Modified peach stones by ethylenediamine as a new adsorbent for removal of Cr (VI) from wastewater

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Abstract: The potential of modified peach stone (PS) for Cr (VI) removal from wastewater was explored in this work. First of all, the properties of the modified peach stone were characterized by SEM, TGA, FT-IR and elemental analysis . Secondly, the modified peach stone were used to absorb Cr (VI). It was found that 3 g/L EPS was good enough for removal of Cr (VI) in feed solution with the maximum adsorption capacity for Cr (VI) of 24.68 mg/g. Either pseudo-second-order model or Langmuir adsorption model was well fitted with the adsorption data. In addition, EPS was found to be able to be reused for a number of cycles for a sustainable operation. This study demonstrates that EPS as a modified natural agriculture waste has great potential to remove Cr(VI) from wastewater.

Keywords: Peach stone; modified; adsorption; Cr (VI); amino; wastewater

1. Introduction

The rapid development of industries and the wide application of different types of technologies bring more and more pollution into our lives, leading to severe harm to the environment and public health. Industrial production such as paper, chrome ore, dyestuff, pigment manufacturing, electroplating, leather tanning, textile industry, refractories and wood corrosion protection[1-2], is the main source of chromium pollution. Heavy metals such as chromium are usually toxic and non-biodegradable. Furthermore, they are very easy to amass in organisms and then to cause harmful side effects on the whole ecosystem through the food chain. Chromium is one of the common heavy metals which exists in the environment in the forms of Cr (III) and Cr (VI) with high toxicity and carcinogenicity even at low concentration [4]. Cr (VI) is 500 times more toxic than Cr (III) [5]. The presence of Cr (VI) may cause allergy, dermatitis, neurotic disorder and even cancer [6]. The maxim limits for Cr (VI) in inland and potable water are 0.1 and 0.05 mg/L [7], respectively. Therefore, it is essential to remove it before being discharged from the industries into the environment.

To effectively remove heavy metals from wastewater, a number of methods have been employed which include precipitation, flocculation, ion exchange and adsorption [8, 9]. Among these methods, adsorption is being widely used due to low cost and high efficiency. In recent years, activated carbon as an effective adsorbent has been widely utilized for wastewater treatment. The application of activated carbon in the practice, however, is limited because of high cost and difficulty for regeneration. To effectively and economically remove heavy metals from wastewater, more and more research has been conducted on developing adsorbents from agriculture wastes due to their abundance, easy availability and low cost or even no cost[9-10],. The agricultural wastes which have been studied for the adsorption of heavy metals from effluents include soybean meal [11], rice husk [12], wheat bran [13] and

walnut shells [14]. However, the adsorption capacity of untreated agricultural materials is not high. A large number of studies have focused on the chemical modifications to enhance their heavy metal removal efficiency [15-17].

Peach stone (PS) as an kind of agricultural waste from peach (Prunus persica) is inevitable to have safe disposal issue and even environmental problem. Like other agricultural residues and by-products, peach stone is mainly composed of cellulose, hemicellulose, and lignin. Peach stone thus can be used as adsorbent to remove Cr (VI) from wastewater at low cost by transformingwaste to highly efficient adsorbent [18]. Although the adsorption capacity of virgin peach stone may not be high enough, different modification methods can be utilized to improve its adsorption capacity.

This study thus aims to develop a new kind of adsorbent with high Cr(VI) adsorption capacity by modifying peach stone with ethylenediamine. It is expected that such kind of adsorbent could be able to effficiently adsorb Cr (VI) from wastewater. The raw and modified materials were characterized by various approaches such as Fourier transformed infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and elemental analyzer to understand their adsorption mechanism. The batch adsorption experiment was performed with variations of initial concentration of Cr (VI), contact time, pH and dosage. Moreover, we also evaluate equilibrium and kinetics aspects of adsorption process as well as regeneration to exploit the future commercial application.

2. Materials and methods

2.1 Peach stone and Chemicals

Peach stones were obtained from Longquan district, Chengdu, China. Sodium hydroxide, ethylenediamine (EDA), epichlorohydrin, potassium dichromate and sodium carbonate were

purchased from Kelong chemical reagent factory (Chengdu, China), which were of analytical grade. Deionized water was used in all experiments, with each experiment triplicated.

2.2 Pretreatment of peach stones

Peach stones were washed with deionized water to remove soil, dust and other impurities, followed by drying in an oven for 24 hr at 90°C. Before being used, dried peach stones were ground in a ball mill and sieved to obtain 50-60 mesh fractions (labeled as PS), and stored in plastic bags for the subsequent experiments[19].

2.3 EDA modification of peach stones
20 grams of the sieved peach stone was immersed in 0.1 M NaOH solution with stirring for 1 hour at room temperature for (what? Better to write the purpose of alkaline immersion for 1hr) .Deionized water was then used to wash peach stone to neutral, followed by drying overnight in the oven at 50°C for the subsequent chemical modificaiton.[19] 10 g dried sample was mixed with 80 ml of 5% NaOH and 30 ml of epichlorohydrin in the round bottom flask containing magnetic stir bar for 5 hr under 50°C [20]. The reaction products were filtered and washed by DI water until the pH reached 7. Then the solid was dried overnight at 50°C. After drying, 2 g of the products was mixed with 0.5g Na_2CO_3 and 50 ml of EDA in a round-bottomed flask with a magnetic stirring bar for hours and washed with deionized till the pH almost approaches near 7. Finally, the products were dried in the oven for 24 hr at 50°C, and labeled as EPS.

2.4 Batch adsorption studies by EDA modified peach stones

All Cr (VI) adsorption experiments were carried out in a shaking table at 250 r/min and 30°C. Cr (VI) stock solution at 50mg/L was prepared by dissolving potassium salts of dichromate into deionized water. The pH values of the solutions were adjusted with ?? M of

NaOH or ?? M of HCl solution. 0.15g absorbents were added into conical flask for all the experiments except the study on the adsorption dose. The adsorption duration from 10 to 300 min was also investigated to figure out the equilibrium time. The adsorption isotherm experiments were studied with different initial Cr (VI) concentrations ranging from 24 to 400mg/L. The initial Cr (VI) concentration, pH and contact time were 50mg/L, 2.5 and 180 min, respectively, except the special note.

