for the electric potential at the mineral surface (Ramasamy et al., 2017, Gu et al., 2021), significantly decreased after HT and sulfonation (Fig. S7). The value increased after the adsorption of Cu(II) (Fig. 6B), indicating electrostatic adsorption (Fig. 7). However, only a slight increase in zeta potential was observed after the Cr(VI) adsorption, implying that other mechanisms govern Cr(VI) adsorption onto HS-PVC.

To further explore the mechanism of the adsorption of Cr(VI) onto HS-PVC, XPS analysis was used to investigate the adsorption behavior of hydrochar. The C1s XPS spectra were separated, and the characteristic C=C, C-C, C-O, and C=O bonds were quantified in HS-PVC before and after Cr(VI) adsorption. The intensity of C=C in HS-PVC decreased from 35.5% (Fig. 6C) to 28.5% (Fig. 6D) after adsorption of Cr(VI) (Fig. 6C), suggesting the involvement of this bond in Cr(VI) removal. According to solid-state ^{13}C NMR, aromatic functional groups decreased from 55.0% (Fig. 6 E) to 51.4% (Fig. 6F) after Cr(VI) adsorption, also supporting a decrease of C=C intensity after the adsorption of Cr(VI). In addition, the degree of graphitization of HS-PVC decreased after Cr(VI) adsorption according to the decrease in the ratio of I_G/I_D from 0.77 to 0.73 (Fig. 6G), which might be related to the reduction of Cr(VI). Interestingly, Cr(III) was detected in HS-PVC after the adsorption of Cr(VI) (Fig. 6H). These results indicated that the functional group C=C and aromatic groups might reduce Cr(VI) to Cr(III). In addition, there were shifts of the ring vibration peak in the FTIR spectra after adsorption of Cr(VI) (arrows in Fig. 6I). Since a ligand aligns itself to a metal, the energy of the ligand material will most likely be perturbed, leading ultimately to subtle shifts in the absorption peaks (Sergios et al., 2010). Thus, HS-PVC might also bind Cr(VI), which was consistent with Cr(III) and Cr(VI) in Fig. 6H. It has been reported that Cr(VI) was complexed with phenolic -OH using hydrochar derived from leaves and wood sticks. The adsorbed Cr(VI) was subsequently reduced to Cr(III) by the hydrochar along with the decrease of the functional group C=C (Chen et al., 2017, Chen et al., 2021). In this study, the Cr(VI) was supposed to be complexed by the phenolic -OH (Fig. 6I) existed in HS-PVC and reduced by the C=C in the aromatic structure formed by HT (Fig. 7).

Note that the removal efficiency of Cr(VI) significantly decreased from 63.8 ± 2.0% in the presence of K(I) to 28.2 ± 5.1% after K(I) was precipitated by $HClO_4$ (Fig. S8). The introduction of H^+ ions increased the proportion of H_2CrO_4, thereby breaking the equilibrium balance of $HCrO_4^-$ and $Cr_2O_7^{2-}$ due to negative charges. This, in turn, suggested that K(I) ions might neutralize the negatively charged HS-PVC surface, thereby facilitating the binding of dichromate ions on HS-PVC (Fig. 7).

3.6. Versatility of HS-PVC

Natural water contains ions and organic compounds (Jeon et al., 2020), which might hinder Cu(II) and Cr(VI) removal by HS-PVC. Due to the competitive adsorption of co-existing ions, the efficient removal of Cu(II) and Cr(VI) decreased only by 19.2% and 25.0% (Fig. 8), respectively, indicating low interference. In addition, HS-PVC was particularly suitable for the removal efficiencies of Cu(II) and Cr(VI) at low concentrations (20 mg/L) (99.6 ± 0.1% and 94.3 ± 2.5%, respectively) (Fig. 8). Further, the removal efficiencies of Cu(II) and Cr(VI) using HS-PVC from waste pipes increased by 13.7% and 43.9% (Fig. 8), which were higher than those of HS-PVC derived from PVC powder (Fig. 1). The better performance of HS-PVC (pipes) might be attributed to plasticizers and mineral fillers in the PVC (Correa et al., 2019). The removal efficiencies of other metals such as Mn(II), Cd(II), Ni(II), and Co(II) amounted to 81.2 ± 2.3%, 80.8 ± 1.7%, 70.8 ± 1.8%, and 70.1 ± 3.2% (Fig. S9), respectively, indicating that HS-PVC is suitable for the treatment of complex industrial wastewater. Moreover, the adsorption of Cu(II) and Cr(VI) decreased only by 10.0% and 31.0% (Fig. S10) after three adsorption-desorption cycles (1 mol/L HCl as eluent), indicating excellent recyclability.

