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Polyethyleneimine/activated carbon paper-based material for low-concentration hexavalent chromium removal

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Abstract In this study, softwood pulp, activated carbon powder, and polyester fiber were prepared into activated carbon paper-based materials (ACPBM) by papermaking. Then the polyethyleneimine (PEI) is loaded on the activated carbon paper-based material by dipping to prepare a high-performance, green PEI/activated carbon composite paper-based adsorbent material (PPCA) to remove low concentrations of Cr(VI) in water. The surface characteristics of the ACPBM and PPCA were analyzed by SEM, EDX, BET, and FT-IR, which showed that PEI had been successfully loaded on the surface of ACPBM. It was found that when the impregnated PEI concentration is 1%, the adsorbent dosage is 3 g·L⁻¹, the contact time is 180 min, the concentration of initial Cr(VI) is 5 mg·L⁻¹, and the pH is 2, the maximum adsorption capacity for Cr(VI) can reach 1.58 mg·g⁻¹. The process of PPCA adsorption of Cr(VI) conformed to the Freundlich isotherm model and the quasi-second-order kinetic model, indicating that the adsorption is multi-molecular layer adsorption with the adsorption mechanism of ion exchange and electrostatic attraction. In adsorption thermodynamics, $\Delta H_0 > 0$, $\Delta G_0 < 0$, and $\Delta S_0 > 0$, indicating that the

process of adsorbing Cr(VI) by the 1%PPCA is an endothermic entropy increase reaction that can proceed spontaneously. This study shows that a green, recyclable, and degradable high-performance PPCA adsorbent has been prepared through traditional papermaking processes and physical impregnation methods, which has a significant removal effect on low-concentration hexavalent chromium ions and can be industrialized.

Keywords Activated carbon paper-based material; Polyethyleneimine; Adsorption; low-concentration hexavalent chromium

1. Introduction

It is a global issue that the drinking water's security and no polluted drinking water is becoming a scarce resource (Liu et al.2021). In recent years, fast development continually along with industrialization and urbanization, industries the electronics industry, electroplating, petrochemical industry, leather tanning, and papermaking have brought benefits while also leaving pollution, especially chromium slag pollution (Ellis et al.2002; Koby et al.2004). These chromium slags are not equipped with anti-seepage measures. Under the scouring of rainwater, they may seep into the ground, causing certain pollution to underground drinking water and threatening human health (Fu et al.2011). Chromium presences in two forms in water systems; one is Cr(III), the other is Cr(VI) (Guan et al.2019). Cr(III) is one of the essential elements in animals (Huang et al. 2019). However, Cr(VI) is a very toxic substance, it is easily absorbed by the skin, causing cancer in human cells (Zhang et al. 2010; Lai et al. 2008). It has been considered as one of the heavy metals to be removed preferentially. Therefore, it is urgent to develop an efficient and environmentally friendly way to remove Cr (VI) in water (Chowdhury et al. 2016; Azimi et al. 2017).

The current methods for removing Cr(VI) in water commonly include membrane separation (Kozłowski et al. 2002), photocatalysis (Xu et al. 2019), ion exchange (Rengaraj et al. 2001), electrodialysis (Jin et al. 2016), and adsorption (Zhang et al. 2019; Sun et al. 2010) etc. The adsorption method is often used to remove Cr(VI) in water due to its flexible utilization, and easy availability. (Pang et al. 2011; Jin et al. 2017). There are a variety of adsorbents, including barks (Sudaryanto et al. 2021), chitosan (Zhang et al. 2021), nano-crystalline-cellulose (Tasrin et al. 2020), mesoporous silica (Li et al. 2021), activated carbon (Mojdeh et al. 2010), and synthetic hydrogel (Zhao et al. 2021), etc.

Activated carbon is widely used because relatively large specific surface area and rich pore distribution (Sun et al. 2013). Activated carbon can be divided into fibrous, granular, and powder form according to the appearance and shape. Among them, activated carbon powder has the best adsorption effect (Choi et al. 2008). When activated carbon powder is put into sewage alone, some may be dissolved in the water, causing secondary pollution and increasing energy consumption for treatment. In the household water purifier, the activated carbon powder is compressed into a cake shape, which reduces the loss of the activated carbon powder. However, the operation method of this method is relatively cumbersome, and it cannot be recovered. For further improvement, activated carbon powder can be combined with other substrates to construct activated carbon-based bulk materials. This method not only solves the problem of the loss of activated carbon powder but also the method is simple in process, the adsorbent is easy to recover.