The concentration of Cr (VI) in the solution was measured by flame atomic absorption spectrophotometry (FAAS, AA-7020, Beijing, China). The adsorption capacity (q_e mg/g) and removal rate (w %) were calculated according to the following equations:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

$$w = \frac{C_0 - C_e}{C_0} \times 100\% \qquad (2)$$

Where q_e and w were the uptake amount (mg/g) and the removal rate (%) at equilibrium, respectively. C_0 and Ce were the initial and equilibrium concentration of Cr (VI) in solution; V was the volume of solution and m was the mass of absorbent.

2.5 Characterization of absorbents

CHN Elemental Analyzer (Var10EL-III, Germany) was used to obtain the C, H and N contents of the materials before and after modification. The surface of the nascent as well as the spent absorbents were characterized by using FTIR spectrometer (WQF520, China). The surface morphology of samples were observed by using a scanning electron microscopy (SEM, JSM-7500F) at 10.0kV. The changes in physical and chemical properties of PS and EPS with temperature were monitored by using the thermal gravity analysis (TGA, NETZSCH STA 449F3) under air atmosphere scanned from 40 to 650°C.

3. Results and discussion

3.1 Effects of key conditions on modification of peach stone

To explore the effects of EDA concentration, reaction time and temperature on modification, batch modification experiments were carried out at variable EDA concentrations from 0.5 to 2.25 M, reaction time from 2-6 h, reaction temperature from 40 to 100℃. The best modification conditions were confirmed by measuring increased N content. The modification mechanism was illustrated in **Fig.1**.
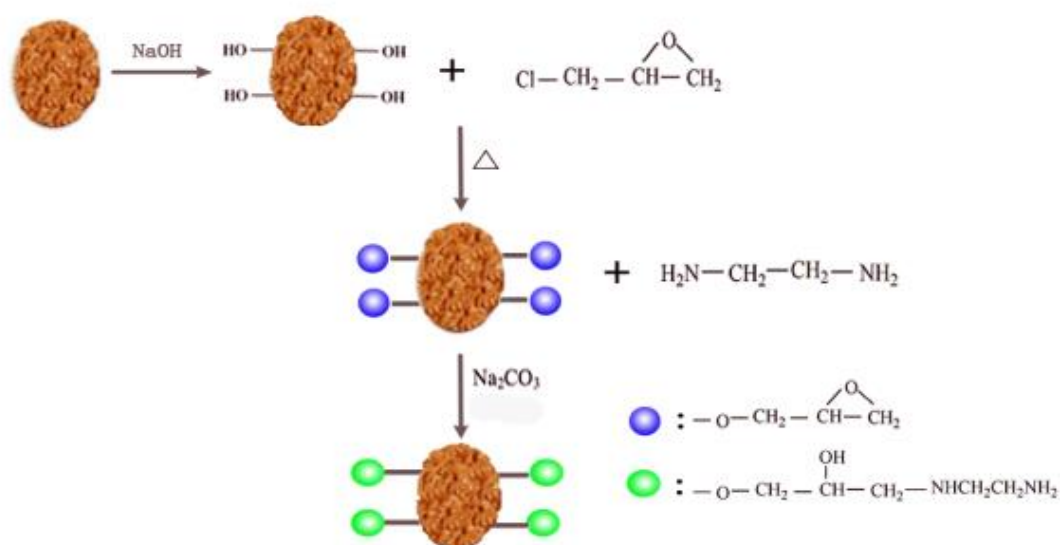

Fig.1 Reactions involved during the ethylenediamine modification of peach stones

Fig.2 shows the effects of modification conditions on N content of modified peach stons. It was found that the N content of the modified peach stones increased sharply with the increase in EDA concentration from 0 to 0.75 M whileplateaued with 0.75-1.25 M EDA concentration. When EDA concentration further increased to 2.25 M, N content decreased slightly. The maximum N content was achieved at EDA concentration of 1.25 M. N% profiles of EPS with reaction time and temperature are similar, and the optimal reaction time and temperature for the maximum N% were found at 4 hr and 60℃, respectively. Therefore,

1.25 M EDA, 4 hr reaction time and 60℃ were chosen as the optimum conditions for the modification of peach stones as absorbents for the subsequent batch adsorption experiments.
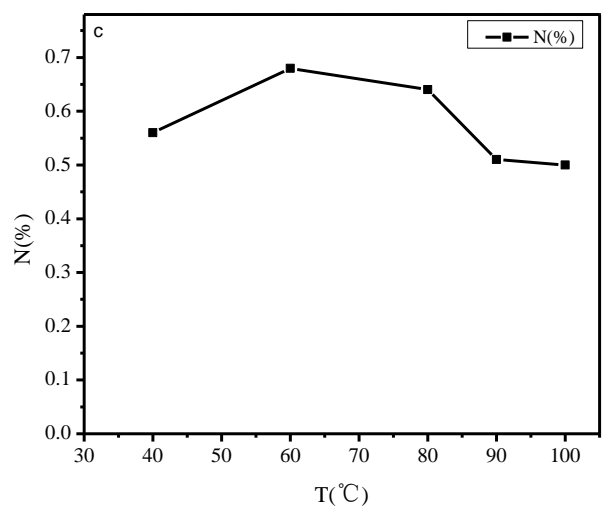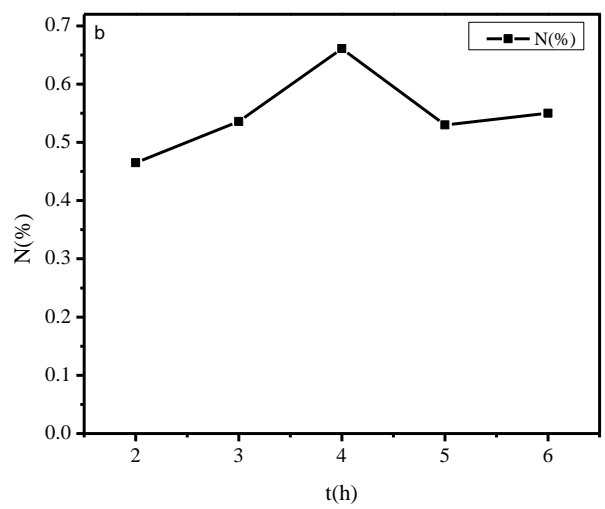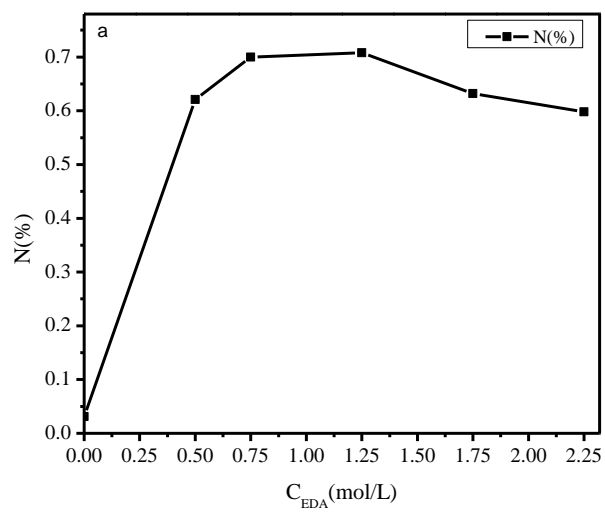
Fig.2 Effects of the concentration of EDA (a), reaction time (b) and temperature (c) on N

