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**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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21 **Abstract**

22 The reuse of waste polyvinyl chloride (PVC) has drawn much attention as it can reduce  
23 plastic waste and associated pollution, and provide valuable raw materials and products. In  
24 this study, sulfonated PVC-derived hydrochar (HS-PVC) was synthesized by two-stage  
25 hydrothermal treatment (HT) and sulfonation, and shown to be a versatile adsorbent. The  
26 removal of Cu(II) cations and Cr(VI) anions using HS-PVC reached  $81.2 \pm 1.6\%$  and  $60.3 \pm$   
27  $3.8\%$ , respectively. The first stage of HT was crucial for the dichlorination of PVC and the  
28 formation of an aromatic structure. This stage guaranteed the introduction of  $-\text{SO}_3\text{H}$  onto  
29 PVC-derived hydrochar through subsequent sulfonation. HT intensities (i.e., temperature and  
30 time) and sulfonation intensity strongly determined the adsorption capacity of HS-PVC.  
31 Competitive adsorption between Cu(II) and Cr(VI) onto HS-PVC was demonstrated by  
32 binary and preloading adsorption. The proposed Cu(II) cations adsorption mechanism was  
33 electrostatic adsorption, while Cr(VI) were possibly complexed by the phenolic  $-\text{OH}$  and  
34 reduced to Cr(III) cations by  $\text{C}=\text{C}$  groups in HS-PVC. In addition, HS-PVC derived from  
35 PVC waste pipes performed better than PVC powder for Cu(II) and Cr(VI) removal ( $> 90\%$ ).  
36 This study provides an efficient method for recycling waste PVC and production of efficient  
37 adsorbents.

38

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

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## 42 **1. Introduction**

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

49 Mechanical recycling (25.5%), incineration (9.3%), and landfill disposal (36.0%) are  
50 currently the main solutions for solving the problem of PVC waste (Yu et al., 2016, Ye et al.,  
51 2017, Liu et al., 2020). However, mechanical recycling is still rudimentary and only suitable  
52 for source-separated PVC waste. Incineration and landfill disposal of PVC waste normally  
53 release hazardous compounds, such as polychlorinated dibenzo-p-dioxins and  
54 polychlorinated dibenzofurans. Furthermore, the land requirements of landfills must be  
55 considered (Wiedinmyer et al., 2014). Thus, reliable alternative methods to treat PVC waste  
56 safely and efficiently in an environmentally sound and high value-added way are worth  
57 pursuing (Lau et al., 2020). Such an approach is in line with the European Union's strategy  
58 for plastics in a circular economy (Matthews et al., 2021).

59 Hydrothermal treatment (HT), conducted at relatively low temperatures of 160 to 300°C,  
60 can pretreat PVC waste for dehydrochlorination (Ma et al., 2019, Ning et al., 2020),  
61 permitting subsequent pyrolysis to produce chars and liquid hydrocarbons with a low Cl  
62 content, such as alkene and polyene (Poerschmann et al., 2015, Jiang et al., 2021). However,

63 cost- and energy-intensive conditions, such as noble metal catalysts and high temperature  
64 (500°C), are typically adopted for lighter oil production by catalytic pyrolysis of plastic  
65 (Kunwar et al., 2016, Maity et al., 2020). On the other hand, PVC waste can be converted  
66 into coal-alternative fuels by HT processes amended with cellulose (Shen et al., 2017),  
67 pinewood sawdust (Huang et al., 2019), and corncob (Lu et al., 2020). Yet, another important  
68 recycling method has been undervalued and ignored, i.e., the potential transformation of  
69 PVC-derived hydrochar (H-PVC) into an effective adsorbent for the removal of contaminants,  
70 such as heavy metals.

71 Unfortunately, the adsorption capacity of organic compounds by H-PVC is very low,  
72 primarily because surface-related adsorption prevails over hydrophobic partitioning  
73 (Poerschmann et al., 2015). Several studies showed that the adsorption of hydrochar derived  
74 from natural biomass sources was enhanced by introducing functional groups, such as –OH,  
75 –COOH, and –NH<sub>2</sub>, which could trap heavy metal ions from aqueous solutions (Azzaz et al.,  
76 2020, Yang et al., 2021). Sulfonation is an attractive modifications method for various carbon  
77 materials due to the unique surface chemistry and low production costs. Large amounts of  
78 oxygen functionalities, such as –OH, –COOH, and lactones, along with –SO<sub>3</sub>H groups, are  
79 introduced into the surface of the carbon materials, improving their hydrophilic/oxyphilic  
80 properties after sulfonation. Sulfonated carbon materials have been widely applied in the  
81 catalysis of esterifications, acetalization, etherifications, and transesterifications (Konwar et  
82 al., 2019). However, sulfonated PVC-derived hydrochar (HS-PVC) has rarely been reported,  
83 albeit potentially being a cost-effective adsorbent for heavy metals.

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

95

## 96 **2. Materials and methods**

### 97 **2.1. Preparation of PVC-derived adsorbents**

98 Raw PVC powder (sieved through a 100 mesh) was purchased from a plastic chemical  
99 company (Guangdong, China). Hydrothermal batch reactions were conducted by loading 10 g  
100 of Raw PVC with 40 mL distilled water in 100-mL airtight stainless-steel tubular reactors  
101 with internal polyphenylene containers. The reactors were heated to 250 °C for 6 h in a  
102 homothermic oven (DHG-9013A, China). The reactors were then cooled to room temperature  
103 in a water bath to prepare the H-PVC. Ten grams of Raw PVC was sulfonated in flasks (250  
104 ml) with concentrated sulfuric acid (98%) at a sulfonation intensity of 1:10 (g/mL) in a shaking

105 bath (70 °C and 110 rpm for 12 h) to produce the sulfonated PVC (S-PVC). Unless otherwise  
106 specified, sulfonation intensity refers to the ratio of adsorbent mass to the volume of sulfuric  
107 acid in this paper. Specifically, a relatively low temperature of sulfonation (70 °C) was chosen  
108 according to the literature (Xiao and Hill 2020). The HS-PVC was synthesized by sulfonation  
109 of H-PVC with the same process as described for S-PVC. The S-PVC and HS-PVC were  
110 washed three times with distilled water to eliminate the unreacted sulfuric acid. The Raw PVC,  
111 H-PVC, S-PVC, and HS-PVC were dried in a homothermic oven at 105 °C for 24 h. The dried  
112 PVC-derived adsorbents were then ground and sieved through a 100 mesh (147 µm) before  
113 adsorption of Cu(II) and Cr(VI).