Previous studies commonly focused on the conversion of waste PVC into coal-alternative fuel (Lu et al., 2020) or lighter oil (Maity et al., 2020). Using HT and sulfonation modifications, the present study provided a novel strategy for resource recovery of PVC waste by producing efficient adsorbents for Cu(II) cations and Cr(VI) anions removal. The sulfonation intensity was mild in this study (98% sulfuric acid at 70°C). Fuming H_2SO_4, $ClSO_3H$, aryldiazonium sulfonates, and higher temperatures (80–150°C) could be considered for additional optimization. In addition, as it is a “sulfonated carbon” (Konwar et al., 2019), HS-PVC may show promising catalytic performances in various organic transformations, including esterifications, ester exchange (transesterifications), acetalization, etherifications, condensation, and multi-component organic reactions that should be studied in the future.

4. Conclusion

This study provided a novel method to fabricate efficient adsorbent (HS-PVC) from waste PVC for both Cu(II) cations and Cr(VI) anions removal. The removal efficiencies of Cu(II) and Cr(VI) using HS-PVC reached 81.2 ± 1.6% and 60.3 ± 3.8%, respectively. The first stage of HT was crucial for the dichlorination of PVC and the formation of an aromatic structure, guaranteeing the introduction of $-SO_3H$ onto PVC-derived hydrochar through subsequent sulfonation. In addition, sulfonation also significantly increased the hydrophilicity of HS-PVC. The adsorption of Cu(II) was sensitive to HT temperature, while that of Cr(VI) was more sensitive to HT time. Adsorption isotherm data were accurately fitted by the

Langmuir isotherm model with a maximum adsorption capacity of 48.9 mg/g for the adsorption of Cu(II) and 20.2 mg/g for the adsorption of Cr(VI) at 45℃. Competitive adsorption of Cu(II) and Cr(VI) occurred, and the selectivity of HS-PVC for the removal of Cu(II) was higher than that of Cr(VI). The adsorption mechanism of Cu(II) was electrostatic adsorption, while Cr(VI) were possibly complexed by the phenolic -OH and reduced to Cr(III) cations by C=C groups in HS-PVC. In addition, HS-PVC was particularly suitable for the adsorption of both metals at low concentrations (＞94% at 20 mg/L). HS-PVC derived from PVC waste pipes also showed high absorption efficiencies for Cu(II) and Cr(VI) (＞90%).

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Table 1

PFO and PSO model parameters for Cu(II) and Cr(VI) adsorption onto HS-PVC.

Metals	q_{exp}	PFO			PSO		
	(mg/g)	q_1 (mg/g)	R_1^2	k_1 (min^{-1})	q_2 (mg/g)	R_2^2	k_2 (g/(mg·min))
Cu(II)	40.34	38.18	0.86	17.92	40.24	0.95	0.70
Cr(VI)	17.75	15.41	0.88	2.39	16.23	0.94	0.25