content of EDA modified peach stones

3.2 Characterization of adsorbents

3.2.1 FTIR analysis

FTIR spectra analysis is used to examine the functional groups of the absorbents. The FTIR spectra of PS, epichlorohydrin-PS, EPS, and Cr (VI) absorbed EPS were shown in **Fig.3**. It can be seen that for PS, there was a strong and broad peak at around 3,441 cm^{-1} which was attributed to hydroxyl groups. The peak at 2,907 cm^{-1} was ascribed to the CH stretching band and the characteristic vibration peak at 1,745 cm^{-1} was assigned to the carboxyl groups in hemicellulose. The adsorption peak at 1,254 cm^{-1} was due to the syringyl ring and CO stretching in lignin and hemicellulose and the band around 1,039 cm^{-1} was the characteristic of the COC and OH groups of primary hydroxyl stretching in cellulose and hemicellulose [2, 21]. Compared with the spectrum of PS, it was found that for epichlorohydrin-PS, the characteristic absorption peak at 1,039 cm^{-1} shifted to 1,029 cm^{-1}, and the peak became sharper probably due to the etherification of -OH on cellulose with epichlorohydrin. In addition, the phenomena that some peaks of PS at 1,195 cm^{-1} to 1,742 cm^{-1} disappeared, the peak at 1,639 cm^{-1} widened, the intensity of peaks at 1,639 cm^{-1} and 3,434 cm^{-1} increased, confirmed a successful etherification of the functional groups on PS surface with epichlorohydrin by [22]. Meanwhile, the shift of peak position and the change of peak intensity at 1,038, 1,639 and 3,434 cm^{-1} further confirmed that the etherification process was mainly achieved between epichlorohydrin and -OH. After the further modification of epichlorohydrin-PS by EDA, the peak at 1,029 cm^{-1} became narrower with the peak intensity enhanced. The peaks at 1,639 cm^{-1} and 3,434 cm^{-1} obviously broadened which were attributed to the introduction of -NH$_2$.

After the adsorption of Cr (VI) by EPS, the characteristic peak at 1,029 cm^{-1} broadened further in accompany with the reduced intensity. The peak intensity [2] at 1639 and 3,434 cm^{-1} decreased too. It is probably due to the contribution of –NH$_2$, -OH, -COOH and some other groups to the adsorption of Cr (VI). It thus can be concluded that the modification of peach stone by EDA by introducing a lot of –NH$_2$ to change the function groups on PS surface is successful as expected to enhance the adsorption capacity to Cr (VI).
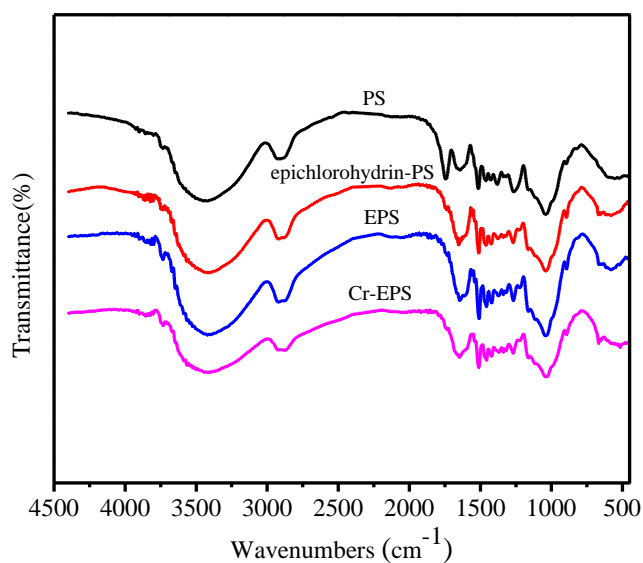

Fig.3 FTIR spectra of PS, epichlorohydrin-PS, EPS, Cr (VI)-EPS

3.2.2 Elemental analysis of PS and EPS

Peach stone was mainly composed of cellulose, hemicelluloses and lignin, which shows the easiness for chemical modification. Based on elemental analysis as shown in **Table 1**, EPS has high contents of C and O, but low N content. After modification by EDA, both contents of H and N increased while C content decreased, indicating the successful introduction of -NH$_2$ by substitution reaction