## 114 **2.2. PVC-derived adsorbents for highly efficient removal of Cu(II) and Cr(VI)**

### 115 **2.2.1. Cu(II) and Cr(VI) removal using Raw PVC, H-PVC, S-PVC, and HS-PVC**

116 A stock solution of 500 mg Cu(II)/L (7.87 mM) was prepared by dissolving 1965 mg of  
117 copper sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O) in 1 L of ultrapure water. A stock solution of 250  
118 mg Cr(VI)/L (4.81 mM) was prepared by dissolving 770 mg of potassium dichromate  
119 (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) in 1 L of ultrapure water. Batch experiments of Cu(II) and Cr(VI) removal were  
120 performed by adding 10 g/L of Raw PVC, H-PVC, S-PVC, and HS-PVC to flasks (250 mL)  
121 in a water bath shaker (25 °C and 100 rpm) for 12 h. All samples were withdrawn from the  
122 flasks and filtered through membrane filters with a pore size of 0.22 µm for subsequent Cu(II)  
123 and Cr(VI) determination.

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

$$125 \text{ Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

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

### 131 **2.2.2. Cu(II) and Cr(VI) removal using HS-PVC under different intensities of HT** 132 **temperature, HT time, and sulfonation and correlation analyses**

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

### 143 **2.2.3. Adsorption kinetics and isotherms of Cu(II) and Cr(VI) removal using HS-PVC**

144 The adsorption kinetics of Cu(II) and Cr(VI) removal were studied based on the removal  
145 efficiencies of HS-PVC as described in Section 2.2.1. Adsorption isotherm experiments were  
146 carried out with different initial concentrations of Cu(II) (i.e., 100, 200, 300, 400, 500, 600,

147 and 800 mg/L) and Cr(VI) (50, 100, 150, 200, 250, and 300 mg/L) at three different  
148 temperatures (25, 35, and 45 °C) using 10 g/L HS-PVC under optimum operational  
149 conditions (250°C, 6 h, and a sulfonation intensity of 1:10).

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

$$153 \quad \ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$154 \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

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

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

$$162 \quad q_e = \frac{b q_m C_e}{1 + b C_e} \quad (4)$$

$$163 \quad q_e = K_F C_e^{1/n} \quad (5)$$

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



168 Levenberg-Marquardt method at the 95% confidence level.

#### 169 **2.2.4. Competitive adsorption of Cu(II) and Cr(VI) onto HS-PVC in binary solution and** 170 **preloading adsorption**

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

$$175 \quad \alpha_2^1 = \frac{q_{e1} \times C_{e2}}{C_{e1} \times q_{e2}} \quad (6)$$

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

180 Preloading adsorption tests for Cr(VI) were performed by incubating 2.5 g HS-PVC in  
181 250 mg/L Cr(VI) solution for 12 h. Then, the HS-PVC preloaded with Cr(VI) was used for  
182 the adsorption of Cu(II) for 12 h, as described in Section 2.2.1. The preloading adsorption  
183 tests for Cu(II) were performed under the same experimental conditions as those for Cr(VI).  
184 The removal efficiencies of Cu(II) and Cr(VI) were calculated to evaluate the competitive  
185 adsorption between Cu(II) and Cr(VI) onto the HS-PVC.

#### 186 **2.2.5. Effect of K(I) on Cr(VI) removal**

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

189 mL, calculated as described in Text S1) was added to precipitate K(I) ( $K_{sp}$  of  $\text{KClO}_4$   $1.5 \times 10^{-2}$ )  
190 in the Cr(VI) solution (total volume 100 mL). Then, HS-PVC (10 g/L) was added to the  
191 treated Cr(VI) solution for adsorption for 12 h. Finally, the removal efficiency of Cr(VI) was  
192 calculated to evaluate the impact of K(I) on the adsorption of Cr(VI) using HS-PVC.

### 193 **2.2.6. Low concentration Cu(II) and Cr(VI) removal using HS-PVC**

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

### 199 **2.2.7. Cu(II) and Cr(VI) removal in natural water**

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

### 205 **2.2.8. Cu(II) and Cr(VI) removal using HS-PVC derived from PVC waste pipes**

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

210 h adsorption (at 25°C and 100 rpm).

### 211 **2.3. Characterizations of PVC-derived adsorbents**

#### 212 **2.3.1. Characterizations of Raw PVC, H-PVC, S-PVC, and HS-PVC**

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

#### 226 **2.3.2. Characterizations of HS-PVC before and after adsorption of Cu(II) and Cr(VI)**

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

231 Scientific, K-Alpha, USA), FTIR, solid-state  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy  
232 (NMR) (Agilent, 600M, USA), and Raman spectroscopy (Thermo Fisher, DXR, USA). The  
233 C1s XPS spectra were separated and characterized by C=C (284.8 eV), C-C (285.1 eV), C-O  
234 (286.1 eV), and C=O groups (288.7 eV). The regions of functional groups derived from the  
235 solid-state  $^{13}\text{C}$  NMR spectra were divided into Carboxylic (220-161), Aromatic (161-113),  
236 Anomeric (113-93), Carbohydrate (93-44), and Alkyl (44-0) (Wang et al., 2016, Li et al.,  
237 2019).

#### 238 **2.4. Statistical analysis**

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

### 246 **3. Results and discussion**

#### 247 **3.1. Highly efficient Cu(II) cations and Cr(VI) anions removal using HS-PVC**

248 Regarding Cu(II) removal, HS-PVC was significantly more efficient ( $81.2 \pm 1.6\%$ )  
249 compared to Raw PVC ( $28.5 \pm 1.7\%$ ) and PVC solely pretreated by either HT ( $14.5 \pm 3.2\%$ )  
250 or sulfonation ( $20.6 \pm 4.8\%$ ) within 12 h (Fig. 1A). In addition, HS-PVC was also highly  
251 efficient in removing Cr(VI) ( $60.3 \pm 3.8\%$ ) compared to Raw PVC ( $6.1 \pm 1.3\%$ ) and PVC

252 solely pretreated by either HT ( $14.0 \pm 4.6\%$ ) or sulfonation ( $7.0 \pm 4.8\%$ ) within 12 h (Fig.  
253 1B). The adsorption of Cu(II) reached equilibrium within 30 min while the adsorption  
254 efficiency of Cr(VI) was only  $49.3 \pm 1.0\%$  at 30 min and then slowly increased to equilibrium  
255 within 3 h (Fig. S1). This suggested different adsorption mechanisms for Cu(II) and Cr(VI)  
256 onto HS-PVC. Biomass-derived hydrochar was also widely employed in the adsorption of  
257 metal cations, such as Cu(II), Zn(II), and Pb(II) (Deng et al., 2020, Kazak and Tor 2020, Song  
258 et al., 2020) or metal anions, such as Cr(VI) ( $\text{Cr}_2\text{O}_7^{2-}$ ) (Li et al., 2020). Cu(II) and Cr(VI)  
259 could be simultaneously removed by hydrochar derived from chitosan with  $\text{Fe}_2\text{O}_3$   
260 modifications. However, the main adsorption mechanisms were chelation adsorption of Cu(II)  
261 and electrostatic adsorption-coupled Cr(VI) reduction due to the specific dual-core  $\text{Fe}_2\text{O}_3@\text{C}$   
262 structure (Wang et al., 2017). The present study firstly provided a metal-free modification of  
263 hydrochar derived from waste PVC for simultaneous Cu(II) cations and Cr(VI) anions  
264 removal.