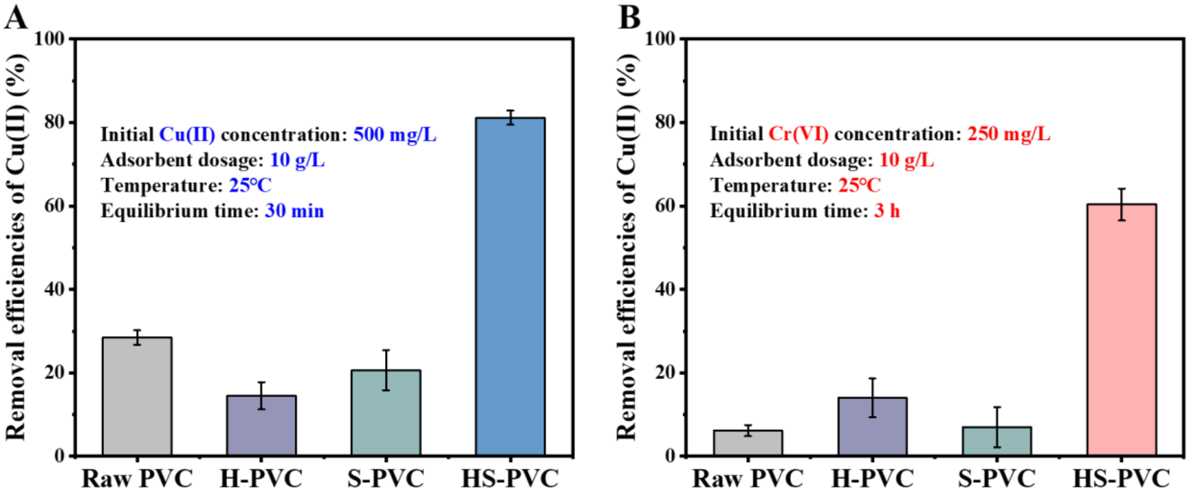

Fig. 1. Cu(II) and Cr(VI) removal efficiencies using Raw PVC, H-PVC, S-PVC, and HS-PVC after adsorption for 12 hours.

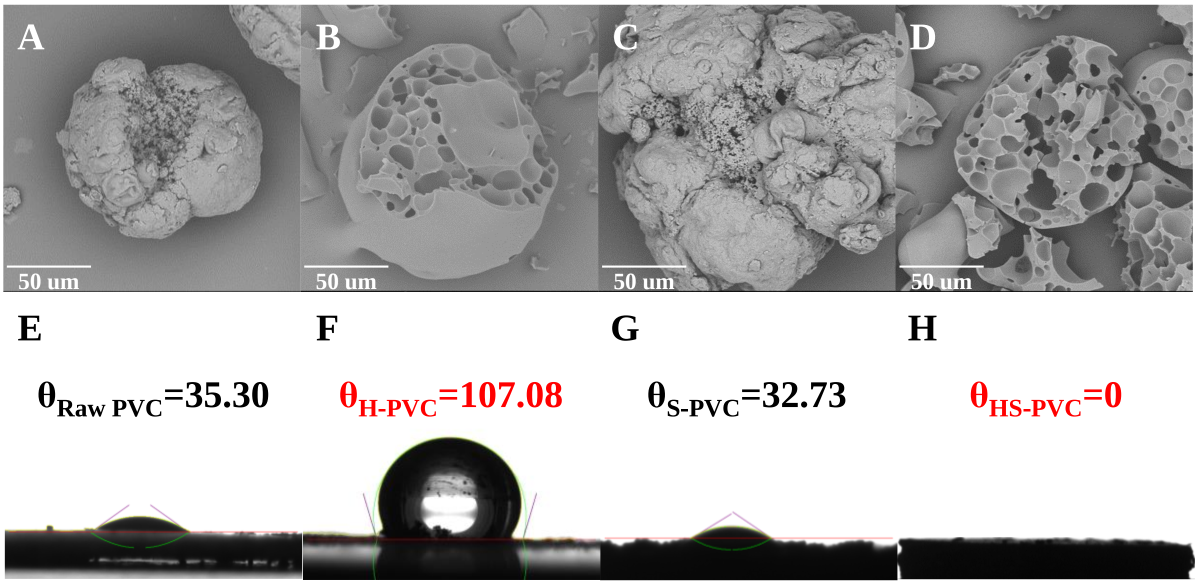

Fig. 2. Surface properties of PVC derived adsorbents: SEM images of Raw PVC (A), H-PVC (B), S-PVC (C), and HS-PVC (D); contact angle (θ) of Raw PVC (E), H-PVC (F), S-PVC (G), and HS-PVC (I).

