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ADSORPTION CHARACTERISTICS OF Cr(VI) ON CARBONIZED *Eupatorium adenophorum* SPRENG

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Abstract

The potential use of a novel low-cost adsorbent, *Eupatorium adenophorum* Spreng, as a solution to remove Cr(VI) ions from aqueous was reported. Effects of various regulating parameters, such as pH value of reaction, adsorbent dosage and temperature, were investigated. To fit the adsorption equilibrium data, Langmuir isotherm and Freundlich isotherm were invoked. Additionally, thermodynamic parameters of the adsorption process, such as ΔG , ΔS and ΔH , were also calculated. The results indicated that carbon temperature 823 K and carbon time 45 min were the optimum conditions to prepare the adsorbent for the removal of Cr(VI), and the condition of pH=1 maximized the adsorption capacity. Cr(VI) was reduced to Cr(III) in the adsorption process. Kinetics studies showed that the adsorption system may be described by the pseudo-second-order equation kinetic model. The Freundlich isotherm adsorption model showed the best fit with experimental data ($R^2=0.9465$) and the overall adsorption process was exothermic and spontaneous.

Keywords: adsorption, Cr(VI), *Eupatorium adenophorum* Spreng, kinetic, thermodynamics

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1. Introduction

Hexavalent chromium [Cr(VI)] is considered as a major water pollutant and mainly exists in wastewater from metallurgy, machinery, electroplating, leather, medicine, textile dyeing and other chemical industries (Sadeghi, 2017). Chromium is considered acutely toxic, carcinogenic and mutagenic to living organisms, hence more hazardous than other heavy metals (Garg et al., 2007). In order to comply with the increasingly strict regulations, it is essential that industries reduce the concentration of Cr(VI) in their effluents to the acceptable levels before recycling or discharging to the natural environment.

The conventional treatment methods applied in these industries include precipitation, ion-exchange, reverse osmosis, electrochemical process, solvent extraction, electrolytic recovery, etc. (Chen and Chen, 2008). By far the most versatile and

effective method to remove hexavalent chromium is adsorption, which helps to dispose the secondary toxic slurries and render the system more economically, especially when low-cost and eco-friendly adsorbents are used. Harmful plants with high biomass may be a good choice of raw material for adsorbents.

As an invasive species, EaS (*Eupatorium adenophorum* Spreng) is now distributed widely in the United States of America, Australia, New Zealand and many countries in Southeast Asia. It was listed as one of the most harmful species in the first batch of invasive species in China. To control its spread effectively, various physical, biological and chemical methods were developed. However, no obvious progress was gained so far. Regarding EaS as a resource has been demonstrated to be effective and practical, which could not only decrease the damage on the local forests, stock farming, agriculture and eco-environment, but also increase

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economical benefits and thus achieve two birds with one stone. In addition, EaS has a loose structure, with a high content of cellulose, hemicelluloses, and lignin. Activated carbon made from EaS was reported in recent years (Sun et al., 2010; Xia et al., 2008). However, the activated carbon made from EaS was expensive and the use of chemical drugs in activation stage resulted in new contaminations, which somewhat limit its development. Meanwhile, EaS could be used as forage for goats and sheep or mixed with other feedstock after pretreatment (Rymer, 2008; Sahoo et al., 2011). Furthermore, Guo et al. (2009) reported to use EaS for the adsorption of lead(II) from aqueous solution and suggested that EaS might be a low-cost adsorbent for effective removal of lead(II) in wastewater. In summary, most of the adsorption studies aimed at the adsorbent prepared by agricultural wastes (Ponou et al., 2011; Narsi et al., 2004; Xin et al., 2010). There are few studies about using carbonized EaS as adsorbent. Therefore, thermodynamics of using carbonized EaS as adsorbent to remove Cr(VI) from aqueous solution and adsorption kinetic of Cr(VI) by carbonized EaS were investigated in this study, which may help to provide the theory basis for heavy metal treatment with carbonized EaS as adsorbent.