265 The adsorption capacity of hydrochar was highly dependent on the functional groups  
266 formed during HT (Tong et al., 2021). However, the structure and component of PVC  
267 ( $[-\text{CH}_2-\text{CHCl}-]_n$ ) were simpler compared to natural biomass, suggesting fewer functional  
268 groups anchored in H-PVC than in natural biomass. This may explain why H-PVC is of little  
269 significance for the adsorption of Cu(II) and Cr(VI) (Fig. 1), which was in line with poor  
270 adsorption in wastewater remediation (Poerschmann et al., 2015). Sulfonation was also an  
271 efficient modification of adsorbents derived from tea waste and cellulose for Cu(II) or Cr(VI)  
272 removal (Dong et al., 2016, Ahsan et al., 2018). However, the adsorption of Cu(II) and Cr(VI)

273 using S-PVC was still low in this study. This paper showed a possible synergistic effect of  
274 HT and sulfonation in the modifications of the methodology to produce a highly efficient  
275 adsorbent.

### 276 **3.2. Characterization during the fabrications of HS-PVC from Raw PVC in** 277 **combination with HT and sulfonation**

278 The microstructure of the PVC-derived adsorbents was characterized by SEM (Fig. 2A  
279 to 2D). A rough surface and non-porous structures were observed in Raw PVC (Fig. 2A).  
280 After HT treatment, the surface of H-PVC became smoother with an internal porous structure  
281 (Fig. 2B) mainly due to dehydrochlorination, aromatization, and depolymerization reactions  
282 during HT (Ning et al., 2020). There was no apparent difference between Raw PVC and  
283 S-PVC in the SEM images (Fig. 2A and 2C), indicating that sulfonation possessed a marginal  
284 impact on the surface structure. In contrast, the HS-PVC was fragmented with an internal  
285 porous structure due to HT and sulfonation (Fig. 2D), which was consistent with a significant  
286 decrease of particle size in HS-PVC compared to the Raw PVC (Fig. 3A and Table S2). In  
287 addition, the hydrophobicity and hydrophilicity of adsorbents may influence the performance  
288 of the adsorption process (Adam et al., 2020). The hydrophobicity of S-PVC was similar to  
289 that of Raw PVC (Fig. 2E and 2G). However, the hydrophobicity was higher after HT (Fig.  
290 2E and 2F), resulting in hydrophobic partitioning as described in the literature (Poerschmann  
291 et al., 2015), which was consistent with the low adsorption efficiency of Cu(II) and Cr(VI) by  
292 H-PVC (Fig. 1). Furthermore, the hydrophilicity of HS-PVC was significantly higher than  
293 that of H-PVC (Fig. 2F and 2H), indicating that sulfonation improved the hydrophilicity of

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

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

302 Elemental analysis (Fig. 3B) showed that the Cl/C molar ratio (0.5) of Raw PVC was  
303 similar to the stoichiometric value of  $([-\text{CH}_2-\text{CHCl-}]_n)$ . However, the molar ratio of Cl/C on  
304 the surface of Raw PVC ( $0.85 \pm 0.37$ ) was higher than 0.5 according to EDS element  
305 mapping (Fig. 3C), suggesting that most of the -Cl functional groups were on the surface of  
306 Raw PVC. The Cl/C ratio of H-PVC significantly decreased (Fig. 3B and 3C) compared to  
307 the Raw PVC after pretreatment by HT due to the dehydrochlorination (Poerschmann et al.,  
308 2015). The elemental composition of the entire Raw PVC and S-PVC was similar (Fig. 3B),  
309 but surface Cl was lower, and surface O slightly higher in S-PVC than in Raw PVC (Fig. 3C).  
310 This indicated that sole sulfonation only impacted the chemical composition on the surface of  
311 Raw PVC (Fig. 3C), causing no obvious chemical modifications to the entire Raw PVC (Fig.  
312 3B). Additionally, the O/C and S/C ratios of HS-PVC increased, resulting in an O/S ratio of  
313 3.04 (elemental analysis in Fig. 3B) or 3.16 (EDS element mapping in Fig. 3C). Thus, it  
314 could be hypothesized that the introduction of S-containing functional groups such as -SO<sub>3</sub>H

315 (O/S=3) into HS-PVC occurred. The absorption peaks of HS-PVC from the FTIR at 1030  
316  $\text{cm}^{-1}$  (O=S=O) and 1169  $\text{cm}^{-1}$  (-SO<sub>3</sub>H) verified this assumption (Fig. 3D) (Chen et al., 2019).  
317 The functional group -SO<sub>3</sub>H was only detected in HS-PVC, indicating that the introduction of  
318 -SO<sub>3</sub>H onto HS-PVC was attributed to the synergy effect of HT and sulfonation. In addition,  
319 the thermostability of HS-PVC was higher than that of Raw PVC according to the TGA  
320 patterns (Fig. S3), which was mainly due to aromatization during HT (Park et al., 2016). It  
321 has been reported that the presence of aromatic groups was essential for the sulfonation of  
322 petroleum coke by concentrated H<sub>2</sub>SO<sub>4</sub> (Xiao and Hill 2020). In this study, HT was crucial to  
323 forming an aromatic structure (Fig. 3D) for the introduction of -SO<sub>3</sub>H during sulfonation to  
324 fabricate HS-PVC for highly efficient Cu(II) and Cr(VI) removal. Moreover, the functional  
325 group C=C in HS-PVC (Fig. 3D) was crucial for removing Cr(VI), which was confirmed in  
326 the following section.

### 327 **3.3. Correlations of Cu(II) and Cr(VI) removal with HT intensities and sulfonation**

328 The adsorption properties of HS-PVC were highly dependent on HT temperature and  
329 time (see time curves in Fig. S4 and Fig. S5). The adsorption efficiencies of Cu(II) and Cr(VI)  
330 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  
331 250 °C, but declined to 63.7 ± 3.2% and 57.2 ± 1.3% at 260 °C, respectively (Fig. 4A). In  
332 addition, the adsorption efficiencies of Cu(II) and Cr(VI) also increased from 56.5 ± 1.7%  
333 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 ±  
334 2.0% and 2.2 ± 1.2% at 8 h, respectively (Fig. 4B). Higher HT intensities benefited PVC  
335 dehydrochlorination (Zhang et al., 2020), providing more sites for subsequent SO<sub>3</sub>H



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

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

348 As summarized in Fig. 4D, the adsorption efficiency of Cu(II) increased by 117.4%  
349 while that of Cr(VI) only by 34.1%, when increasing the temperature from 220 °C to 250 °C.  
350 In contrast, the adsorption efficiency of Cu(II) improved only by 41.6%, while that of Cr(VI)  
351 increased by 534%, with HT time increasing from 2 to 8 h. These results indicated that the  
352 adsorption of Cu(II) was sensitive to HT temperature while the adsorption of Cr(VI) was  
353 rather sensitive to HT time. However, the impact of sulfonation intensity on the adsorption of  
354 Cu(II) (increasing 112.5% from 1:1 to 1:10) was similar to the adsorption of Cr(VI) (increasing  
355 110.3% from 1:1 to 1:10).