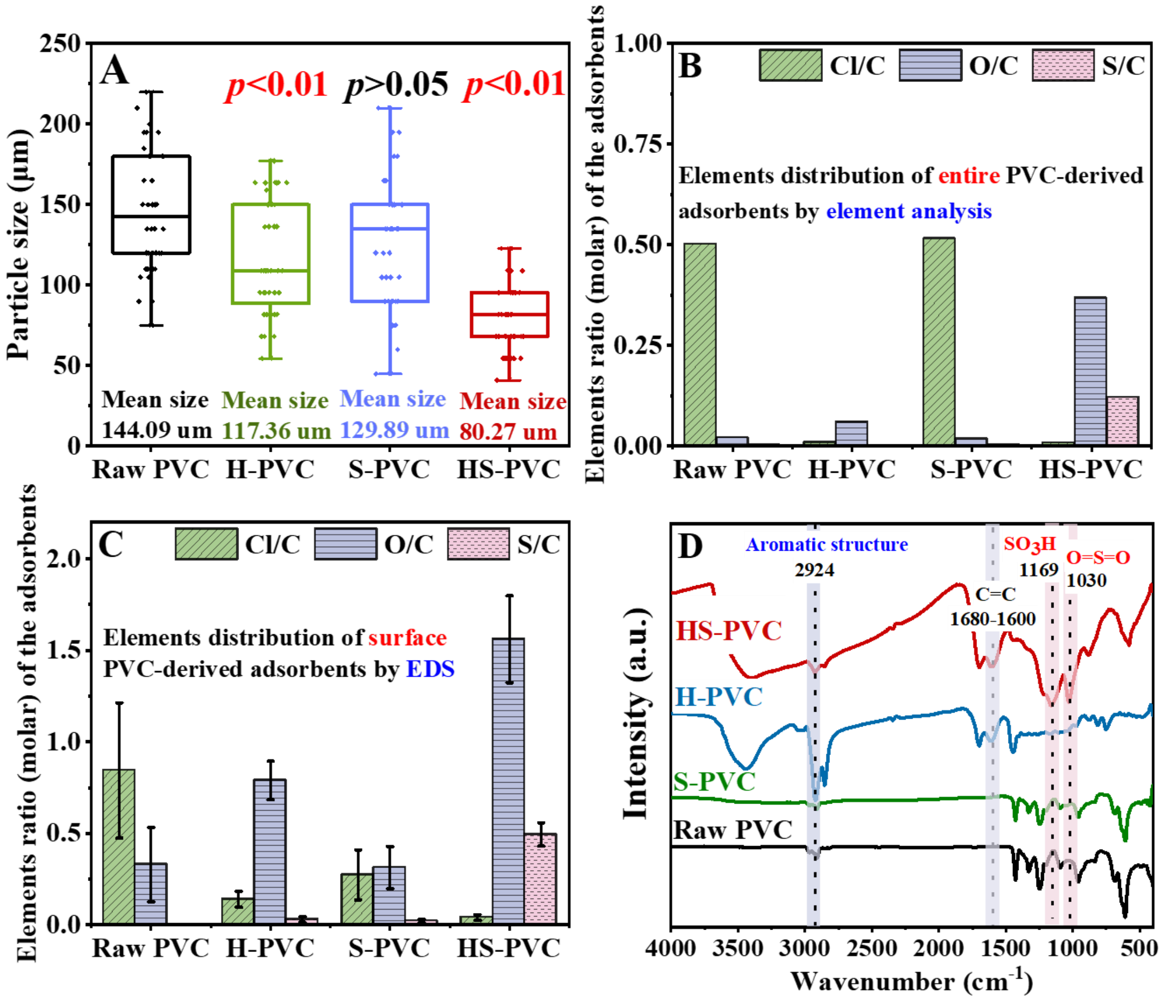

Fig. 3. Characterization of Raw PVC, H-PVC, S-PVC, and HS-PVC: particle size distribution (A), elemental analysis (B), EDS element mapping (C), and FTIR spectra (D).