Table 1 The elemental analysis results of PS and EPS

	C(%)	O(%)	H(%)	N(%)
PS	48.13	45.64	6.201	0.031
EPS	47.59	45.41	6.342	0.661

PS: peach stone; EPS: peach stone modified by ethylenediamine

3.2.3 Themogravimetric analysis of PS and EPS

TG analysis was conducted to understand the thermal stability of PS and EPS. The TG curves of PS and EPS were showed in **Fig. 4**. It can be seen that there are three stages of mass loss, which could correspond to water loss, pyrolysis and combustion of organic matters in PS, respectively More weight loss (about 5%) was observed in EPS compared to PS at temperature about 151℃, which was due to the loss of free water. When temperature went up further to 370℃, both PS and EPS experienced substantial mass loss (the weight loss of both PS and EPS was approximately 45%), which was mainly attributed to the thermal decomposition of cellulose, hemicellulose and lignin [23, 24]. When temperature continued to rise PS mass loss mainly occurs in the temperature range of 368 to 514℃, which was mainly attributed to the combustion of fixed carbon of lignin and cellulose in PS[19]. Above514℃, , the mass of PS did not changes any more, indicating that only ash was left. For EPS, the mass loss at the third stage lasted from 368 to 600℃, which is very different from PS. This suggests that the modification of PS changes its thermal characteristics. The ash content for both PS and EPS are equivalent, which further indicates that the change of thermal characteristics is mainly caused by chemical modification.
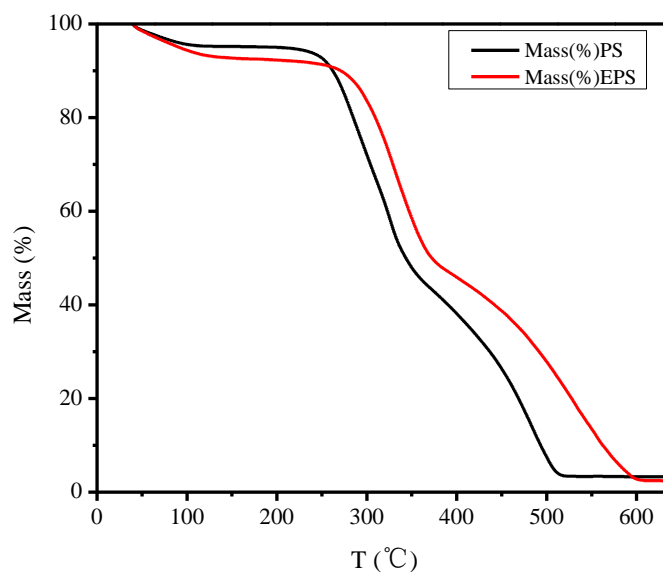
Fig.4 TG curves of PS and EPS

3.2.4 SEM analysis of PS and EPS

The scanning electron micrographs of PS and EPS were shown in **Fig. 5**. The micrographs showed a large amount of impurities on the surface of PS. In addition, a large number of pores on the surface of PS were blocked (**Fig.5 (a)**). However, after the PS was modified by EDA as shown in **Fig.5 (b)**, the surface became cleaner and the number of holes was significantly improved. This is mainly because that the impurities and pigments on PS surface were removed during the modification process. The more pores in EPS indicates the higher specific surface area, which is favorable to adsorption of Cr (VI).
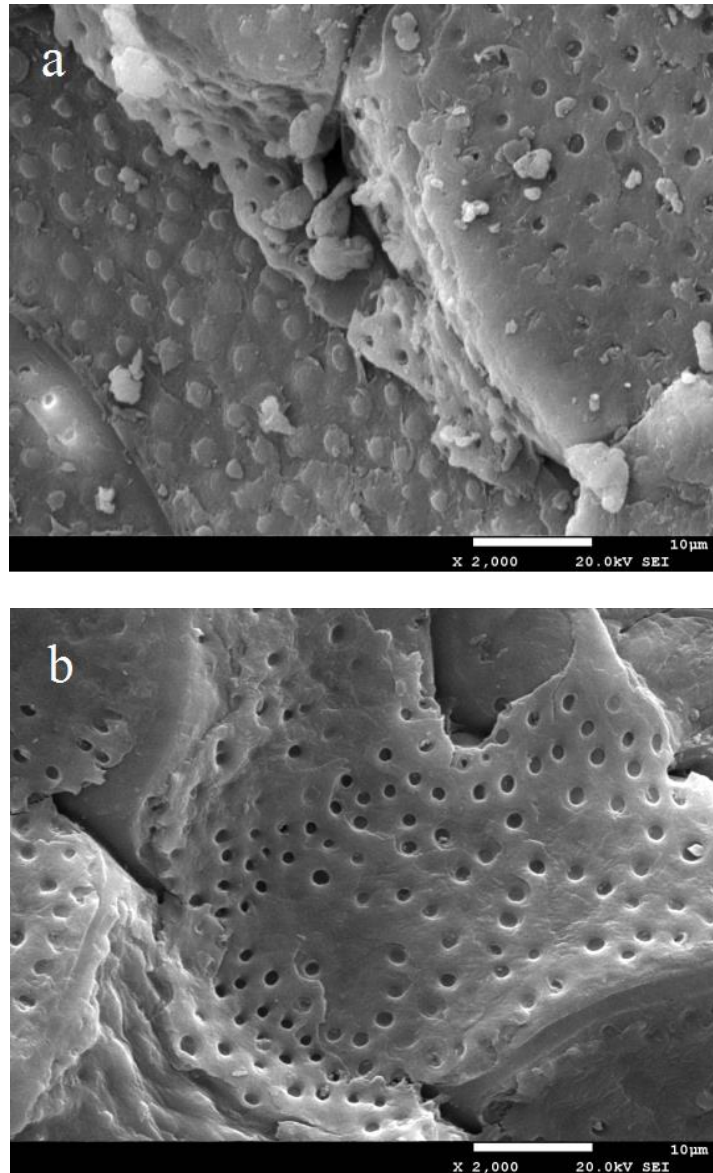
Fig.5 SEM micrographs of PS (a), and EPS (b)