2. Material and methods

2.1. Material

2.1.1. Adsorbent preparation

EaS was collected from Sichuan Province, P.R. China. The raw materials (stems of EaS) were dried at 378 K, crushed and sieved to particles with meshes of which the size range is 35-60. After sieving, the material was heated in the electric furnace under nitrogen atmosphere at different temperatures (673K, 723K, 773K, 823K) for 15 min, 30 min, 45 min and 60 min, respectively. The products were then cooled down to room temperature. Lignin was measured according to the National Standard of China (GB/T 20805-2006) *Determination of acid Detergent Lignin in Feedstuffs*; crude fiber was measured according to the National Standard of China (GB/T 5009-2003) *Determination of Crude Fiber in Vegetable Foods*. The contents of lignin and crude fiber in the EaS sample were 31.8% and 43.5%, respectively.

2.1.2. Reagents

The stock solution (50 mg/L) of Cr (VI) was prepared by dissolving (0.1415±0.0001)g of potassium dichromate (K₂Cr₂O₇) (AR grade) in 1000- mL deionized water. The stock solution was finally diluted to obtain standard solutions.

2.1.3. Equipment

A digital pH meter (PHS-25, Shanghai, China) was used for pH measurements. The pH meter was standardized using buffer solutions (sodium tetraborate and mixed phosphate) of pH values 9.18

and 6.86. An electronic thermostatic reciprocating shaker (SHZ-88, Jintan, China) was used to agitate the samples. 722N Visible Spectrophotometer was used to determinate the chromium content in standard and treated solutions. The carbonization of EaS was made by using electric furnace (TMF-4-13, Shanghai, China).

2.2. Adsorption studies and the measurement of chromium content

Groups of studies were conducted to investigate the parametric factors such as pH, adsorbent dosage, solution temperature and contact time. Selected adsorbents were added in a 150 mL stopper conical flask with 100 mL of test solution. Solutions with different initial concentration of Cr(VI) were prepared by proper dilution from 50 mg/L Cr(VI) standard stock solution. 0.1mol/L HCl and 0.1 mol/L NaOH solution were applied to modulate pH of the solution. The contents of the flask were filtered and the filtrates were analyzed for remnant Cr(VI) concentration in the sample. Every treatment was conducted twice.

1, 5-Diphenylcarbazide Spectrophotometry method (GB 7467-87, China) was used for the analysis of Cr(VI) ions in the aqueous solutions. The amount of Cr(VI) was measured. Diphenyl carbazide color method (GB7466-87, China) was used for the analysis of total Cr in the aqueous solutions.

Then, the removal percentage of Cr (VI) was calculated by (Eq. 1):

$$\phi = \left(1 - \frac{C_{final}}{C_{initial}}\right) \times 100\% \quad (1)$$

where ϕ is the removal percentage of Cr(total), C_{final} , $C_{initial}$ are final and initial total concentration of Cr in the aqueous solutions.

2.3. Adsorption isotherms and thermodynamic experiments

Langmuir and Freundlich models were employed to describe the uptake of Cr(VI) by carbonized EaS. The model parameters were determined from the following equations (Eqs. 2-3):

Langmuir isotherm (Eq. 2):

$$q_e = \frac{Q_m K_c C_e}{1 + K_c C_e} \quad (2)$$

Freundlich isotherm (Eq. 3):

$$\ln Q_e = \ln K_f + \frac{1}{n} C_e \quad (3)$$

where K_c and K_f are the equilibrium constants; C_e is the equilibrium concentration of solution (mg/L); n is Freundlich constant; Q_m is the maximum adsorption capacity (mg/g); Q_e is the amount of Cr(VI) adsorbed by per gram adsorbent (mg/g).

The thermodynamic parameters such as Gibbs free energy change ΔG^0 , enthalpy change (ΔH^0), entropy change (ΔS^0) were calculated to evaluate the feasibility and the nature of the adsorption process.

The Gibbs free energy change ΔG^0 of the reaction was obtained using the following equations (Eqs. 4-5).

$$\Delta G^0 = -RT \ln K_c \quad (4)$$

$$\lg K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (5)$$

where K_c is the thermodynamic equilibrium constant (L/mol); R is gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$); ΔH^0 is enthalpy change (J/mol); ΔS^0 is entropy change ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$); T is the thermodynamic temperature.

2.4. Adsorption kinetic experiments

Experiment of the adsorption kinetic of Cr(VI) from an aqueous solution was carried out as follows. Firstly, 0.35g of the prepared adsorbent was added to 50 mg/L of Cr(VI) solutions (100mL) in the stopper conical flask. Secondly, the pH value of the solution was adjust to 1.0. Finally, the stopper conical flasks were shaken at a frequency of 150 r/min at the temperature of 298K for different lengths of time ranging from 0 to 80 minutes. In the biosorption kinetic study, pseudo-second-order equation was employed to estimate the adsorption rates and possible reaction mechanisms.