Polyethyleneimine (PEI) is a high molecular polymer with abundant amino and imino groups, which can chelate with heavy metals (Ma et al. 2014). However, PEI directly applied as an adsorbent shows the disadvantages of easy loss. PEI needs to be fixed to another matrix to remove heavy metals. Common fixation methods include physical impregnation and chemical grafting or cross-linking (Xing et al. 2021). Mojdeh Owlad (Mojdeh et al. 2010) immersed activated carbon in PEI water solution to prepare an adsorbent to remove Cr(VI). When the initial concentration of hexavalent chromium ions is $10 \text{ mg}\cdot\text{L}^{-1}$, its adsorption capacities reach $22 \text{ mg}\cdot\text{g}^{-1}$ with a maximum removal rate of 80%, and the remaining hexavalent chromium concentration is $2 \text{ mg}\cdot\text{L}^{-1}$. To further improve the loading rate of PEI, Pan (Pan et al. 2018) used glutaraldehyde as cross-linking agent to combine PEI with activated carbon by crosslinking method and explored the material's capacity to adsorb Cr(VI) in wastewater. We can find that when the initial concentration of Cr(VI) is $350 \text{ mg}\cdot\text{L}^{-1}$, the removal rate is up to 98%, and the adsorption capacity is up to $500 \text{ mg}\cdot\text{g}^{-1}$. The concentration of remaining hexavalent chromium ion is $7 \text{ mg}\cdot\text{L}^{-1}$. Even though they have a certain adsorption effect on Cr(VI), the remaining hexavalent chromium does not meet the industry's highest emission standard ($\leq 0.5 \text{ mg}\cdot\text{L}^{-1}$) and the highest chromium content standard in drinking water ($< 0.05 \text{ mg}\cdot\text{L}^{-1}$). Moreover, the cross-linking agent is commonly toxic and harms the human body.

In this paper, we use the traditional papermaking method to prepare an activated carbon paper-based matrix material made of activated carbon powder, softwood pulp, and polyester fiber, which improved the utilization value of activated carbon powder. In addition, a non-toxic adhesive of polyvinyl alcohol

(PVA) was used to realize the facile fixing of PEI to the matrix by a straightforward way of dip-coating. The influence of pH, PEI concentration, Contact time, temperature, adsorbent dosage, and Cr(VI) initial concentration on the Cr(VI) adsorption capacity in water were extensively explored, and the adsorption mechanism of adsorbent for hexavalent chromium was further discussed.

2. Experimental section

2.1 Materials

Softwood pulp was purchased from Dalian Yangrun Trading Co., Ltd. (Dalian, Liaoning). The polyester fiber was provided by Weifang Long Fiber Co., Ltd. (Weifang, Shandong). Cationic polyacrylamide (CPAM) was purchased from Puyi Environmental Protection Technology Co., Ltd (Shanghai, China). Activated carbon (20 mesh), purchased from Luzhi, Pingdingshan City Original Activated Carbon Co., Ltd. (Pingdingshan, Henan). Potassium dichromate, diphenylcarbazide, polyethyleneimine, acetone, sulfuric acid, and polyvinyl alcohol used in the experiment were all analytically pure and they were Provided by Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China).

2.2 Preparation of activated carbon paper-based materials

First, weigh a certain amount of softwood pulp, polyester fiber, and activated carbon powder(The oven-dry basis ratio is 42:10:48, The basis weight is 240 g·m⁻²) into a decomposing tank, decompress 2000 r to prepare an even suspension. Secondly, add diluted CPAM and PAE (The additive amount of CPAM is 0.08%, PAE is 0.8%) to dissolve 2000 r. The decomposed mixed raw materials are converted into wet paper using a paper sheet former. The wet paper is placed in a blast drying oven (temperature controlled at 115 °C) for 20 min to make activated carbon paper-based materials (ACPBM).

