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Radiation-induced grafting of 4-vinyl pyridine onto cellulose microsphere for Cr(VI) removal

Youwei Zhang[a,b,1], Hui-Ling Ma[b,c,1], Jing Peng[b], Ling Xu[d], Jiuqiang Li[b], Maolin Zhai[b,*]

[a] *Aviation Key Laboratory of Science and Technology on Stealth Materials, Beijing Institute of Aeronautical Materials, Beijing 100095, China, Tel. +86 10 62497288, Fax +94 10 62496510, email: ywzhang_pku@163.com (Y. Zhang)*
[b] *Beijing National Laboratory for Molecular Sciences, Department of Applied Chemistry and the Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China, Tel. +86 10 62753794, Fax +94 10 62753794, email: huiling_1027@163.com (H.L. Ma), jpeng@pku.edu.cn (J. Peng), jqli@pku.edu.cn (J. Li), mlzhai@pku.edu.cn (M. Zhai)*
[c] *Beijing Key Laboratory of Radiation Advanced Materials, Beijing Research Center for Radiation Application, Beijing 100015, China*
[d] *Peking University Shenzhen Institute, Shenzhen 518055, China, email: lingxu@xmu.edu.cn (L. Xu)*
[1] *These authors contributed equally to this work*

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ABSTRACT

A novel amino-functionalized cellulose microsphere adsorbent (named C-VP) was prepared by radiation-induced grafting 4-vinyl pyridine (4VP) onto cellulose microsphere and subsequent protonation process. The graft polymerization conditions on the influence of grafting yield such as total absorbed dose, dose rate, solvent mixture ratio and monomer concentration, have been studied in detail. The obtained C-VP was tested for the abilities to remove Cr(VI) in batch experiments. The results demonstrated that the Cr(VI) adsorption was highly pH dependent and the maximum Cr(VI) uptake was obtained as the pH of solvent was 2.74. The adsorption isotherms of the C-VP for Cr(VI) fit the Langmuir model. The adsorption rate was considerably fast, and the adsorption reached equilibrium within 25 min. In addition, the Cr(VI) ions could be effectively desorbed using a 0.1 mol L^{-1} NaOH solution. Moreover, the reusability of the obtained C-VP was tested for several times and only slight loss in adsorption capacity was observed. Our work demonstrated the as-prepared adsorbent could possess a promising potential in the practical field of water treatment.

Keywords: Cellulose microsphere; Radiation grafting; 4-vinyl pyridine; Adsorbent; Cr(VI)

1. Introduction

Chromium is a common pollutant in effluents originated from industries including leather, mining, metal cleaning, electroplating, chemical manufacturing and so on [1,2]. It is mainly present in Cr(VI) and Cr(III) forms in the environment. Compared with Cr(III), Cr(VI) holds a higher toxicity due to its powerful carcinogenic effect to living organisms and high solubility in water [3]. The USEPA made clear regulations that the maximum Cr(VI) concentration in drinking water should be below 0.05 mg L^{-1} [4]. Therefore, it is imperative to explore effective methods and materials for treating Cr(VI) contaminated wastewater before being discharged into the environment.

To meet the strict environmental regulations, various techniques have been applied to reduce/remove Cr(VI) from wastewater, such as chemical precipitation, membrane separation [5,6], solvent extraction [7,8] and adsorption. Compared with these methods, adsorption is considered as the more efficient and economically favorable technology with several advantages including less

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*Corresponding author.

release of sludge, low cost and easy to operate [9]. The adsorbents with different structures have been prepared and evaluated for removing Cr(VI) from wastewater, such as fiber [10], membrane [11], microsphere [12] and powder adsorbents [13,14]. Among these adsorbents, microsphere-based adsorbents have attracted a great deal of attention because of their high mechanical stability, easy operation and large surface area [15]. However, most of the microsphere-based adsorbents are hardly degradable. On the contrary, cellulose has been extensively used as matrix to prepare functional adsorbents due to its low cost and biodegradation [16]. However, the utilization of cellulose microspheres-based adsorbent for Cr(VI) removal has rarely been reported.