### 356 3.4. Kinetics and isotherms of the adsorption of Cu(II) and Cr(VI) onto HS-PVC

357 Adsorption kinetics were essential to investigate the adsorption process (Song et al.,  
358 2020, Wang and Guo 2020). The adsorption of Cu(II) and Cr(VI) onto the HS-PVC (Fig. 5A  
359 and 5B) increased rapidly in the first 30 min and then decreased as the reaction approached  
360 equilibrium due to the saturation of active adsorbent sites. The values of  $q_e$  and rate constants  
361 ( $k_1$  and  $k_2$ ) obtained from the kinetic models (Fig. 5A and 5B) were shown in Table 1, along  
362 with the correlation coefficients ( $R^2$ ). The  $R^2$  value of the PSO model was higher than that of  
363 the PFO model for both Cu(II) and Cr(VI) adsorption. In addition, the  $q_e$  calculated by the  
364 PSO model was more consistent with the experimental value compared to that of the PFO  
365 model (Table 1). Hence, the adsorption process of Cu(II) and Cr(VI) onto HS-PVC could be  
366 well described by the PSO model, indicating that chemisorption might be the rate-limiting  
367 step. In addition, more active sites were reported with the PSO model compared to the PFO  
368 model (Wang and Guo 2020), which was crucial to the adsorption of Cu(II) and Cr(VI) onto  
369 HS-PVC.

370 Adsorption isotherms play a crucial role in investigating the chemical interactions  
371 between adsorbates and adsorbents (Yang et al., 2019, Wang and Guo 2020). The adsorption  
372 isotherms of the adsorption of Cu(II) and Cr(VI) onto HS-PVC at three different temperatures  
373 (25, 35, and 45°C) were shown in Fig. 5C-5F. During the adsorption of Cu(II), the  $R^2$  values  
374 of the Langmuir model (0.94–0.96) were higher than those of the Freundlich model (0.82–  
375 0.89) at all tested temperatures (25, 35, and 45 °C) (Fig. 5C, 5D, and Table S4), indicating  
376 that the adsorption of Cu(II) by HS-PVC was a monolayer process. Similarly, the adsorption

377 of Cr(VI) was also a monolayer process due to the higher  $R^2$  values of the Langmuir model  
378 (0.94 at 25 °C and 0.95 at 35 °C) compared to those of the Freundlich model (0.90 at 25 °C  
379 and 0.89 at 35 °C) (Fig. 5E, 5F, and Table S4). However, the adsorption of Cr(VI) was fitted  
380 by the Langmuir and Freundlich model equally well according to  $R^2$  values of 0.96 at 45°C.  
381 In addition, the values of  $K_F$  and  $q_m$  increased with the increasing temperature (Table S4),  
382 indicating an endothermic adsorption process (Xu et al., 2019).

### 383 3.5. Mechanisms for the adsorption of Cu(II) and Cr(VI) onto HS-PVC

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

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

419 and reduced by the C=C in the aromatic structure formed by HT (Fig. 7).

420 Note that the removal efficiency of Cr(VI) significantly decreased from  $63.8 \pm 2.0\%$  in  
421 the presence of K(I) to  $28.2 \pm 5.1\%$  after K(I) was precipitated by HClO<sub>4</sub> (Fig. S8). The  
422 introduction of H<sup>+</sup> ions increased the proportion of H<sub>2</sub>CrO<sub>4</sub>, thereby breaking the equilibrium  
423 balance of HCrO<sub>4</sub><sup>-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> due to negative charges. This, in turn, suggested that K(I) ions  
424 might neutralize the negatively charged HS-PVC surface, thereby facilitating the binding of  
425 dichromate ions on HS-PVC (Fig. 7).

### 426 3.6. Versatility of HS-PVC

427 Natural water contains ions and organic compounds (Jeon et al., 2020), which might  
428 hinder Cu(II) and Cr(VI) removal by HS-PVC. Due to the competitive adsorption of  
429 co-existing ions, the efficient removal of Cu(II) and Cr(VI) decreased only by 19.2% and 25.0%  
430 (Fig. 8), respectively, indicating low interference. In addition, HS-PVC was particularly  
431 suitable for the removal efficiencies of Cu(II) and Cr(VI) at low concentrations (20 mg/L)  
432 ( $99.6 \pm 0.1\%$  and  $94.3 \pm 2.5\%$ , respectively) (Fig. 8). Further, the removal efficiencies of Cu(II)  
433 and Cr(VI) using HS-PVC from waste pipes increased by 13.7% and 43.9% (Fig. 8), which  
434 were higher than those of HS-PVC derived from PVC powder (Fig. 1). The better performance  
435 of HS-PVC (pipes) might be attributed to plasticizers and mineral fillers in the PVC (Correa et  
436 al., 2019). The removal efficiencies of other metals such as Mn(II), Cd(II), Ni(II), and Co(II)  
437 amounted to  $81.2 \pm 2.3\%$ ,  $80.8 \pm 1.7\%$ ,  $70.8 \pm 1.8\%$ , and  $70.1 \pm 3.2\%$  (Fig. S9), respectively,  
438 indicating that HS-PVC is suitable for the treatment of complex industrial wastewater.  
439 Moreover, the adsorption of Cu(II) and Cr(VI) decreased only by 10.0% and 31.0% (Fig. S10)

440 after three adsorption-desorption cycles (1 mol/L HCl as eluent), indicating excellent  
441 recyclability.

442 Previous studies commonly focused on the conversion of waste PVC into  
443 coal-alternative fuel (Lu et al., 2020) or lighter oil (Maity et al., 2020). Using HT and  
444 sulfonation modifications, the present study provided a novel strategy for resource recovery  
445 of PVC waste by producing efficient adsorbents for Cu(II) cations and Cr(VI) anions removal.  
446 The sulfonation intensity was mild in this study (98% sulfuric acid at 70°C). Fuming H<sub>2</sub>SO<sub>4</sub>,  
447 ClSO<sub>3</sub>H, aryldiazonium sulfonates, and higher temperatures (80–150°C) could be considered  
448 for additional optimization. In addition, as it is a “sulfonated carbon” (Konwar et al., 2019),  
449 HS-PVC may show promising catalytic performances in various organic transformations,  
450 including esterifications, ester exchange (transesterifications), acetalization, etherifications,  
451 condensation, and multi-component organic reactions that should be studied in the future.