2.3 Preparation of PEI/PVA solution

First, 20 g of PVA was added into a beaker with 250 mL of deionized water and mechanically stirred for 1 h at 60 °C, followed by raising the temperature to 90 °C and continue stirring for another 2 h to prepare 8 wt.% PVA solution. Secondly, use deionized water to dilute 50% PEI solution to 0.5%, 1%, 2%, and 5% for use. Finally, the desired amount of PVA and PEI solutions (a mass ratio of 4:1) were mixed and magnetically stirred in a water bath for 30 min at 30 °C to prepare PEI/PVA solutions with different concentrations.

2.4 Preparation of PEI/PVA composite activated carbon paper-based material

A desired amount of ACPBM was immersed in PEI/PVA mixture solutions with different

concentrations for 2 min, taken out, followed by drying in a 70 °C blast drying oven for 1 h. The PEI/activated carbon paper-based composite materials (PPCA) were prepared. PPCA impregnated with different concentrations of PEI are named 0.5%PPCA, 1%PPCA, 2%PPCA, and 5%PPCA.

2.5 Characterization of adsorbent

The surface morphology and size of ACPBM, 1%PPCA before and after the adsorption of Cr(VI) were characterized using scanning electron microscopy (SEM). Energy-dispersive X-ray spectroscopy (EDX) elemental maps were obtained during SEM testing. The surface functional groups of PPCA at different impregnation concentrations were analyzed using an FT-IR spectrometer (FTS-3000) at 600-4000 cm⁻¹. The pore size distribution and specific surface area of the sample are evaluated using the N₂ adsorption and desorption isotherm obtained by BET at 77k.

2.6 Adsorption experiments

Weigh 0.1414 g of potassium dichromate baked to a constant weight at 105-110°C and dissolve it with 500 mL of pure water to prepare a Cr(VI) stock solution with 100 mg·L⁻¹, which was diluted to a series of concentrations as needed. A Cr(VI) solution with a certain concentration was put into 50 mL colorimetric tubes with stoppers and diluted to the mark by adding deionized water. Subsequently, 2.5 mL of 10 wt.% sulfuric acid solution and 2.5 mL of 2.5 g·L⁻¹ diphenylcarbazide solution were added immediately. After standing for 10 min, put it in a 1cm colorimetric tube and measure the absorbance with a dark box three-purpose ultraviolet spectrophotometer at a wavelength of 540 nm. The standard curve of Cr(VI) is shown in Figure.1.

Fig.1 Standard curve diagram of Cr⁶⁺

First, accurately measure 100 mL of a certain concentration of Cr(VI) aqueous solution into a 250

mL conical flask, then add a certain quality of ACPBM and PPCA, which was placed in a shaker with a pre-set temperature, and magnetically stirred at 170 rpm for various time duration. Subsequently, after taking it out, filter the solution with a 0.45 μm filter membrane, The absorbance was measured by the above method, and the concentration of Cr(VI) is obtained according to Figure 1.

The experiment separately explored the influence of concentrations of PEI/PVA solution (0.5, 1, 2, 3, and 5%), pH (2, 4, 6, 8, and 10), and adsorbent dosage (1, 3, and 5 $\text{g}\cdot\text{L}^{-1}$) on the Cr(VI) adsorption performance. To study the adsorption mechanism of 1% PPCA, we conducted an experimental investigation on its adsorption kinetics. Briefly, 0.3 g of 1%PPCA was added in a solution of 100 mL, pH of 2, hexavalent chromium concentration of 5 $\text{mg}\cdot\text{L}^{-1}$, and a temperature of 303 K for different absorption time (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, and 6 h). In addition, in the adsorption thermodynamic experiment, other conditions remain unchanged, and the adsorption was carried out at 293, 303, and 313 K for 3 h. The adsorption isotherm experiment was carried out by changing the initial concentrations of Cr(VI) solution (1, 5, and 15 $\text{mg}\cdot\text{L}^{-1}$) and keeping the temperature at 303 K to adsorb for 3 h. Based on the obtained adsorption data, thermodynamic parameters (ΔG_0 , ΔH_0 , and ΔS_0) were determined.