In our previous study [17], a cellulose microsphere-based adsorbent was prepared by radiation-induced grafting of styrene onto the surface of microsphere, followed by acylation and amination processes. The as-prepared adsorbents exhibited a good binding affinity to Cr(VI). However, the complex preparation and the poor mechanical strength of the adsorbent because of acylation and amination processes have limited its applications for Cr(VI) removal from wastewater. Therefore, for practical utility there is still a requirement for developing a facile strategy to prepare surface-functionalized cellulose microspheres. Herein, the object of this work is to provide a facile strategy to modify the cellulose microspheres by radiation-induced grafting 4-vinyl pyridine onto the surface of them using gamma ray and subsequent protonation to endow the good adsorption capacity for Cr(VI).

2. Experimental

2.1. Materials

Microcrystalline cellulose microspheres with an average diameter of ~230 µm were obtained as a gift sample from Mitsubishi Corporation (Japan). 4-Vinyl pyridine (4VP) with purity of more than 99% was supplied by Acros Organics (Morris Plains, NJ). Potassium dichromate was purchased from Shan Xi Xi Long Chemical Factory. Diphenylcarbazide was obtained from Sinopharm Chemical Reagent Co., Ltd. Methanol, hydrogen chloride, sodium hydroxide and sodium chloride were supplied by Beijing Chemical Works. All the reagents were analytical-grade chemical products and were used as received without further purification.

2.2. Preparation of the adsorbent

The preparation procedure of the C-VP adsorbent is illustrated in Fig. 1. The cellulose microspheres were immersed into the methanol/water solution containing various concentrations of 4VP in glass tubes and left for 24 h to facilitate the swelling of the cellulose microspheres [17]. The samples were bubbled with nitrogen for 30 min to remove oxygen and then quickly sealed to keep the nitrogen atmosphere prior to irradiation. Subsequently, the samples were directly irradiated using a ^{60}Co source at the Department of Applied Chemistry of Peking University for various dose and dose rate at ambient temperature. After irradiation, the products were washed in a Soxhlet extractor with methanol for 24 h to remove the residual monomer and homopolymer. The products were then dried in a vacuum oven at 60°C to constant weight. The grafting yield (GY) was determined by the percentage increase in weight as follows:

$$GY(\%) = (W_g - W_0)/W_0 \times 100 \tag{1}$$

where W_g and W_0 are the weights of the grafted and control cellulose microspheres in dry state, respectively.

After that, the grafted cellulose microspheres were protonated in 1 mol L^{-1} HCl solution for 24 h. The resulting products (C-VP) were dried in a vacuum oven at 60°C for 24 h. Two kinds of adsorbents were prepared and used for further batch experiments. GY of 4VP for C-VP-I and C-VP-II were 36% and 48%, respectively.

2.3. Characterization of C-VP

A Fourier transform infrared spectrometer (Magna-IR 750, Nicolet) was used to characterize the original cellulose microsphere and the C-VP. The spectra were obtained in the absorbance mode in range of 2000–600 cm^{-1} by averaging 16 scans at 1 min intervals to minimize the effects of dynamic scanning. Morphology of the samples was observed by scanning electronmicroscope (SEM) (Hitachi S4700).

2.4. Cr(VI) adsorption onto C-VP

Cr(VI) adsorption studies were carried out using batch adsorption method. All the experiments were performed in the 50 mL Cr(VI) solutions (100 mg L^{-1}) with 50 mg C-VP for 24 h at room temperature. The influences of pH, adsorbent feed, Cr(VI) and temperature on Cr(VI) uptake were also conducted using a very similar procedure. The pH of