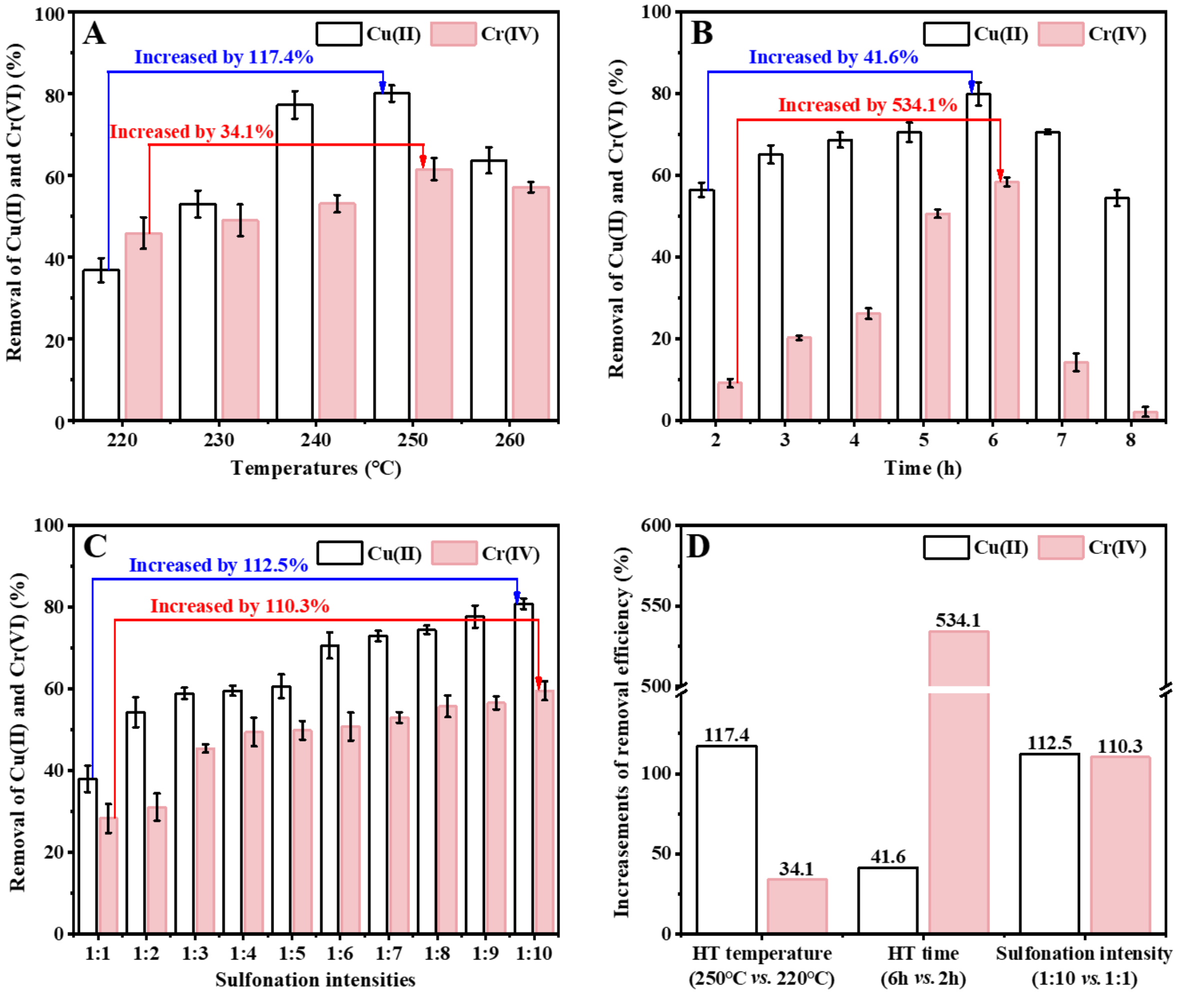

Fig. 4. Effects of HS-PVC preparation intensities on Cu(II) and Cr(VI) removal: HT temperature (A), HT time (B), sulfonation intensity (C), and comparison of Cu(II) and Cr(VI) removal efficiencies between the optimal and the lowest efficiency (D) (HT temperature: 250 °C *vs.* 220 °C, HT time: 6 h *vs.* 2 h, and sulfonation intensity: 1:10 *vs.* 1:1). The initial concentrations of Cu(II) and Cr(VI) were 500 and 250 mg/L. The adsorbent dose was 10 g/L and the temperature 25 °C.