#### 452 **4. Conclusion**

453 This study provided a novel method to fabricate efficient adsorbent (HS-PVC) from  
454 waste PVC for both Cu(II) cations and Cr(VI) anions removal. The removal efficiencies of  
455 Cu(II) and Cr(VI) using HS-PVC reached  $81.2 \pm 1.6\%$  and  $60.3 \pm 3.8\%$ , respectively. The first  
456 stage of HT was crucial for the dichlorination of PVC and the formation of an aromatic  
457 structure, guaranteeing the introduction of -SO<sub>3</sub>H onto PVC-derived hydrochar through  
458 subsequent sulfonation. In addition, sulfonation also significantly increased the hydrophilicity  
459 of HS-PVC. The adsorption of Cu(II) was sensitive to HT temperature, while that of Cr(VI)  
460 was more sensitive to HT time. Adsorption isotherm data were accurately fitted by the

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

469

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649 **Table 1**

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

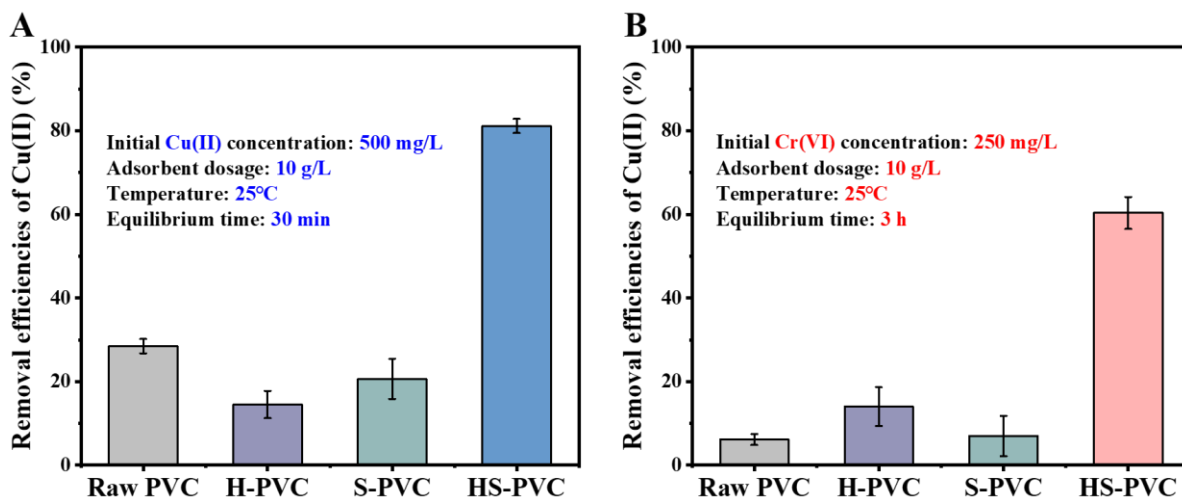
Metals	$q_{\text{exp}}$ (mg/g)	PFO			PSO		
		$q_1$ (mg/g)	$R_1^2$	$k_1$ (min <sup>-1</sup> )	$q_2$ (mg/g)	$R_2^2$	$k_2$ (g/(mg·min))
Cu(II)	40.34	38.18	0.86	17.92	40.24	0.95	0.70
Cr(VI)	17.75	15.41	0.88	2.39	16.23	0.94	0.25

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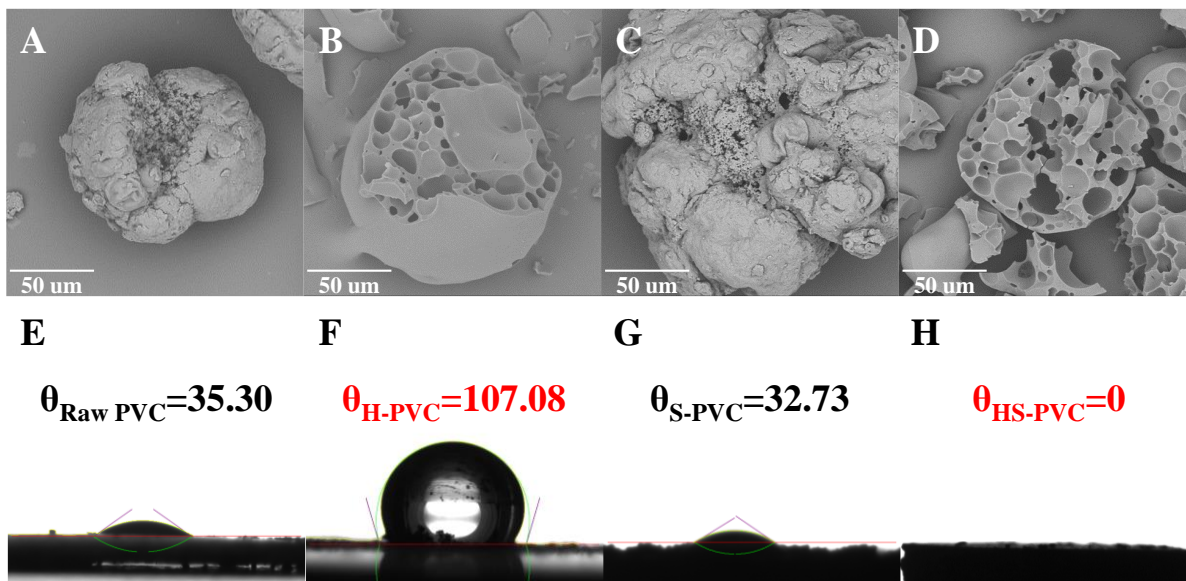


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656 Fig. 1. Cu(II) and Cr(VI) removal efficiencies using Raw PVC, H-PVC, S-PVC, and