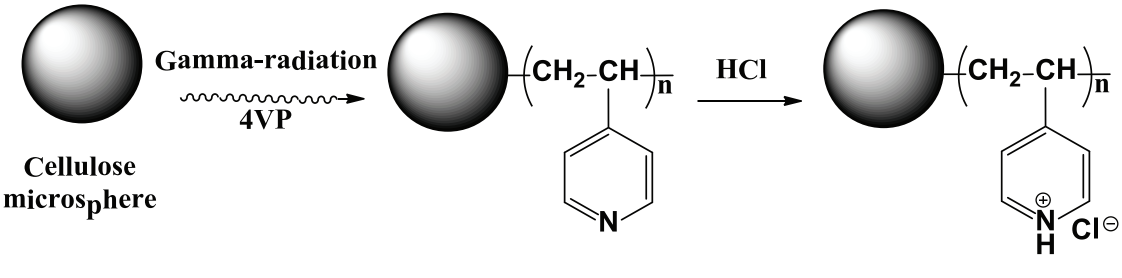

Fig. 1. Synthetic route of C-VP.

the Cr(VI) solutions were ranged from 1.1 to 11.8, the temperature were ranged from 298 K to 313 K and the Cr(VI) concentrations were ranged from 50 to 250 mg L^{-1}. Cr(VI) concentration was measured by UV-vis spectrophotometer (UV-3010, HITACHI) at 540 nm by 1, 5-diphenyl carbamide method [18]. The Cr(VI) uptake by C-VP was calculated by Eq. (2):

$$\text{Cr(VI) uptake} = (C_0 - C_e) \times V / m \tag{2}$$

where C_0 and C_e are the initial and residual concentrations of Cr(VI), respectively; V is the volume of the Cr(VI) solution and m is the weight of dry adsorbent.

2.5. Desorption and regeneration

Adsorbed Cr(VI) anions were desorbed from C-VP by treatment in a beaker with 100 mL NaOH solution (0.1 M). The beaker was then placed in an incubator shaker (140 rpm) at room temperature for 2 h. The concentration of Cr(VI) ions in the eluent was determined as described above. The C-VP-II was subsequently protonated in 1 mol L^{-1} HCl solution. The Consecutive adsorption–desorption cycles were repeated five times by using the same C-VP.

All the above experiments were carried out in duplicate and average values were reported. Standard deviations were found to be within ±3%.

3. Results and discussion

3.1. The preparation and characterization of C-VP

3.1.1. Effect of solvent composition

It has been established that the radiation grafting of vinyl monomers occurs according to the grafting front mechanism. Grafting often starts at the surface of the matrix, then proceeds toward to the middle of the matrix by the progressive diffusion of the monomer through the swollen grafted layer [19]. Therefore, best grafting is expected to occur in the solvent which will be beneficial to the swelling of matrix. It is reported that methanol is a good solvent for swelling cellulose [17]. Besides, the chain transfer to solvent also influences the radiation grafting. Low GY will be obtained in the solvent with high chain transfer constant. Water is a very good reaction medium for radiation grafting on account of its zero chain transfer constant [20]. Therefore, water and methanol were chosen as the mixture solvent for radiation grafting of 4VP onto cellulose microsphere. The effect of MeOH/H_2O co-solvent composition on the GY is shown in Fig. 2. The GY increased by increasing the ratio of water content in the mixture. However, 4VP was scarcely grafted on the cellulose microspheres in pure water, and it is because the cellulose matrix could not be swollen by water. The addition of methanol can contribute to the increase GY of 4VP. But excess methanol restrained the grafting polymerization because methanol was a nonsolvent for poly(4-vinyl pyridine) moieties. These results indicate that solubility parameter and chain transfer constant are both important factors to affect the GY of 4VP.