3. Results and discussion

3.1 Characterization

The surface morphology of ACPBM and 1% PPCA were observed by SEM. It can be seen from Figure 2a that softwood pulp fiber is the main component of ACPBM. Because the surface of polyester fiber is relatively smooth, it has a poor binding force with plant fibers. Therefore, the polyester fiber is arranged alternately with softwood pulp fiber in a network form. Activated carbon powder adheres to the surface of the fiber. From figure 3b, it can be seen that there is a glue-like substance between the fiber and the fiber, which makes the pore size of the material smaller, indicating that the PEI has been successfully loaded on ACPAM. Figure 2c is the SEM image of 1% PPCA after Cr(VI) adsorption. From Figure 2c, it can be seen that softwood pulp fibers swell due to water immersion, while polyester fibers are not affected. We also performed EDX analysis on the adsorbed material, we found that besides C, N, and O elements, there is also the presence of Cr element in the material, which also fully shows that the 1%PPCA has an adsorption effect on Cr(VI).

From Figure 3a, we can get that the nitrogen adsorption capacity of the adsorbent increases with the increase of relative pressure. According to the classification of isotherms, it belongs to category VI

isotherms. In the lower P/P_0 zone, the capillary condensation of nitrogen occurs and agglomerates in the micropores on the inner surface area, which increases the adsorption capacity, the isotherm rises rapidly, and the curve is convex. With the increase of P/P_0 , when all pores have capillary aggregation, adsorption only occurs on the outer surface, much smaller than the inner surface, and the adsorption amount rises slowly. When the relative pressure is close to 1, nitrogen is adsorbed on the macropores, and the curve rises. In the range of P/P_0 of 0.43-1.0, the isotherm shows an obvious hysteresis loop. According to the classification of IUPAC, it belongs to the category VI mesoporous hysteresis ring, which shows that ACPBM is mainly composed of mesopores and micropores, and the pore structure is irregular. As shown in Figure 3a, it was found that as the concentration of impregnated PEI/PVA becomes larger, the adsorption capacity becomes smaller, which implies that PEI/PVA may adhere to the pores of activated carbon, resulting in a decrease in the specific surface area (Table 1) of the material and a decrease in the adsorption sites provided for nitrogen. The adsorption amount becomes smaller. It can be seen from the figure that the pores of ACPBM are mainly distributed between 2-16nm, and the pores of 1%PPCA and 2%PPCA are mainly distributed between 2-10nm. This is mainly because the addition of PEI blocks the macropores.

The surface chemical structure of adsorbent impregnated with different concentrations of PEI/PVA solution was analyzed by infrared spectroscopy, as presented in Figure 4. The samples all showed typical characteristic absorption peaks of cellulose, such as -OH stretching vibration (3270 cm^{-1}), CH_2 -stretching vibration (2880 cm^{-1}), C-H bending vibration (1558 cm^{-1}), and C-O-C stretching vibration (1057 cm^{-1}) (Shao et al.2021). The characteristic absorption peaks at 1705 cm^{-1} are the C=O stretching vibrations in the polyester fiber, respectively (Ricardo et al , 2015). From figure 4, we can also get that as the concentration of the coated PEI increases, there is an obvious small peak near 1650 cm^{-1} , which is the result of the N-H bending vibration of PEI. In addition, PEI should have N-H stretching vibration peaks and C-N stretching vibration peaks at 3270 cm^{-1} and 1045 cm^{-1} (Hong et al, 2021). However, we found that ACPBM, 0.5%PPCA, 1%PPCA, and 2%PPCA all have characteristic peaks at these two wavelengths. The N-H and the C-N stretching vibration peak in the PEI are covered by the O-H and the C-O-C stretching vibration peak in the cellulose, respectively. The above analysis shows that PEI has been successfully loaded onto the ACPBM.

Fig.2 SEM image of ACPBM (a) and 1% PPCA (b); SEM image of 1% PPCA after adsorption of Cr (VI) (c); EDX elemental mapping images of the 1% PPCA after adsorption of Cr (VI) (d, e, f, and g)

Fig.3 N₂ adsorption-desorption isotherms (a) and pore size distribution (b) of ACPBM, 1% PPCA and 2% PPCA

Table 1 Pore structure characteristics of ACPBM, 1%PPCA 和 2%PPCA

Specific surface area(m ² ·g ⁻¹)	Total pore volume(cm ³ ·g ⁻¹)
---	--

ACPBM	521.86	0.4088
1%PPCA	454.25	0.3322
2%PPCA	424.61	0.3103

Fig.4 FTIR spectra of ACPBM,0.5%PPCA,1%PPCA and 2%PPCA (a); zeta-potential of 1%PPCA with various pH in deionized water (b)