3.3. Comparison of Cr(VI) adsorption by PS and EPS

In order to compare the adsorption of Cr(VI) by peach stones before and after modification, 0.15 g of PS and EPS were used to adsorb Cr(VI) from 50 mL solution with Cr (VI) concentration of 50 mg/L Cr (VI) at pH 2.5 and temperature of 30°C. It can be seen from **Fig.6.** that over the time, the adsorption of Cr(VI) by EPS increased exponentially at first and then increased slowly and gradually reached a steady state. For PS, no obvious adsorption in the first three hours was observed although there was a slight adsorption from

200 to 300 minutes and then plateaued. The maximum adsorption capacity of EPS to Cr(VI) is 13.90 mg/g while it is only 4.14 mg/g for PS, indicating that the Cr(VI) adsorption capacity after the modification by ethylenediamine is significantly improved.
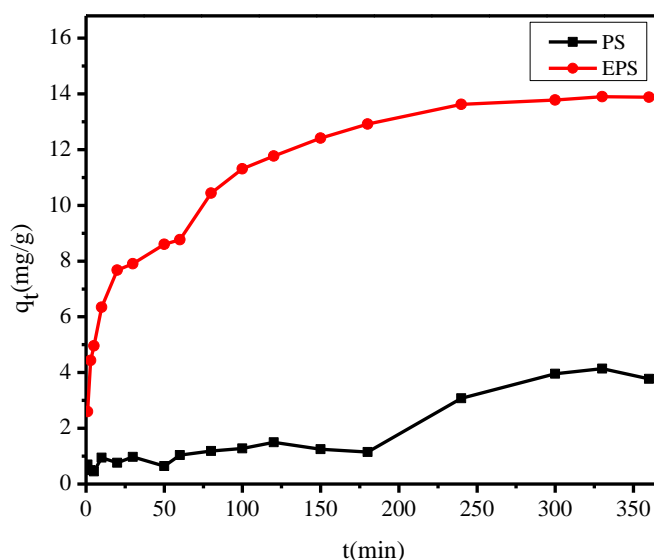

Fig.6 Comparison of Cr (VI) adsorption by PS and EPS

3.4. Effects of pH on Cr (VI) adsorption by EPS

The pH of the solution was an important parameter to the Cr (VI) removal because of the surface charge and ionic competition. The effect of initial pH varying from 2.0 to 9.0 for Cr (VI) removal was shown in **Fig.7**. It was observed that the adsorption capacity of Cr (VI) decreased dramatically with the increase in wastewater pH when pH is above 2.5. The maximun Cr (VI) adsorption capacity was achieved at pH 2.5. At lower pH, positive charges were the dominant species on the surface of absorbent due to the protonation, thus the electrostatic attraction between the positive charges on the adsorbent surface and the negatively charged $HCrO_4^-$, $Cr_2O_2^{7-}$, CrO_2^{4-} could give rise to the increase in the adsorption capacity [25]. Meanwhile, the presence of $-NH_3^+$ introduced by the modification also contributes to Cr (VI) adsorption by electrostatic attraction. The increase in pH resulted in the

decreased the adsorption of Cr (VI) due to the strong competition between hydroxyl ions and $HCrO_4^-$, $Cr_2O_2^{7-}$, and CrO_2^{4-}. With pH change in the wastewater, the forms of Cr (VI) in the solution was diversified. Thus, the competition existed not only between Cr (VI) ions in each form, but also between Cr (VI) ions and OH^-. 2.5 was thus chosen as the optimal pH to carry out the subsequent investigation.
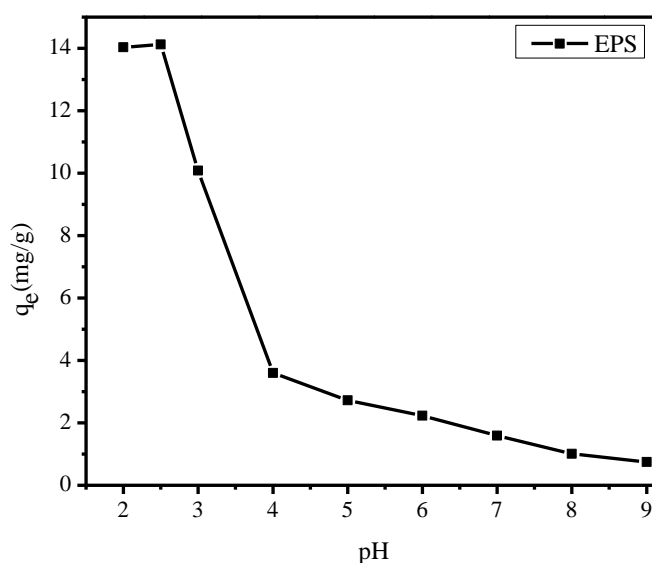

Fig.7 Effect of solution pH on Cr (VI) adsorption onto EPS

3.5. Effects of adsorbent dosage

The effects of adsorbent dose on the removal of Cr (VI) were studied at temperature of 30°C and pH at 2.5 in the medium solution where the initial concentration of Cr (VI) in the solution was 50 mg/L. In this study, the adsorption of Cr (VI) by EPS was examined with an adsorbent dosage ranging from 1 g/L to 6 g/L (**Fig. 8**). It shows that the specific adsorption capacity decreased with the increase in adsorption dosage. The maximum Cr (VI) removal efficiency was achieved with 3 g/L of EPS dosage and a further increase in adsorbent dose showed no quantitative effect on Cr (VI) removal efficiency. It may be due to more active sites and big surface area offered by the adsorbent. So 3 g/L was chosen as the optimum dose to remove Cr (VI) from the solution.
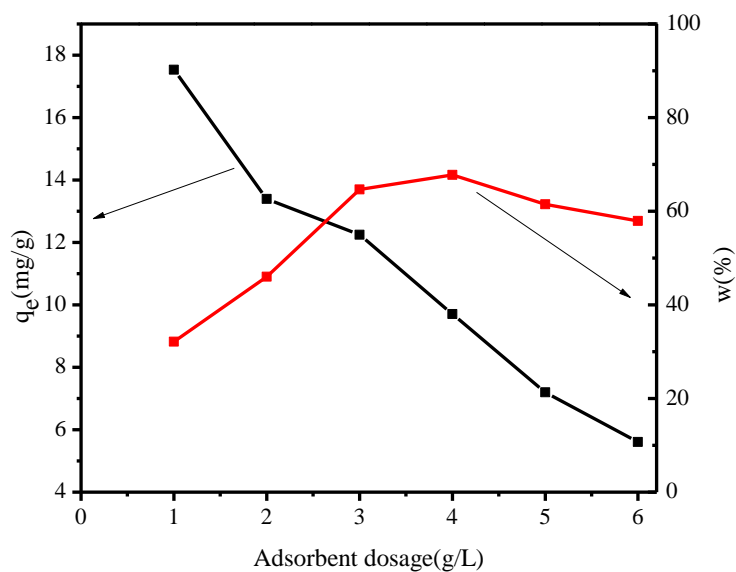
Fig.8 Effect of adsorbent dosage on Cr (VI) onto EPS