657 HS-PVC after adsorption for 12 hours.

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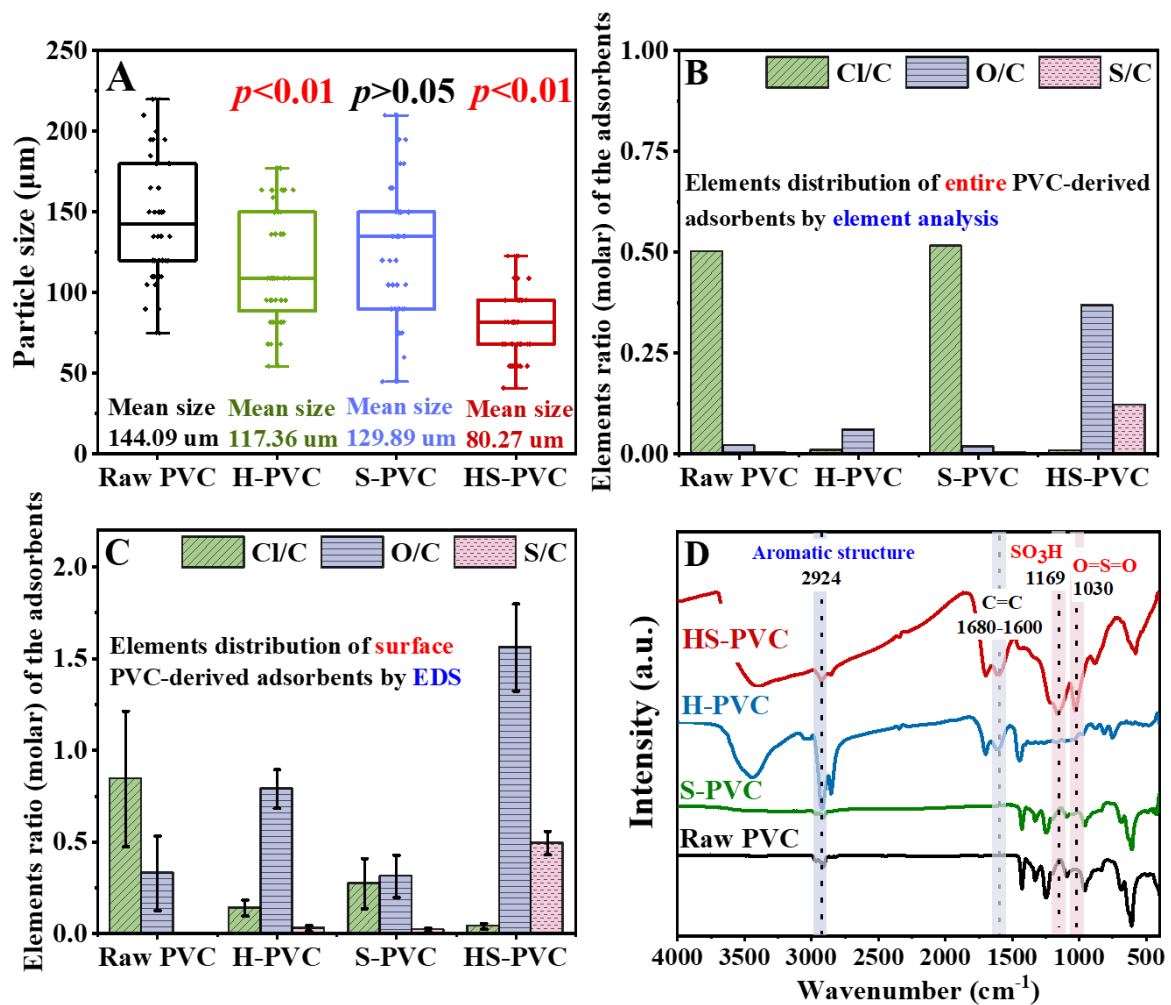
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660 Fig. 2. Surface properties of PVC derived adsorbents: SEM images of Raw PVC (A), H-PVC

661 (B), S-PVC (C), and HS-PVC (D); contact angle ( $\theta$ ) of Raw PVC (E), H-PVC (F), S-PVC

662 (G), and HS-PVC (I).

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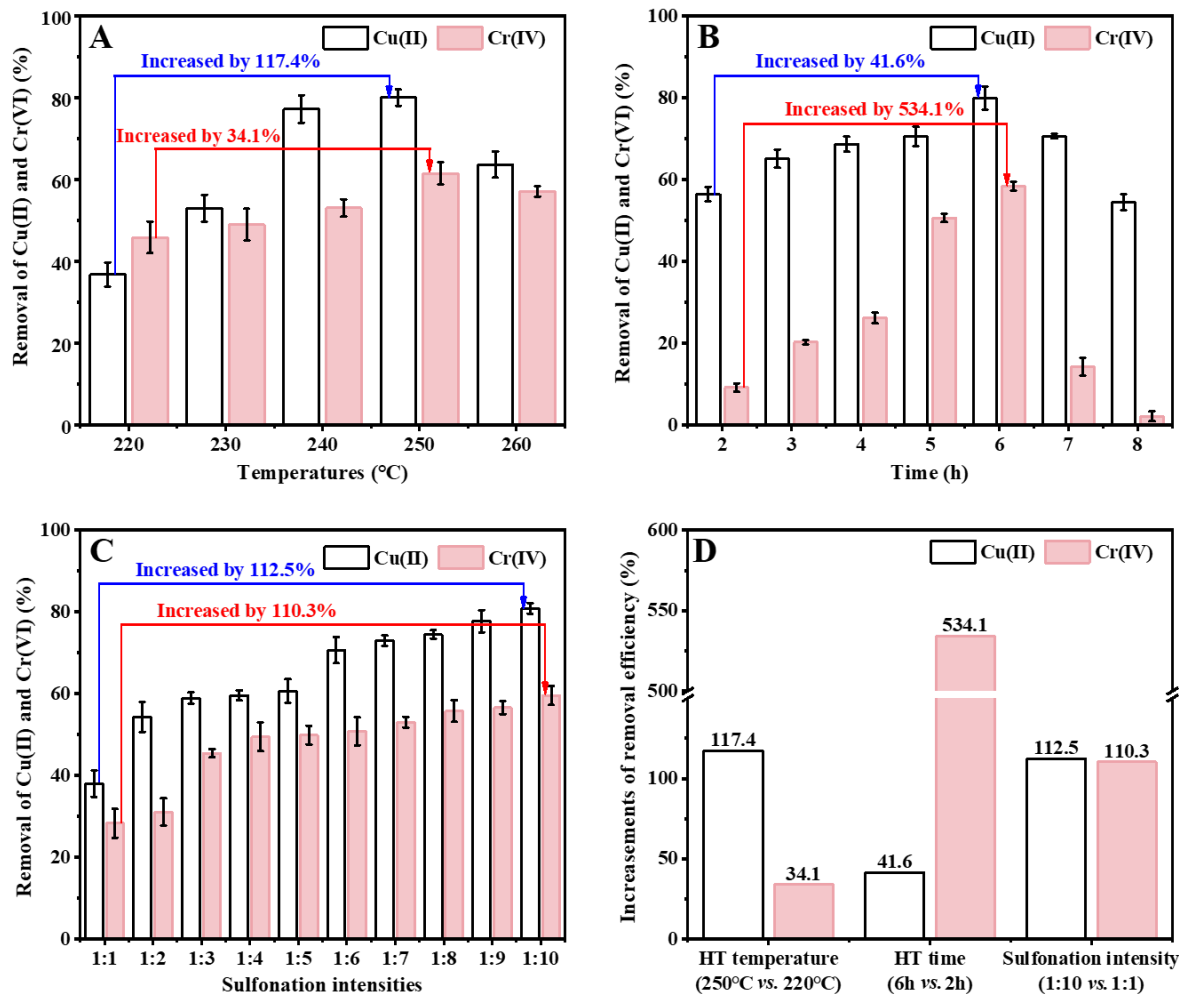


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665 Fig. 3. Characterization of Raw PVC, H-PVC, S-PVC, and HS-PVC: particle size distribution

666 (A), elemental analysis (B), EDS element mapping (C), and FTIR spectra (D).