3.2 Effects of PEI&PVA solution concentration

Fig.5 The effect of PEI concentration (a), pH (b), dosage (c) and Cr(VI) initial concentration(d) on the Cr (VI) adsorption capacity and removal rate

Figure 5a shows the effect of PPCA impregnated with different concentrations of PEI&PVA on the removal rate and adsorption amount of Cr(VI). From figure 5a, we can get that the removal rate is 90.15%, and the adsorption amount of Cr(VI) by ACPBM is $1.50 \text{ mg} \cdot \text{g}^{-1}$. The adsorption capacity and removal rate of the adsorbent for Cr(VI) increase with the impregnated PEI/PVA concentration. When the impregnated PEI/PVA concentration is 1%, the adsorption amount and removal rate of adsorbent to Cr(VI) reaches the maximum value of $1.58 \text{ mg} \cdot \text{g}^{-1}$ and 94.88%, respectively. This is mainly because not only the activated carbon has an adsorption effect on Cr(VI), but also the amino groups in PEI can remove Cr(VI) through chelation. As the concentration of impregnation increases, the amino groups in the adsorbent increase so that the ability to remove Cr(VI) becomes stronger. The concentration of impregnation continues to increase, and the adsorption effect of adsorbent on Cr(VI) decreases. This is mainly because a large amount of PEI adheres to the surface of the activated carbon, resulting in a decrease in the specific surface area (Table 1) of the activated carbon and a decrease in the adsorption sites provided for Cr(VI), giving rise to the decreasing of the adsorption performance of Cr(VI).

3.3 Effects of initial PH

Cr(VI) mainly exists in three forms: $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , and HCrO_4^- in solution, and the mutual conversion between them is affected by pH (Pan et al. 2018). Under acidic conditions, Cr(VI) in the solution mainly exists in the form of $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- . With the increase of pH, the content of hydrogen ions decreases, and the conversion proceeds in the direction of generating HCrO_4^- . Under alkaline conditions or neutral conditions, Hexavalent chromium ions mainly exists in CrO_4^{2-} (Sun et al. 2013; MA et al. 2014).

PEI is a polymer with a high cationic charge, and the protonation of surface amino groups is the main factor that affects the density of PEI cationic charge. The stronger the protonation ability of the amino groups on the PEI surface, the greater the cationic charge density on the surface. It has a strong adsorption effect on the anions existing in the solution.

From figure 5b, we can find that when $\text{pH}=2$, the removal rate reaches the maximum value of 95%. As the pH value increases, the removal rate gradually decreases. This is mainly because, in the acidic solution of $\text{pH}=2$, there is more hydrogen ion content in the solution, making the amino groups in PEI easier to protonate. Thereby, HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ existing in the form of anions in the solution can be

better electrostatically absorbed. With the pH increases, the content of hydrogen ions in the solution decreases, which weakens the protonation ability of the amino groups in PEI, and reduces the electrostatic adsorption performance of the 1%PPCA to hexavalent chromium ions. From the results of Zeta potential (Fig. 4b), we can find that the high adsorption efficiency under low pH conditions is due to a strong electrostatic attraction between the positively charged nitrogen (N^+) and the Cr(VI) existing in the form of anions. When pH=2, 1%PPCA has the best adsorption performance for Cr(VI), so a pH 2 is selected for the following experiments.

3.4 Effects of dosage

From figure 5c, we know that when the dosage of 1%PPCA increased from $1\text{ g}\cdot\text{L}^{-1}$ to $3\text{ g}\cdot\text{L}^{-1}$, the removal rate of Cr(VI) increased significantly, from 44.44% to 94.45%. The main reason is that in the initial stage of the adsorption, 1%PPCA is small, and the adsorption sites provided are few. With the increase in the amount of 1% PPCA, the adsorption sites of chromium ions increase, which significantly improves the adsorption effect. Continue to increase the amount of input, and the Cr(VI) removal rate will remain balanced. This is mainly because the adsorption of hexavalent chromium ions in water by 1% PPCA has reached adsorption equilibrium. Even if the dosage is increased, the removal rate of Cr(VI) will not be significantly improved.

3.5 Effects of time and temperature

From figure 6a, we can get that as the adsorption contact time increases, the adsorption capacity also increases. When the contact time is 180 min, the adsorption capacity reaches the maximum value of $1.58\text{ mg}\cdot\text{g}^{-1}$. This is mainly because the 1%PPCA did not reach the adsorption equilibrium in the initial adsorption stage. As the contact time increases, the adsorbent can continue to adsorb Cr(VI). When the contact time further increases from 180 min to 360 min, the adsorption capacity is unchanged, which indicates that the adsorption has reached the adsorption equilibrium.