3.6. Variation of contact time and adsorption kinetics

Contact time was an important parameter to determine the adsorption efficiency. The variation of contact time indicated that the removal efficiency of Cr (VI) increased with the prolongation of adsorption. As shown in **Fig.9,** the initial adsorption was very rapid. After 180 min, the adsorption equilibrium was nearly established although there is still a certain level of increase in the adsorption capacity. The equilibrium indicates that initially all available active sites on adsorbents are saturated now with $HCrO_4^-$, $Cr_2O_2^{7-}$, and CrO_2^{4-}, Therefore, 180 min was selected as the adsorption time for further experiments.
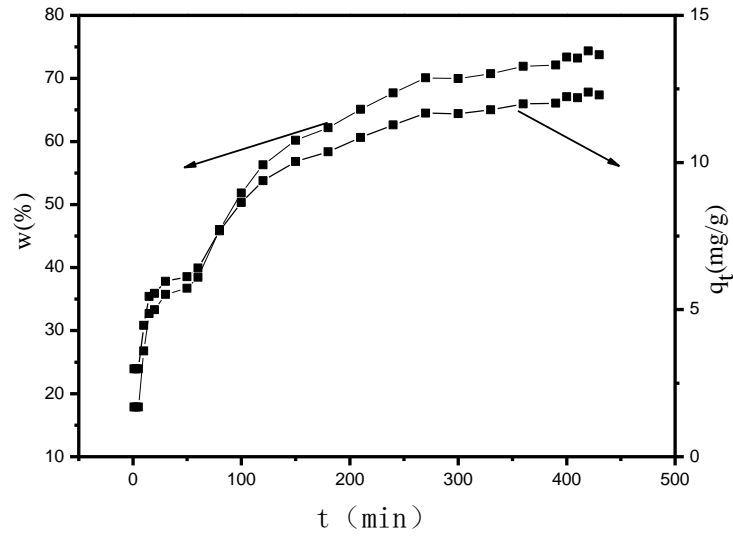
Fig.9 Effect of contact time on Cr (VI) adsorption by EPS

To understand the adsorption process further, the pseudo-second-order and intra-particle diffusion models, respectively, were applied to simulate the adsorption data. The pseudo-second-order rate model [26] is described in the following equation:

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

The intraparticle diffusion model [27] can be used to analyze the kinetic data to provide insights to the diffusion mechanism, which is expresses as below:

$$q_t = k_p t^{0.5} + C \qquad (4)$$

Where q_e (mg/g) and q_t (mg/g) denote the adsorption uptake of Cr (VI) by EPS at equilibrium and at time t, respectively. K (g.mg^{-1}.min^{-1}) is the pseudo-second-order rate constant calculated from the plots of t/q_t against t, and k_p (mg.h$^{0.5}$.g^{-1}) is the intra-particle diffusion rate constant gained from the slope of straight-line portions of the plots of q_t against $t^{0.5}$, and C is the constant obtained from the intercept of the plots.

Adsorption kinetic was studied at temperature: 30°C; initial Cr (VI) concentration: 50mg/L; adsorbent dose: 3g/L and pH: 2.5. All values of kinetic parameters were shown in **Table 2**.

Table 2 Kinetic parameters for Cr (VI) adsorption by EPS

Heavy metals	Pseudo-second-order kinetic model			Intra-particle diffusion kinetic model		
	k_2(g/(mg.min))	q_e (mg/g)	R^2	k_p mg/(min$^{0.5}$.g)	C	R^2
Cr (VI)	0.004724	14.55	0.9930	0.7240	3.463	0.9557