667



668

669 Fig. 4. Effects of HS-PVC preparation intensities on Cu(II) and Cr(VI) removal: HT

670 temperature (A), HT time (B), sulfonation intensity (C), and comparison of Cu(II) and Cr(VI)

671 removal efficiencies between the optimal and the lowest efficiency (D) (HT temperature: 250 °C

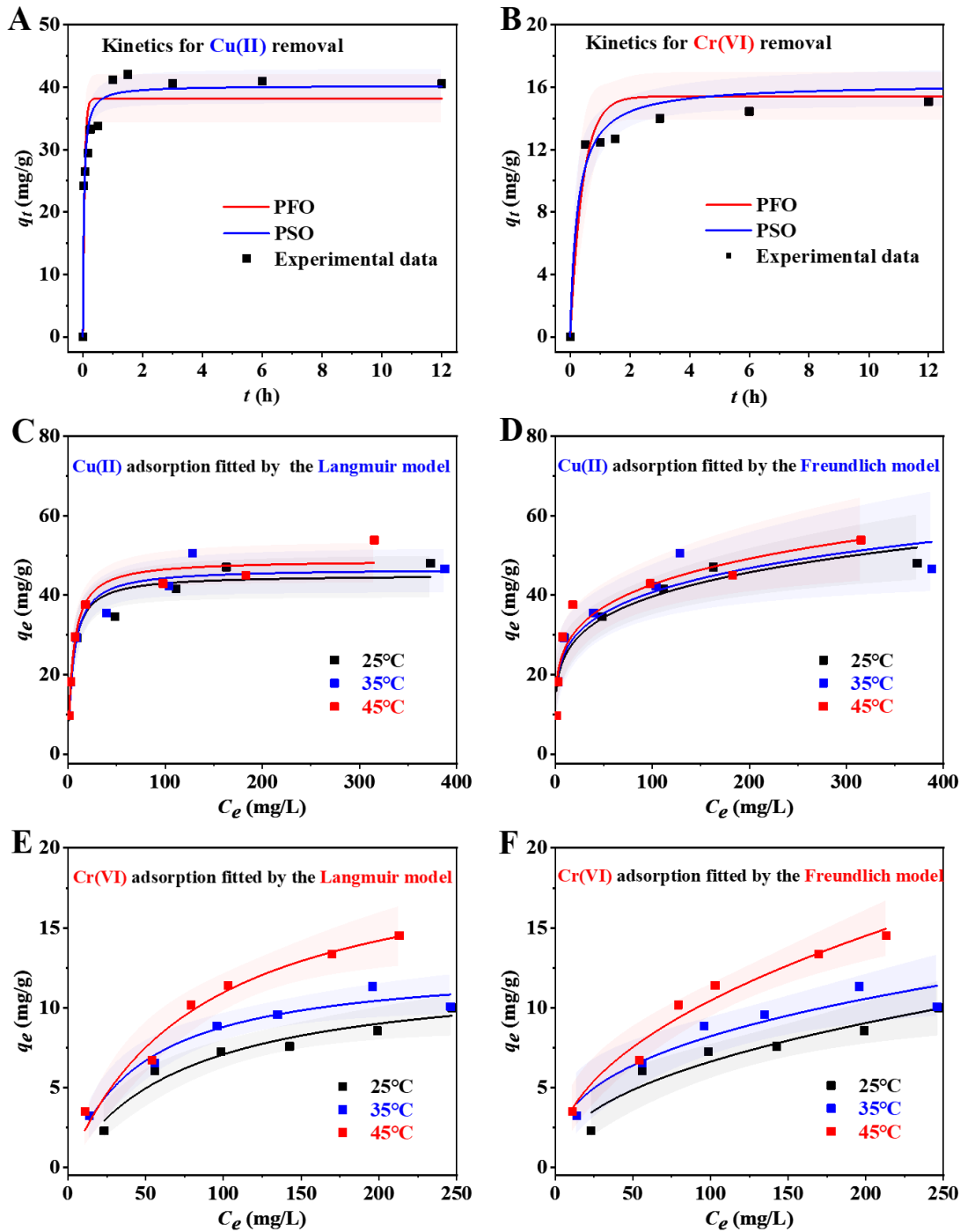
672 vs. 220 °C, HT time: 6 h vs. 2 h, and sulfonation intensity: 1:10 vs. 1:1). The initial

673 concentrations of Cu(II) and Cr(VI) were 500 and 250 mg/L. The adsorbent dose was 10 g/L

674 and the temperature 25 °C.