From figure 6a, we also can get that the amount of adsorption increases with the increase of temperature, which shows that temperature rise is conducive to the adsorption of Cr(VI) in water. When the temperature increased from $20\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$, the adsorption capacity increases significantly from $1.37\text{ mg}\cdot\text{g}^{-1}$ to $1.53\text{ mg}\cdot\text{g}^{-1}$. When further increases the temperature from $30\text{ }^{\circ}\text{C}$ to $40\text{ }^{\circ}\text{C}$, the adsorption capacity increases slowly. Thus, the temperature of $30\text{ }^{\circ}\text{C}$ is the optimal adsorption condition.

3.6 Adsorption kinetics

Adsorption kinetics is mainly used to describe the adsorption rate of the adsorbent. There are three adsorption kinetic models, namely the quasi-first-order, the quasi-second-order adsorption kinetic equation, and the intra-particle diffusion model (Xiao et al. 2017). Fitting the adsorption data with these three equations can explore the adsorption mechanism of the adsorbent.

The quasi-first-order adsorption kinetic equation is the proportional relationship between the reaction adsorption rate and the concentration of reactants, and its linear expression (Indra et al. 2005) is:

$$\log(Q_e - Q_t) = -k_1 t + \log Q_e \quad (1)$$

Where Q_e is the equilibrium adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$), Q_t is the adsorption capacity at time t ($\text{mg} \cdot \text{g}^{-1}$), and k_1 is the reaction rate constant of the quasi-first order adsorption kinetic equation.

The quasi-second-order kinetic equation assumes that the adsorbent and the adsorbate undergo a chemical reaction, and the adsorption rate is affected by the chemical adsorption mechanism. This process involves the gains and losses of electrons or the sharing of electrons. Its linear expression (Indra et al. 2005) is:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e} \quad (2)$$

Where k_2 is the adsorption rate constant of the quasi-second-order kinetic equation, $h = k_2 Q_e$ is the initial adsorption rate constant ($\text{mg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$)

The intra-particle diffusion model is mainly used to describe the process of adsorbent diffusion to the surface of the adsorbent through macropores or micropores. Its linear expression (Indra et al. 2005) is:

$$Q_t = k_3 t^{\frac{1}{2}} + Q_e \quad (3)$$

Where k_3 is the diffusion rate constant within the particle ($\text{mg} \cdot \text{g}^{-1} \cdot \text{h}^{-0.5}$), the larger the value, the easier the adsorbate diffuses inside the adsorbent.

Table 2 Adsorption kinetics and intra-particle diffusion model parameters for the adsorption of Cr(VI) by 1%PPCA

$Q_{e,\text{exp}}$ ($\text{mg} \cdot \text{g}^{-1}$)	Quasi-first-order adsorption kinetic equation			Quasi-second-order adsorption kinetic equation		
	$Q_e(\text{mg} \cdot \text{g}^{-1})$	$K_1(\text{h}^{-1})$	R^2	$Q_e(\text{mg} \cdot \text{g}^{-1})$	$K_2(\text{g} \cdot \text{mg}^{-1} \cdot \text{h}^{-1})$	R^2
1.58512	1.14285	0.65112	0.94274	1.74182	1.24651	0.99485

Intra-particle diffusion model (the first stage)			Intra-particle diffusion model (the second stage)		
$Q_1(\text{mg}\cdot\text{g}^{-1})$	$K_3(\text{mg}\cdot\text{g}^{-1}\cdot\text{h}^{-0.5})$	R^2	$Q_1(\text{mg}\cdot\text{g}^{-1})$	$K_3(\text{mg}\cdot\text{g}^{-1}\cdot\text{h}^{-0.5})$	R^2
0.19407	0.87659	0.99645	1.57232	0.00525	0.99096

According to the data in figure 6 (b,c) and table 2, we can get the R^2 of the quasi-first-order adsorption kinetic equation to be 0.94274, and the adsorption capacity is $Q_e=1.14285 \text{ mg}\cdot\text{g}^{-1}$, the quasi-second-order adsorption kinetic equation is $R^2=0.99485$, $Q_e=1.74182 \text{ mg}\cdot\text{g}^{-1}$. The quasi-second-stage adsorption kinetic equation not only has a high degree of fit, but also its Q_e is closer to $q_{e, \text{exp}}$.