As shown in **Fig. 10a**, Cr (VI) adsorption fits pseudo-second-order kinetics very well with a correlation coefficient (R^2) of 0.993. The fitted q_e value was consistent with the experimental data. This indicated that the adsorption process can be described by chemisorption. On the other hand, it can be seen from **Fig. 10b** with intraparticle diffusion model that there were two different linear curves at the initial adsorption stage, indicating that the adsorption process was controlled by more than one process at the initial stage. The good liner relationship with with a rapid adsorption process may be the external surface adsorption, and the intra-particle diffusion step. the liner plots did not pass the origin, indicating that intra-particle diffusion was not the rate controlling step.
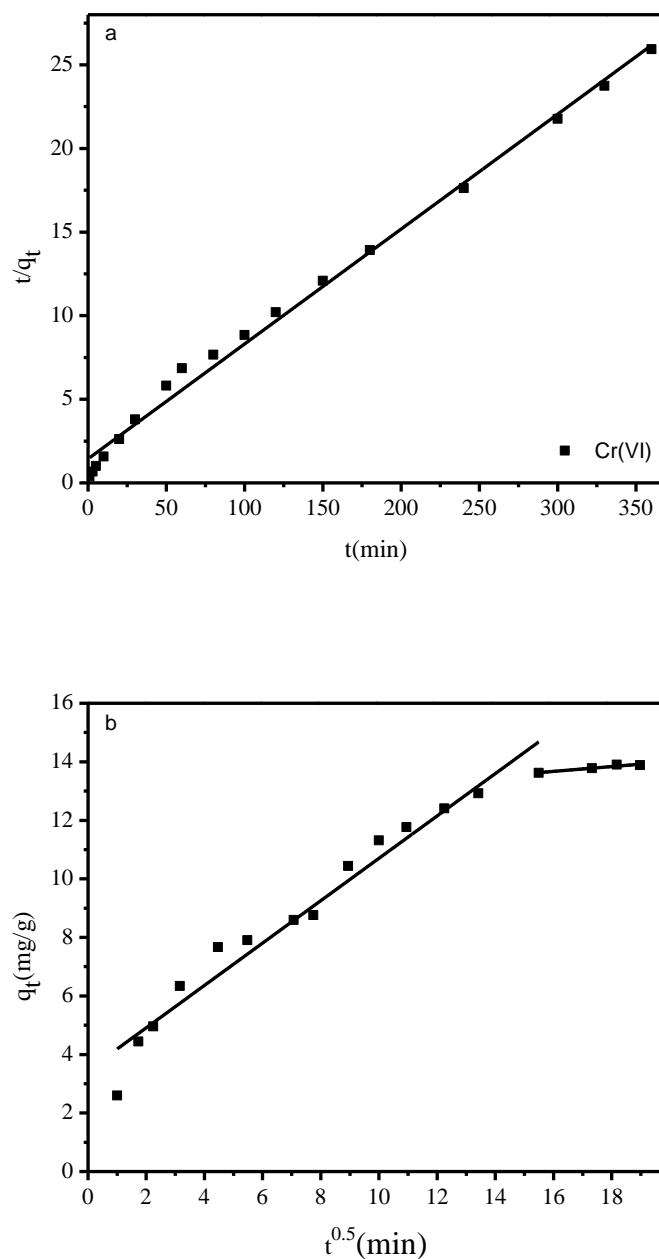
Fig.10 The pseudo-second-order kinetic model (a) and intra-particle diffusion plots (b) on Cr (VI) adsorption by EPS.

3.7. Effect of Cr (VI) concentration and adsorption isotherm

The effect of initial Cr (VI) concentration on adsorption was studied with a concentration ranging from 25 to 400 mg/L and contact time of 180 min, adsorbent dose of 3g/L and pH at 2.5. an increasing trend of adsorption of Cr (VI) with the increase in the initial

Cr (VI) concentration was observed(**Fig. 11**). This was mainly attributed to the fact that as the initial concentration increased, the Cr (VI) concentration difference between the adsorbent surface at time of 0 min and the solution gradually increased, leading to higher concentration difference as the driving force for the adsorption. With the further increase of Cr (VI) concentration, the active sites are saturated, thus the adsorption would gradually reaches saturation, resulting in unchanged Cr (VI) adsorption capacity.
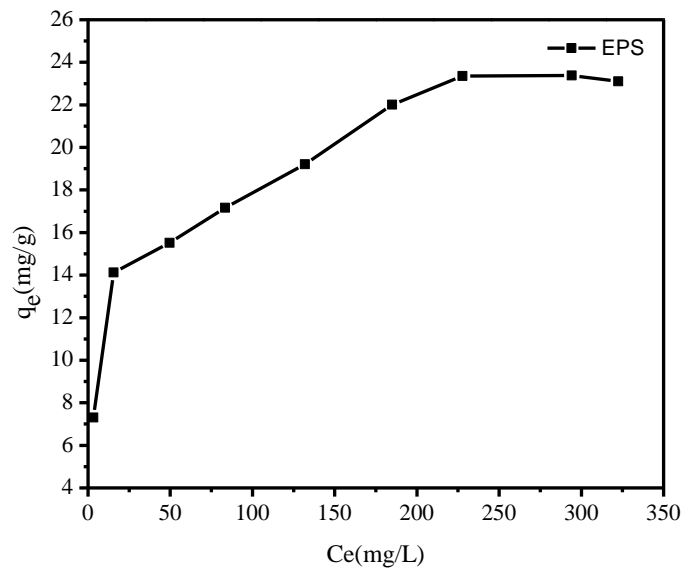

Fig.11 Effect of initial concentration of Cr (VI) on the adsorption by EPS.

To understand the adsorption type, Langmuir and Freundlich isotherm models were employed to simulate the experimental data. The Langmuir isotherm assumes the monolayer adsorption process on the surface of adsorbent [28], while the Freundlich isotherm describes heterogeneous surfaces along with multi-layer adsorption processes. Langmuir isotherm model [29] can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \qquad (5)$$

Where q_e and C_e are the equilibrium adsorption capacity (mg/g) and equilibrium concentration (mg/L), respectively. q_{max} is the maximum adsorption capacity (mg/g), and K_L is the Langmuir constant (L/mg).

Freundlich model [30] can be expressed as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (6)$$

Where q_e and C_e are the equilibrium concentration (mg/L) and equilibrium adsorption capacity (mg/g), respectively. K_f and n are the Freundlich constant. The Langmuir and Freundlich constants of the adsorption of Cr (VI) were calculated from the slopes and intercepts of the plots of Ce/q_e versus Ce (**Fig.12a**) and $\log q_e$ versus C_e (**Fig. 12b**), which were summarized in **Table 3.**

As shown in **Fig. 12** and **Table. 3**, The correlation coefficients (R^2) for both Langmuir and Freundlich isotherm models were larger than 0.94, suggesting that the Cr (VI) might be adsorbed on the surface of adsorbent in the mixed forms of monolayer and multilayer.