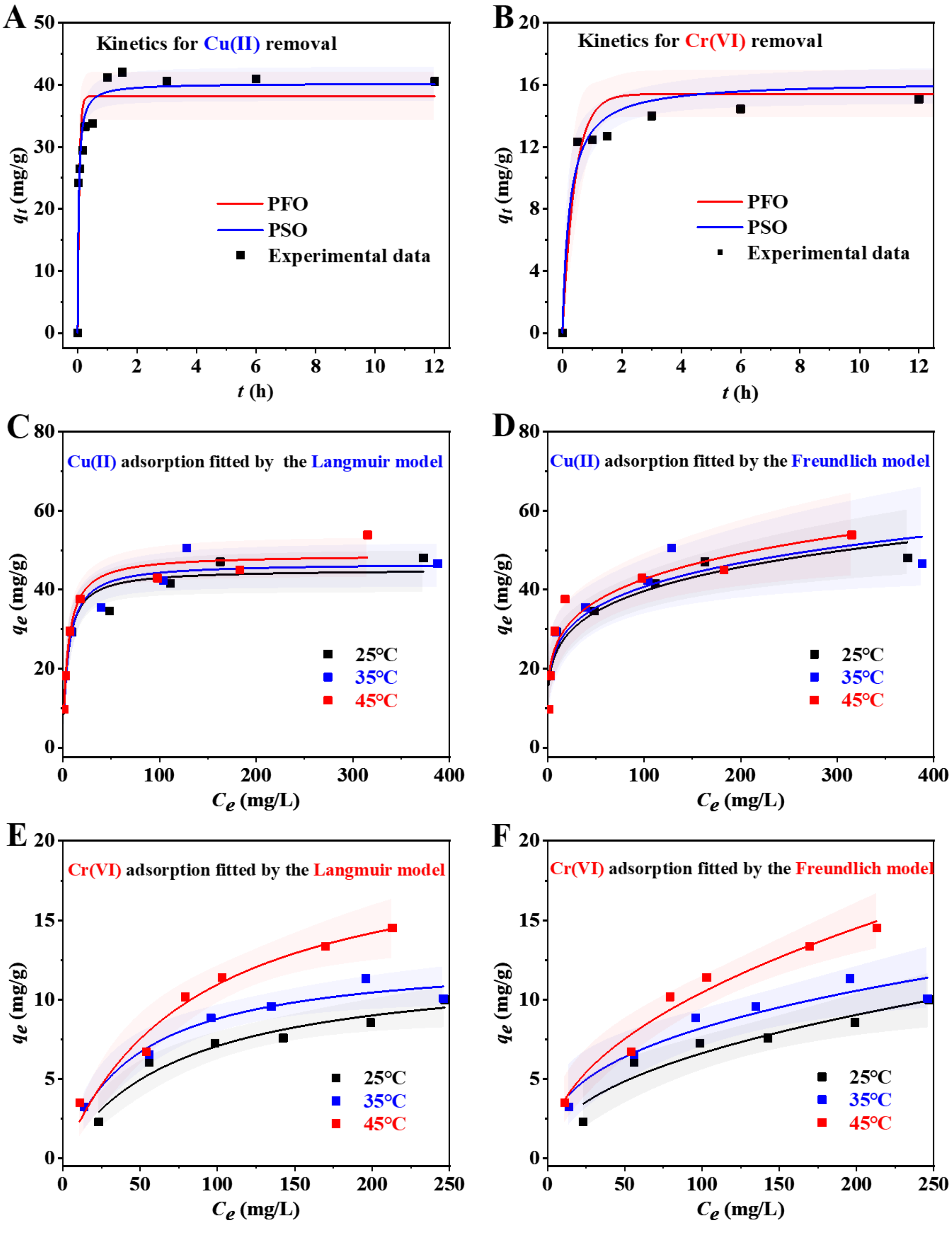

Fig. 5. Adsorption kinetics of Cu(II) (A) and Cr(VI) (B) onto HS-PVC. Equilibrium isotherms of Cu(II) fitted by the Langmuir (C) and Freundlich models (D) at different temperatures (25, 35, and 45 °C). Equilibrium isotherms of Cr(VI) fitted by the Langmuir (E) and Freundlich models (F) at different temperatures (25, 35, and 45 °C). The colored area covers the 95% confidence intervals.