The pseudo-second-order kinetic model could be expressed by Eq. (6):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

The pseudo-first-order kinetic model could be expressed by Eq. (7):

$$\frac{1}{qt} = \frac{1}{qe} + \frac{k_1}{(qet)} \quad (7)$$

The Power function equation model could be expressed by:

$$q = at^b \quad (8)$$

where q_t represents the amount adsorbed during the period of time t (mg/g); k_2 is the equilibrium rate constant for the pseudo-second-order ($\text{g/mg} \cdot \text{min}$); and q_e is the equilibrium adsorption capacity (mg/g). k_1 is the content of pseudo-first-order kinetic, and a , b are the contents of Power function equation.

2.5. Technological parameters optimization for the preparation of EaS adsorbent

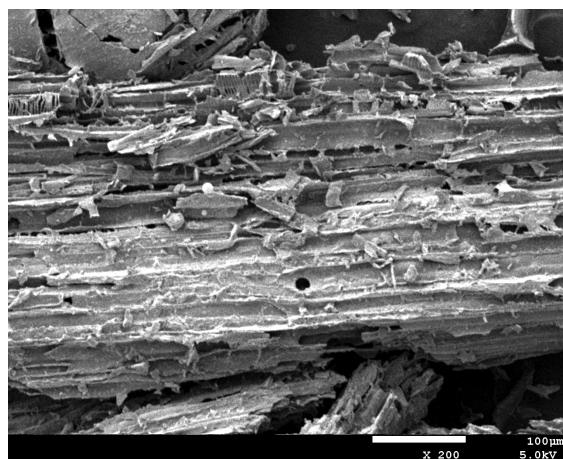
0.3g prepared adsorbent was added to the solutions (100mL) with 50 mg/L of Cr(VI) in the stopper conical flasks. The stopper conical flasks were then shaken in the electronic thermostatic reciprocating shaker at a frequency of 150 r/min for 2h at 298K. The removal percentage of Cr(VI) could be calculated based on the measured value of $C_{initial}$ and C_{final} concentrations. The removal percentages of Cr(VI) for the EaS adsorbents which were prepared with different lengths of time and temperatures were measured and calculated (see Table 1). The results showed that the optimal technological parameters were 823K and 45min. All EaS adsorbent used in the following experiment were prepared in the condition with the optimal parameters.

2.6. Characterizations of the EaS adsorbent

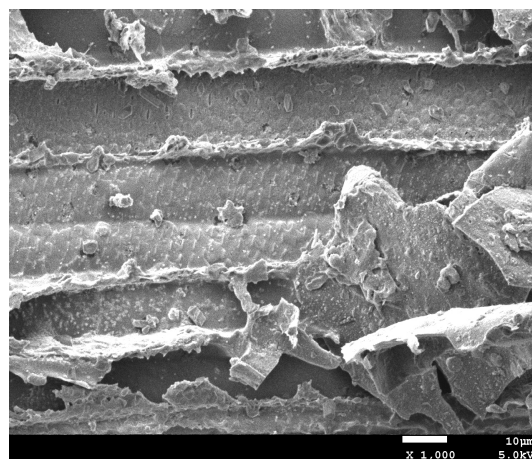
“The Determination of Iodine Adsorption Value of the Wooden Activated Carbon Test Method” (GB/T12496.8-1999) was used to measure iodine number.

Table 1. Results of carbonized experimental data

Serial number	Carbonized temperature (K)	Carbonized time (min)	Cr(VI) removal rate (%)
1	673	15	49.2
2	673	30	52.2
3	673	45	50.4
4	673	60	58.0
5	723	15	64.3
6	723	30	52.2
7	723	45	71.9
8	723	60	77.7
9	773	15	78.3
10	773	30	89.8
11	773	45	90.4
12	773	60	92.8
13	823	15	95.7
14	823	30	96.3
15	823	45	97.3
16	823	60	91.8



(a)



(b)

Fig. 1. SEM photo of the biosorbent sample at different magnifications ($\times 200$, $\times 1000$)

“The Determination of Methylene Blue Adsorption Value of the Wooden Activated Carbon Test Method” (GB/T12496.10-1999) was used to measure the methylene blue. The adsorption value of iodine and methylene blue of EaS adsorbent was 482.89 mg/g and 151.5 mg/g, respectively. The iodine adsorption value was lower than normal values of activated carbon by 900-1100 mg/g, while methylene blue adsorption value was higher than normal values of activated carbon by 100-120 mg/g, which showed that in the carbonized EaS, the porosities are mainly mesoporous (Páez et al., 2011).