Table 3 Langmuir and Freundlich isothermal model parameters for the adsorption of Cr (VI) by EPS

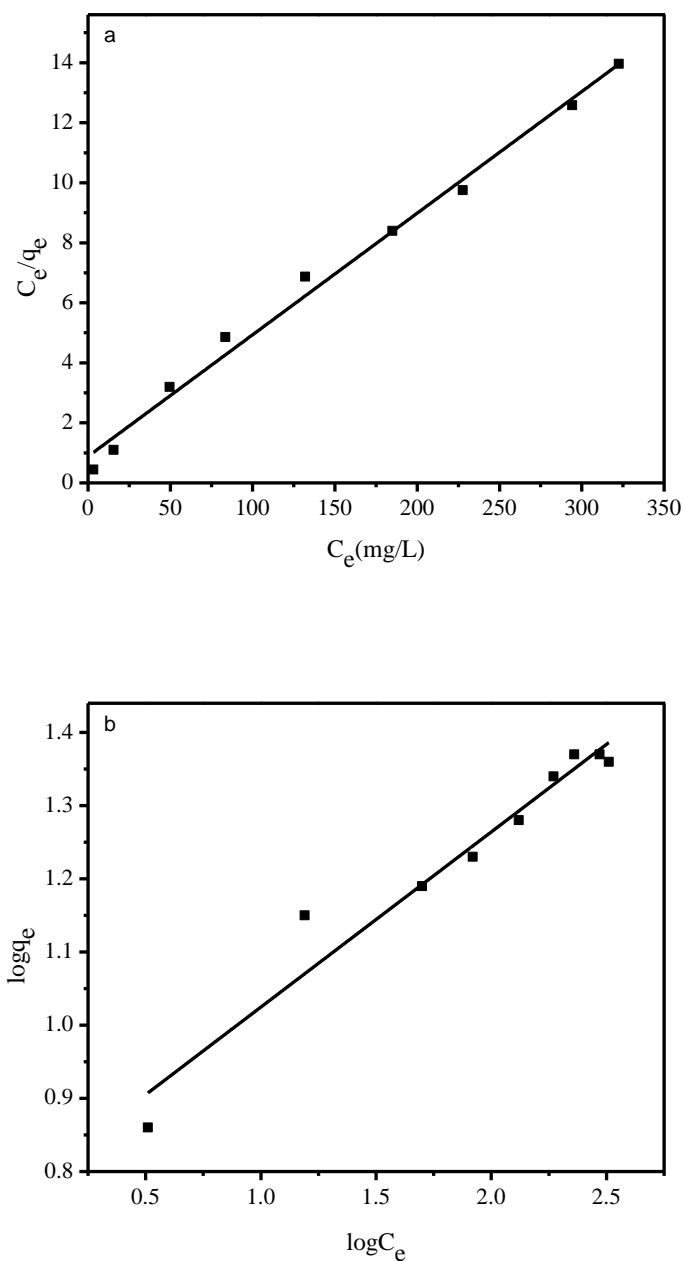| Heavy metals	Langmuir isothermal model			Freundlich isothermal model		
	b(L/mg)	q_{max} (mg/g)	R^2	K_f (mg/g)	n	R^2
Cr (VI)	0.04585	24.68	0.9905	6.100	4.177	0.9455

Fig.12 The models of adsorption (a) Langmuir isotherm model and (b) Freudlich isotherm

model

In the present study, the maximum Cr (VI) uptake capacity was 24.68 mg/g. Compared

with the adsorbents developed by other researchers **(Table 4)**, the adsorption capacities of Cr

(VI) by EPS were similar or even higher than most of them. This result suggests that EPS is a

promising adsorbent to treat effluent containing heavy metals.

Table 4 Comparison of Cr(VI) removal capacities by different adsorbents

Adsorbent	Adsorption capacity (mg/g)	Reference
Rice straw	3.15	[33]
Clarified sludge	26.31	[34]
Natural Akadama clay	4.29	[35]
Composite alginate – goethite beads	29.5	[36]
Red mud	21.1	[37]
Zeolites modified ZVI	2.49	[38]
EPS	24.68	This study

3.8. Regeneration of EPS

To use the adsorbent developed in this study repeatedly to further reduce the cost, it was very essential to investigate the regeneration ability of the adsorbents. As shown in **Fig.13** , it was observed that the adsorbents exhibited the good regeneration performance. The Cr (VI) adsorption capacity by EPS in the first regeneration cycle was 14.15mg/g while it has a very slight decreased from 14.15 to 13.33 mg/g after four regeneration cycles. This result indicated that EPS is promising for Cr (VI) removal in the practical application with regeneration.
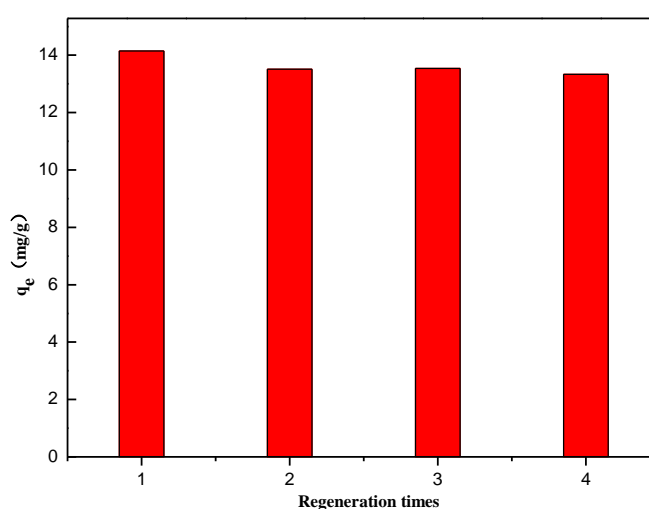

Fig.13 Regeneration study on the Cr (VI) removal by EPS

4 Conclusions

EDA modified PS was developed as a new adsorbent to remove Cr (VI) from wastewater. FTIR, SEM, TGA and elemental analysis confirmed the presence of amino groups in PSafter modification. The pseudo-second-order kinetic model was well fitted with the adsorption data by EPS, implying that the adsorption process is controlled by chemisorption. For isotherm models, Langmuir adsorption model better described the adsorption of Cr (VI) by EPS than Freundlich model. The maximum adsorption capacity of 24.68 mg/g at pH 2.5 by EPS suggested a comparable adsorption capacity compared with absorbents developed by other reseachers. Furthermore, EPS showed negligible adsorption capacity loss after 4 cycle of regeneration. All results from this study suggest that EPS is a promising and environmentally friendly absorbent by utilizing agricuture waste for the removal of Cr (VI) from wastewater.

Acknowledgments

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