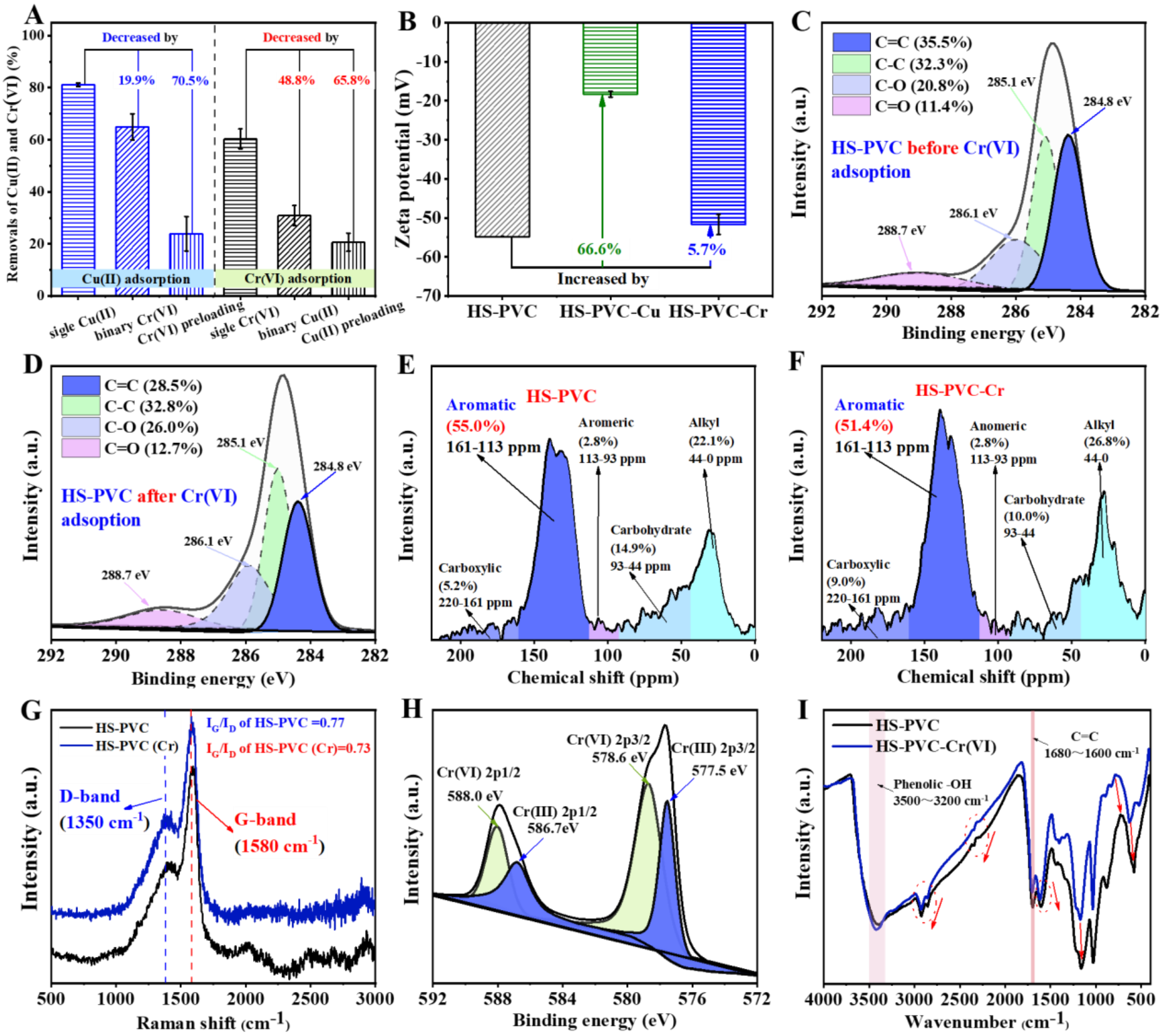

Fig. 6. Mechanisms for the adsorptions of Cu(II) and Cr(VI) by HS-PVC. Competitive adsorption between Cu(II) and Cr(VI) by HS-PVC (A). Zeta potential of HS-PVC, HS-PVC after the adsorption of Cu(II) (HS-PVC-Cu), and HS-PVC after the adsorption of Cr(VI) (HS-PVC-Cr) (B). C 1s XPS spectra of HS-PVC before the adsorption of Cr(VI) (C) and after the adsorption of Cr(VI) (D). Solid-state ^{13}C NMR of HS-PVC before the adsorption of Cr(VI) (E) and after the adsorption of Cr(VI) (F). Raman spectra of HS-PVC before and after adsorption of Cr(VI) (a higher I_G/I_D ratio indicates a