Scanning Electron Microscope (SEM, HITACHIS-450, Japan) was used to characterize the micro-structure of the samples, which was operating at an acceleration voltage of 5 kV. The surface composition of the GAC was analyzed with the aid of EDX(Oxford Instruments 7200) (Lai et al., 2012).

The SEM clearly revealed the carbon surface texture and morphology of the granules (Fig. 1) at different magnifications. The coarse, porous nature of the biosorbent could be clearly observed. There were many small convex globular particles (diameter 1-2 μm) in the biosorbent, which increased both the surface roughness and specific surface area.

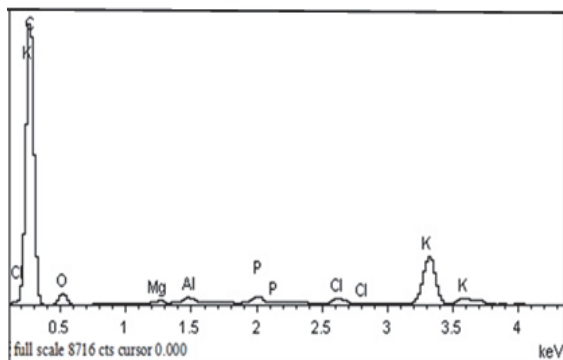


Fig. 2. EDX pattern of the biosorbent sample

EDX analysis of the samples showed that main elements in the biosorbent were O, K, and C

(Fig. 2). There was no harmful element in the biosorbent, which indicated the biosorbent from EaS was environment-friendly.

3. Results and discussions

3.1. Effect of contact time and conformation change of Cr(VI)

Experiments were carried out at temperature of 298K with 100mL solution with 50mg/L concentration of Cr(VI), using 0.35g adsorbent at pH 1.0. The solutions were kept shaking at a frequency of 150 r/min for 3h. The sample times were 10, 20, 30, 40, 50, 60, 90, 120, 150 and 180min. The Cr(VI) and total chromium were measured. The results were showed in Fig. 3.

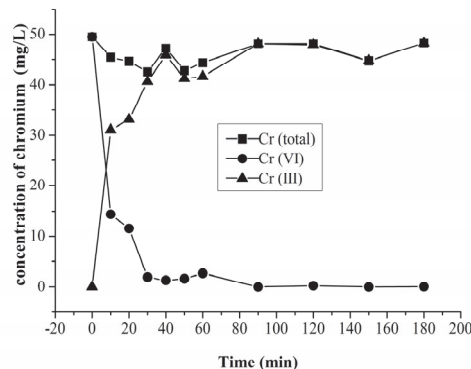


Fig. 3. Effect of contact time on Cr(VI) adsorption

As Fig. 3 shows, Cr(VI) in the solutions decreased sharply with the adsorption time and reached adsorption equilibrium after 90 min, when the concentration of Cr(VI) in the solution became zero. Total chromium was in slightly waves in the whole adsorption process while Cr(III) was generated, and the concentration of Cr(VI), Cr(III) and total chromium in the solution tended to reach steady after 90 min. These results indicated that almost all the Cr(VI) were reduced to Cr(III) when contacted with the adsorbent, because carbonized

EaS contained a great quantity of reducing C and the Cr(VI) has high redox potential value (above +1.3 V at standard condition). Cr(VI) could easily or spontaneously be reduced to Cr(III) when it contacted with the biomaterials (Nemr, 2009; Li et al., 2009). The concentration change of chromium species in aqueous revealed that the removal mechanism of Cr(VI) by the adsorbent was its reduction into Cr(III).

3.2. Effect of pH on Cr(VI) biosorption

The pH of the aqueous solution is the most important parameter affecting the biosorption process. The effect of pH on the biosorption of Cr(VI) was examined by varying the pH of metal solution in the range of 1- 9. The result was shown in Fig. 4.