From figure 6 (d) and table 2, we can find the process of 1%PPCA adsorption of Cr(VI) can be divided into two stages. The $R^2>0.99$ of the two stages indicates that Q_t has a linear relationship with $t^{0.5}$, and there is intra-particle diffusion in this process. The K_3 of the first stage is 0.87659, and the K_3 of the second stage is 0.00525. It shows that the adsorbent in the first stage is prone to internal diffusion in the adsorbate. This is mainly because there is a large concentration difference between the 1%PPAC surface and the Cr(VI) at the beginning of the reaction, and the mass transfer driving force is large. Particles are mainly diffused by macropores, so particle diffusion is easy with. As the reaction progresses, the adsorption sites on the surface of 1%PPCA are gradually occupied by chromium ions, which reduces the adsorption rate. At this time, the particles diffuse mainly through the micropores inside the adsorbate.

Fig.6 The effect of time and pH on Cr(VI) adsorption(a); The adsorption kinetics of Cr(VI) adsorption by 1%PPCA (b: linear plot of pseudo-first-order; c: pseudo-second-order; d: Intraparticle diffusion model)

3.7 Adsorption isotherm

The adsorption isotherm expresses the relationship between adsorption capacity and solution concentration when adsorption reaches equilibrium at a certain temperature. It can describe the mechanism of action between adsorbate and adsorbent, which has a great effect in exploring the surface characteristics of adsorbate and adsorbent (Guo et al. 2017a; Guo et al. 2017b).

The Langmuir isotherm is used to show that the adsorption reaction is a monolayer surface adsorption. Many uniform adsorption active sites are distributed on the adsorbent, and one molecule can only be adsorbed to one active site. (Charpentier et al. 2016). When the surface adsorption active sites are all occupied, the adsorption capacity reaches the saturation value. The equation (Indra et al. 2005) is:

$$\frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{bQ_e C_e} \quad (4)$$

Convert it into a linear expression (Indra et al. 2005) as:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (5)$$

Where C_e is the equilibrium concentration ($\text{mg}\cdot\text{L}^{-1}$); Q_0 is the maximum adsorption capacity for single-molecule adsorption ($\text{mg}\cdot\text{g}^{-1}$); b is the Langmuir constant, which indicating the binding force between the adsorbent and the adsorbate.

The Freundlich isotherm indicates that the adsorption reaction belongs to multi-molecular layer adsorption (Lin et al. 2017a; Lin et al. 2017b). The active adsorption sites are unevenly arranged on the adsorbent. The equation (Indra et al. 2005) is:

$$\lg Q_e = \lg K_F + \frac{\lg C_e}{n} \quad (6)$$

Where K_F is the equilibrium adsorption constant, which reflects the strength of the adsorption capacity; $1/n$ is the composition factor, which indicates the strength of the adsorption capacity increases with the concentration, and reflects the difficulty of adsorption.

From figure 7 (a, b) and table 3, we can know the parameters of the Freundlich adsorption isotherm are $R^2=0.99074$, $R^2>0.99$. It shows that the Freundlich adsorption isotherm better reflects the adsorption behavior of 1%PPCA to hexavalent chromium ion, which also concludes that the adsorption of 1%PPCA on hexavalent chromium ion is multi-molecular layer adsorption. It can be seen from the table that $n=1.45161$, $n>1$, indicating that the adsorption reaction is easy to proceed with. The parameters of Langmuir adsorption isotherm are $R^2=0.96827$, which also reflects the adsorption behavior. From table 3, We can also find that the maximum adsorption capacity of 1%PPCA for hexavalent chromium ion is $6.62032 \text{ mg}\cdot\text{g}^{-1}$.