higher degree of graphitization) (G). Cr 2p XPS spectra of HS-PVC after the adsorption of Cr(VI) (H). FTIR spectra of HS-PVC before and after the adsorption of Cr(VI) (I).

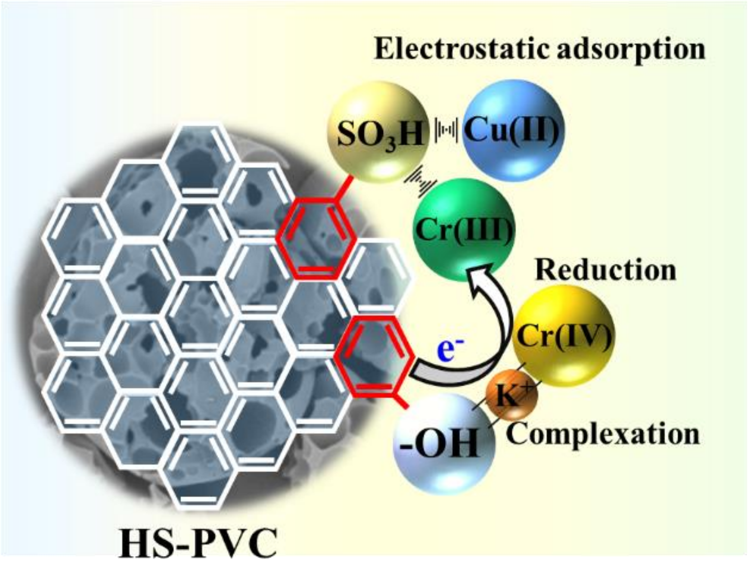

Fig. 7. Schematic adsorption of Cu(II) and Cr(VI) using HS-PVC

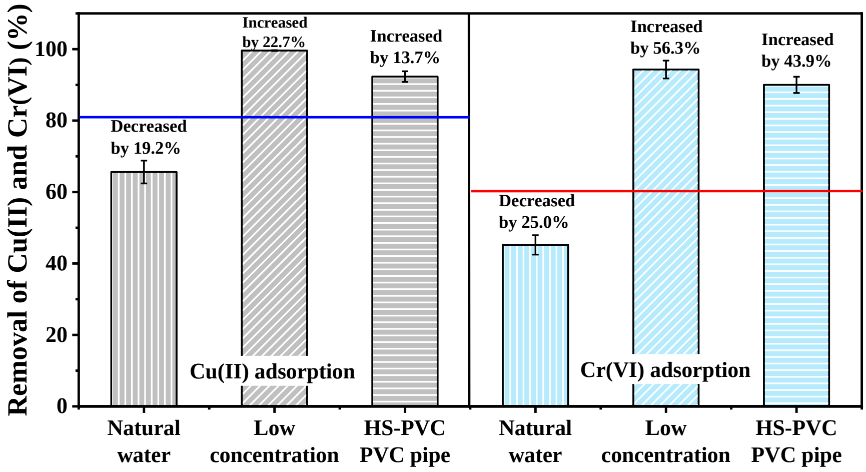

Fig. 8. Versatility of HS-PVC for Cu(II) and Cr(VI) removal efficiencies. Removal of Cu(II) and Cr(VI) by HS-PVC from natural water, at low concentration (20 mg/L), and by HS-PVC derived from waste PVC pipes (blue and red lines represent the removal efficiency of Cu(II) and Cr(VI) by PVC powder in Fig. 1).