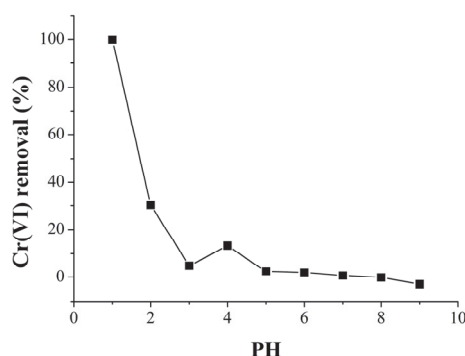


Fig. 4. Effect of pH on Cr (VI) adsorption

The Cr(VI) removal percentage was found to decrease as pH increased from 1 to 3. The removal percentage then maintained at 10% with little fluctuation within the pH range from 3 to 9. The Cr(VI) removal percentage reached its peak value of 99.9% at solution pH 1.0. The change of Cr(VI) removal percentage with pH may be attributed to following reasons. First, when pH is between 1-2, HCrO_4^- mainly exists at pH 1.0 and increasing pH shifted the concentration of HCrO_4^- to $\text{Cr}_2\text{O}_7^{2-}$ and other forms such as CrO_4^{2-} . Finally, when the pH increased to above 7.0, CrO_4^{2-} would be the primary form (Garbisu et al., 1998; Qiu et al., 2009). The results indicated that HCrO_4^- was adsorbed into the biomass preferentially, which was in consistent with previous studies (Acar and Malkoc, 2004; Bhattachaya et al., 2008; Teymouri, 2017).

3.3. Effect of adsorbent dose on Cr(VI) biosorption

Study on the effect of adsorbent dose is important to determine the sorbent-sorbate equilibrium of the system and assessment of adsorbent absorbability. It helps to optimize the adsorbent dosage while meet the removal efficiency demands (Gupta and Babu, 2009). Carbonized EaS dosages varying from 0 to 0.5g at 0.05g interval were studied using 100mL Cr(VI) solution of 50mg/L. pH of the solution was modulated to 1.0. The solutions

were kept shaking at a frequency of 150r/min at 298K. The results were shown in Fig. 5.

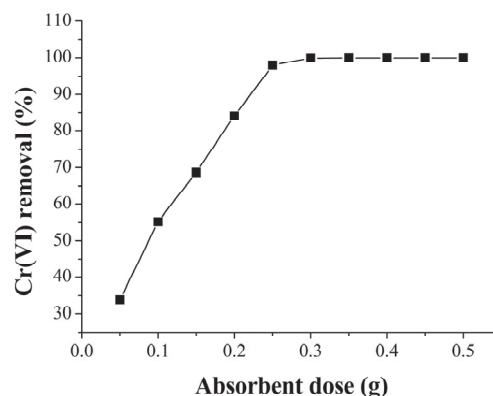


Fig. 5. Effect of sorbent dosage on Cr (VI) adsorption

The Cr(VI) removal percentage increased with the adsorbent dosage from 0 to 0.25g and reached 99.9% at the dosage of 0.25g. After dosage of 0.25g, the removal efficiency gradually reached adsorption equilibrium. The variation in adsorption capacities between various adsorbent dosages were mainly attributed to the adsorption sites available for adsorption. As adsorbent dosage increased, more active sites on the adsorbent became available for the adsorption. Finally, when the adsorption reached equilibrium, increasing adsorbent number had no effect on the adsorbate uptake because it added unavailable sites (Namasivayam et al., 1998). Furthermore, although large adsorbent dosage increased the interference among active groups on the adsorbent surface, the equilibrium concentration of Cr(VI) became lower because the driving force was too low for adsorbate to diffuse onto the adsorbent surface and to be adsorbed. This result is in accordance with other previous studies (Li et al., 2009; Park et al., 2008).

The cost of this product arises mainly from raw material collecting, drying, grinding and carbonizing, which is lower than that of traditional activated carbon. Using EaS as a resource is also a promising way to control its spread and protect local eco-environment. Thus, adsorption of Cr(VI) by carbonized EaS appears to be a cheap, efficient and win-win (from both eco-environment and environmental pollution treatment perspectives) alternative.