Table 3 Adsorption isotherm parameters for the adsorption of Cr(VI) by 1%PPCA

	Freundlich		Langmuir
equation	$Y=0.68889X+0.56174$		$Y=0.15105X+0.10708$
R^2	0.99074	R^2	0.96827
$K_F(\text{mg}\cdot\text{g}^{-1})$	3.64535	$1/Q_0(\text{g}\cdot\text{mg}^{-1})$	0.15105
$1/n$	0.68889	$Q_0(\text{mg}\cdot\text{g}^{-1})$	6.62032
n	1.45161	b	1.41063

3.8 Adsorption Thermodynamics

To explain the effect of temperature on the adsorption of chromium ions, it is very important to calculate the thermodynamic constants of adsorption. The thermodynamic isotherm is mainly used to evaluate the change of energy and entropy of the adsorbent during the adsorption process. The equation between the Gibbs free energy change (ΔG_0) and the distribution coefficient K_D (Indra et al. 2005) is:

$$\Delta G_0 = -RT \ln K_D \quad (7)$$

The equations of enthalpy change (ΔH_0), entropy change (ΔS_0) and ΔG_0 (Indra et al. 2005) are as follows :

$$\Delta G_0 = \Delta H_0 - T\Delta S_0 \quad (8)$$

Combining the two formulas can get the Vanter Hoff equation (Indra et al. 2005):

$$\ln K_D = -\frac{\Delta G_0}{RT} = \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT} \quad (9)$$

Where R is the gas constant $0.008314 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; T is the absolute temperature K.

Figure 7c and table 4, we can find that the adsorption process of 1%CCPA on Cr(VI) is $\Delta H_0=57.67 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta H_0>0$, indicating that this reaction is endothermic. The adsorption performance gradually increases with the increase of temperature. This is also consistent with the aforementioned increase in temperature that is beneficial to the adsorption process, which may be because heating up can speed up the diffusion rate and improve the adsorption performance of 1% CCPA on Cr(VI). The adsorption process of 1%CCPA on Cr(VI) is $\Delta S_0=262.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. We can conclude that during the adsorption process, the entropy increases, and the complexity and stability of adsorption and the degree of freedom of the liquid-solid surface increase. From table 4, we can also find that $\Delta G_0<0$, indicating that this reaction can proceed spontaneously. And as the temperature increases, ΔG_0 gradually becomes smaller, which further shows that increasing the temperature can promote the progress of adsorption.

Fig.7 The adsorption isotherms of the Langmuir (a) and Freundlich (b); the adsorption isotherm equation(c)

Table 4 Adsorption thermodynamics parameters for the adsorption of Cr(VI) by 1%PPCA

	ΔH_0 (kJ·mol ⁻¹)	ΔS_0 (J·mol ⁻¹ ·K ⁻¹)	T(K)	ΔG_0 (kJ·mol ⁻¹)	R ²
Cr(VI)	57.67	262.4	293	-19.213	0.99054
			303	-21.807	
			313	-24.461	

4. Conclusions

In this work, we prepared a PEI/PVA composite activated carbon paper-based adsorbent that can efficiently remove low-concentration Cr(VI). The adsorption effect of the 1%PPCA was greatly affected by the pH, and the optimal pH was 2. At this time, the adsorption capacity can reach 1.58 mg·g⁻¹. We performed a fitting analysis of adsorption kinetics, isotherms, and thermodynamic equations on the adsorption data. The results show that the adsorption kinetics conforms to the quasi-second-stage adsorption kinetic equation, indicating that a chemical reaction between the paper-based material and Cr(VI) and the rate of adsorption is controlled by the mechanism of chemical adsorption. The Freundlich adsorption isotherm better reflects the adsorption behavior of 1%PPCA on

Cr(VI), indicating that the adsorption of Cr(VI) to the adsorbent is multi-molecular layer adsorption. In adsorption thermodynamics, $\Delta H_0=57.67 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta H_0>0$, $\Delta G_0<0$, indicating that the process of adsorbing Cr(VI) by the adsorbent is an endothermic reaction that can proceed spontaneously. And $\Delta S_0=262.4 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; this reaction increases entropy, the complexity, and stability of adsorption and the degree of freedom of liquid-solid surface increase during the adsorption process. In general, this study prepared a green adsorbent through simple papermaking and impregnation physical methods, which has a certain removal performance for drinking water containing low concentrations of Cr(VI). The adsorbent is prepared by traditional papermaking and physical impregnation methods and can be produced in large quantities.

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Material preparation, data collection and analysis were performed by [Tianliang Gao], [Chuanshan Zhao], [Sha Li], and [Xia Li]. The first draft of the manuscript was written by [Tianliang Gao] and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

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