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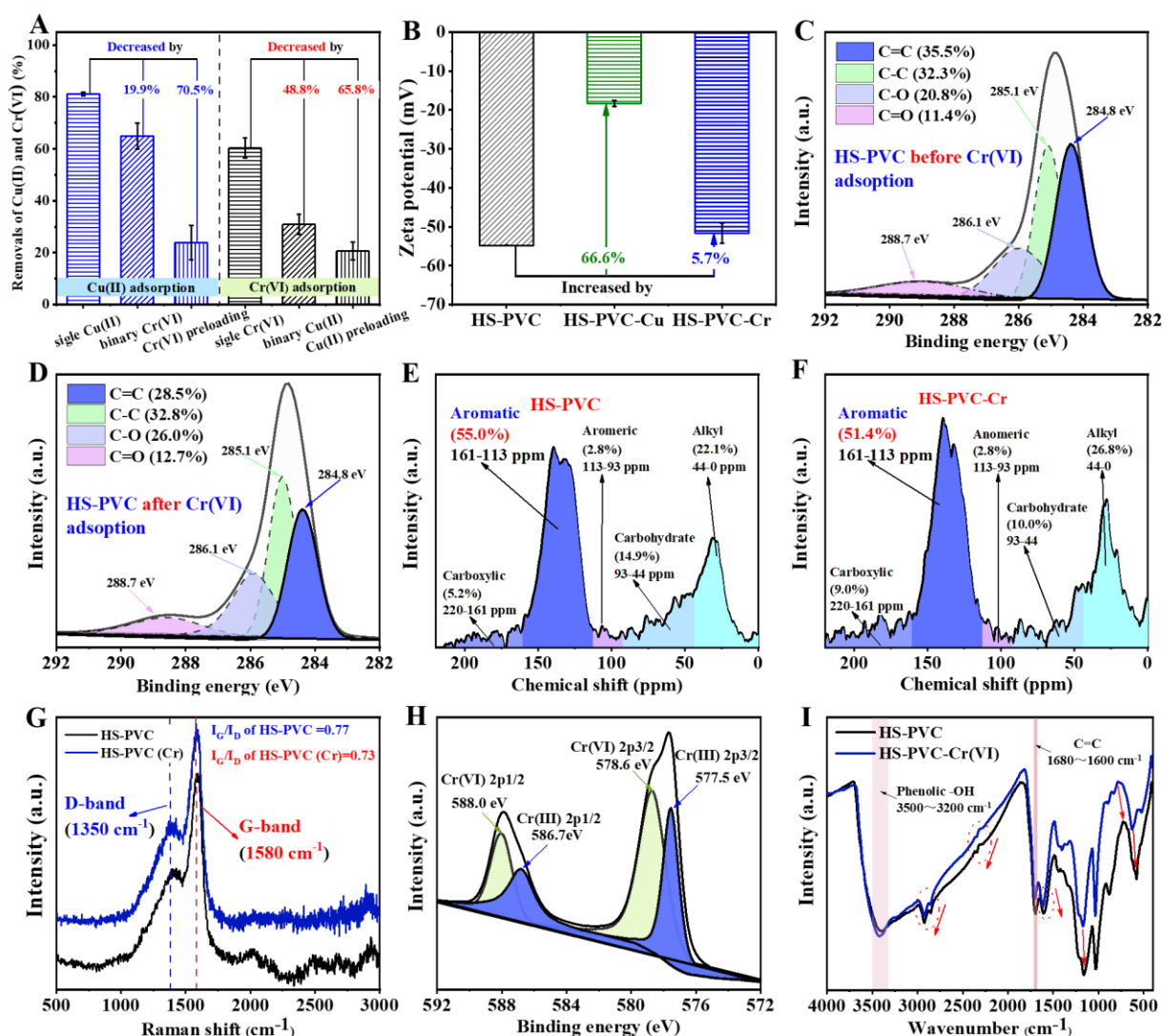
677 Fig. 5. Adsorption kinetics of Cu(II) (A) and Cr(VI) (B) onto HS-PVC. Equilibrium

678 isotherms of Cu(II) fitted by the Langmuir (C) and Freundlich models (D) at different

679 temperatures (25, 35, and 45 °C). Equilibrium isotherms of Cr(VI) fitted by the Langmuir (E)

680 and Freundlich models (F) at different temperatures (25, 35, and 45 °C). The colored area

681 covers the 95% confidence intervals.



682

683 Fig. 6. Mechanisms for the adsorptions of Cu(II) and Cr(VI) by HS-PVC. Competitive

684 adsorption between Cu(II) and Cr(VI) by HS-PVC (A). Zeta potential of HS-PVC, HS-PVC

685 after the adsorption of Cu(II) (HS-PVC-Cu), and HS-PVC after the adsorption of Cr(VI)

686 (HS-PVC-Cr) (B). C 1s XPS spectra of HS-PVC before the adsorption of Cr(VI) (C) and

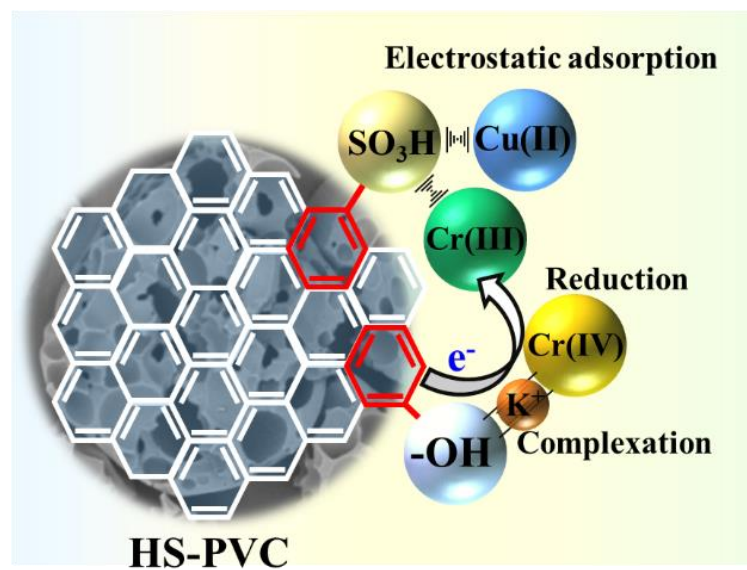
687 after the adsorption of Cr(VI) (D). Solid-state <sup>13</sup>C NMR of HS-PVC before the adsorption of

688 Cr(VI) (E) and after the adsorption of Cr(VI) (F). Raman spectra of HS-PVC before and after

689 adsorption of Cr(VI) (a higher  $I_G/I_D$  ratio indicates a higher degree of graphitization) (G). Cr

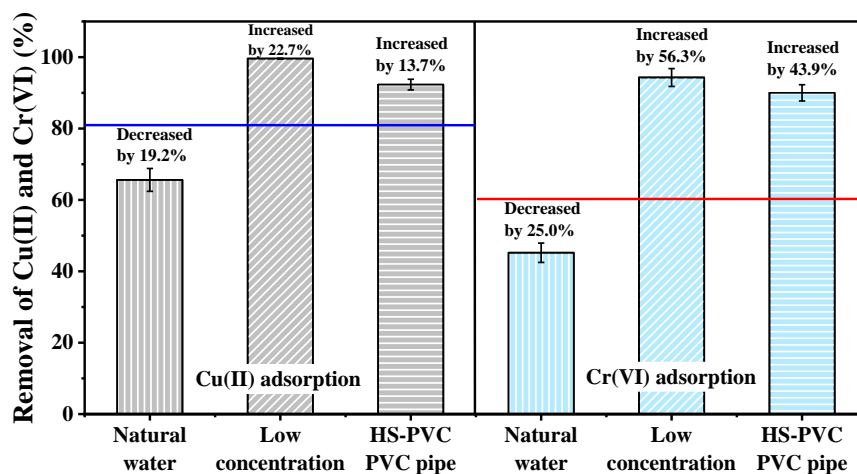
690 2p XPS spectra of HS-PVC after the adsorption of Cr(VI) (H). FTIR spectra of HS-PVC

691 before and after the adsorption of Cr(VI) (I).



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



695

696 Fig. 8. Versatility of HS-PVC for Cu(II) and Cr(VI) removal efficiencies. Removal of

697 Cu(II) and Cr(VI) by HS-PVC from natural water, at low concentration (20 mg/L), and by

698 HS-PVC derived from waste PVC pipes (blue and red lines represent the removal efficiency

699 of Cu(II) and Cr(VI) by PVC powder in Fig. 1).

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