3.4. Adsorption kinetics

The kinetics of Cr(VI) adsorption was studied from the curves of time versus $q_e(\text{mg/g})$. Variation of the equilibrium adsorption capacity of Cr(VI) with adsorption time (min) at 298K was shown in Fig. 6. The adsorption times were 10, 20, 30, 40, 50, 60, 90, 120, 150, 180 min. From Fig. 6, it could be observed that the adsorption amount of Cr(VI) by carbonized EaS increased sharply from 10 to 40 min which indicated that Cr(VI) diffused from the solution to

carbonized EaS adsorbent surface within this time period.

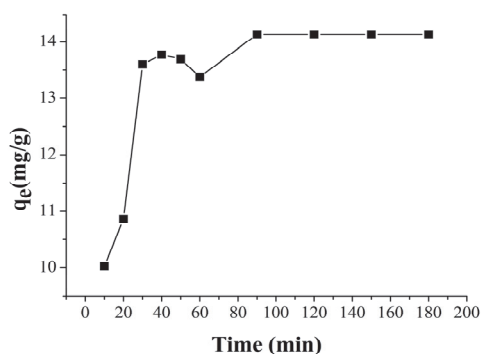


Fig. 6. Adsorption kinetics plot

After 40min, the adsorption amounts changed slightly and finally maintained constant after 90 min, which suggested that in this period Cr(VI) migrated in the carbonized EaS adsorbent and the adsorption reaction reached balance gradually (Ho and McKay, 1999). Pseudo-first-order equation, pseudo-second-order equation and the power function equation were applied to simulate the Cr(VI) adsorption kinetics and analyze the relationship between Cr(VI) ion concentration and adsorption time. The simulated results were shown in Fig. 7, Fig. 8 and Fig. 9.

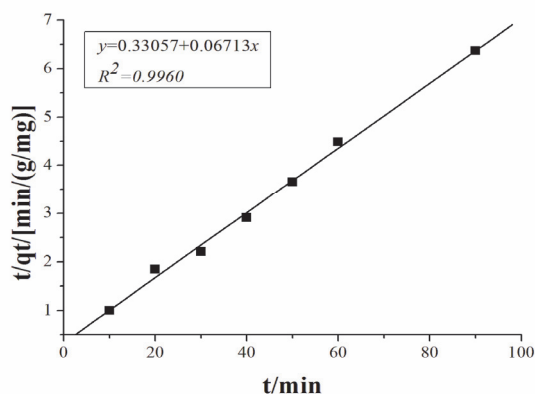


Fig. 7. Linearization of the pseudo-second-order equation for adsorption kinetics

The R^2 of pseudo-second-order kinetics is the highest compared with that of Power function equation and of pseudo-first order kinetics, which demonstrated that the adsorption of Cr(VI) on carbonized EaS could be described better by pseudo-second order kinetics, where the correlation coefficient $R^2=0.9960$, the equilibrium rate constant for the pseudo-second-order $k_2=0.00149$ g/(mg·min), the theoretical equilibrium adsorption capacity $q_e=14.89$ mg/g, and the experimental results $q_e=14.14$ mg/g.

The model calculation showed a good agreement with the experimental results, which indicated that the system studied, was appropriately described by the pseudo-second-order model. It demonstrated that the removal of Cr(VI) proceeds

included two steps: firstly, the electrostatic force attracts Cr(VI) ions towards carbonized EaS; secondly, Cr(VI) ions are reduced to Cr(III) ions by reducing organic carbon (Chang and Juang, 2004). The second result is in consistent with the effect of the contact time on the adsorption process.

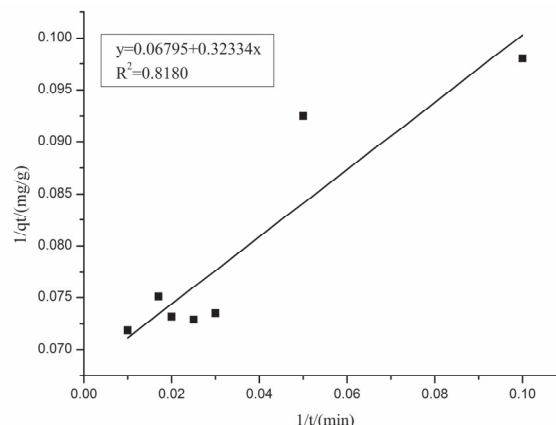


Fig. 8. Linearization of the pseudo-first-order equation for adsorption kinetics

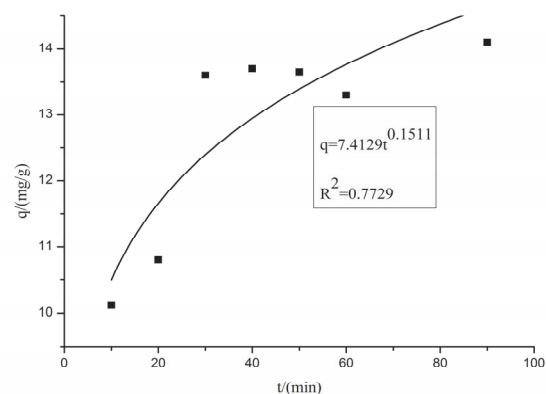


Fig. 9. The power function equation for adsorption kinetics

3.5. Thermodynamic parameters

Equilibrium isotherm was studied at temperature of 298K, 303K, 313K and agitation speed of 150 r/min. Equilibrium time for the test was 90min. 0.35g carbonized EaS was add into 100 mL Cr(VI) solutions of 0, 10, 25, 50, 75, 100, 150 mg/L concentration. Equilibrium data were shown in Table 2. Estimated S. E (standard error) was calculated by Langmuir and Freundlich fitting equation, in which a smaller S.E is better fitting. The linear forms of Langmuir isotherm and Freundlich isotherm were used to determine the isotherm constants.

Table 1 showed that the adsorption amount of Cr(VI) by carbonized EaS decreased with the adsorption temperature. The coefficient of determination R^2 values suggested that Freundlich isotherm provided a good fit for the sorption system, which was based on heterogeneous adsorption of metal ions by biosorbent. The thermodynamic parameters were calculated by Eqs. (4 and 5) and the results were shown in Table 3.

Table 2. Parameters of the Langmuir and Freundlich models

T/K	<i>Langmuir model</i>				<i>Freundlich model</i>			
	Q_m (mg/g)	K_c (L/mol)	R^2	$S.E$	K_f (mg/g)	$n/$ (g/L)	R^2	$S.E$
298	24.95	0.6658	0.7377	0.0186	12.3	5.34	0.8968	0.0078
303	23.83	8.2498	0.7804	0.0134	12.5	4.14	0.8209	0.0103
313	21.92	4.4978	0.8045	0.0112	12.4	5.32	0.9465	0.0023

Table 3. Thermodynamic parameters

T/K	$\Delta G / (kJ \cdot mol^{-1})$	$\Delta S / (J \cdot mol^{-1} \cdot K^{-1})$	$\Delta H / (J \cdot mol^{-1})$
298	-13.23	3.0612	-11263
303	-10.429		
313	-13.844		

It could be seen from Table 3 that ΔG were all negative value and ΔH was negative at 298K, which demonstrated that the adsorption process of Cr(VI) on carbonized EaS was a spontaneous and exothermal reaction. The equilibrium sorption capacity decreased with temperature substantiated that the adsorption process of Cr(VI) on carbonized EaS was exothermal.

The negative values of ΔG and high adsorption capacity demonstrated that both physical and chemical adsorption existed in this adsorbent, but chemical adsorption was dominating, which agreed with the result of pseudo-second-order fitting. In addition, Positive ΔS indicated that this adsorption was a process of entropy increase. The exothermic and non-ordering may be caused by the reduction of Cr(VI) to Cr(III) (Shu and Xiong, 2009).

4. Conclusions

(1) The optimum technological condition of carbonized EaS adsorbent preparation is: carbonization temperature 823K; carbonization time 45 min.

(2) The prepared adsorbent had a high Cr(VI) removal amount (24.95 mg/g) at pH 1.0. The proper adsorption time of the system is 90 min.

(3) The equilibrium isotherms were well fit by the Freundlich models. Regarding the thermodynamic of uptake of Cr(VI), thermodynamic parameters revealed that the adsorption process is spontaneous, exothermic and diffusion-controlled. Adsorption of Cr(VI) obeyed the pseudo-second-order equation.

In summary, this study has demonstrated that carbonized EaS could be used to remove Cr(VI) from aqueous solution and using EaS as an adsorbent is a promising way for resource utilization of EaS.

Acknowledgments

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