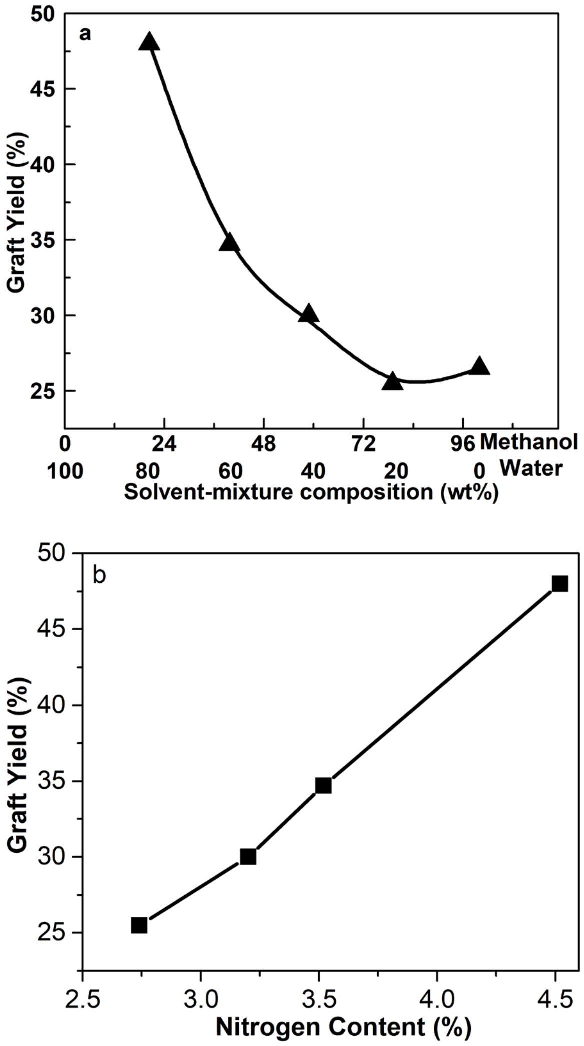

Fig. 2. The effect of solvent composition on the GY (a); the nitrogen content of C-VP with different GY (b). (dose: 20 kGy, dose rate: 20 Gy min^{-1}).

3.1.2. Effect of monomer concentration

It is known that monomer concentration is a very important parameter that can strongly affect the GY, because the diffusion of monomer can play an important role in the radiation polymerization [21]. To study the influence of monomer concentration on the GY of 4VP, radiation-induced graft polymerization were carried out using varying monomer concentrations of 10, 20 30, 40, 50 and 60 wt% (Fig. 3). With the increasing of monomer concentration, the GY reached a maximum at a monomer concentration of 50 wt%, and then decreased sharply at higher monomer concentration. Increasing monomer concentration to a certain degree was beneficial to the reaction between the monomer and free radical sites of the polymer. However, further increasing the monomer concentration will lead to the decreased GY, because the increasing solution viscosity would disturb the penetration of the monomers to reach the active sites or the radicals of the base polymer [22].

3.1.3. Effect of absorbed dose and dose rate

The results presented in Fig. 4a show the influence of absorbed dose on the GY. It was found that the GY ascended with the increase of absorbed dose. More free radicals would be formed and more reactive sites would be generated during the graft polymerization at a higher absorbed dose so that monomer molecular would have more opportunity to react with the radicals. The GY of 4VP onto cellulose microspheres irradiated with a dose of 50 kGy increased to 105.4%. However, abundant homopolymers formed when the absorbed dose exceeded 25 kGy. Therefore, we chose an absorbed dose of 25 kGy for further experiments.

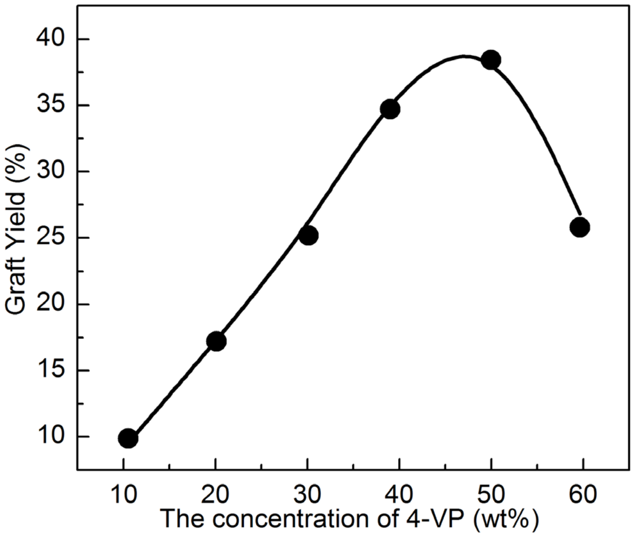

Fig. 3. Effect of monomer concentration on the GY of 4VP. (dose: 20 kGy, dose rate: 20 Gy min^{-1}, MeOH/H_2O = 3:2).

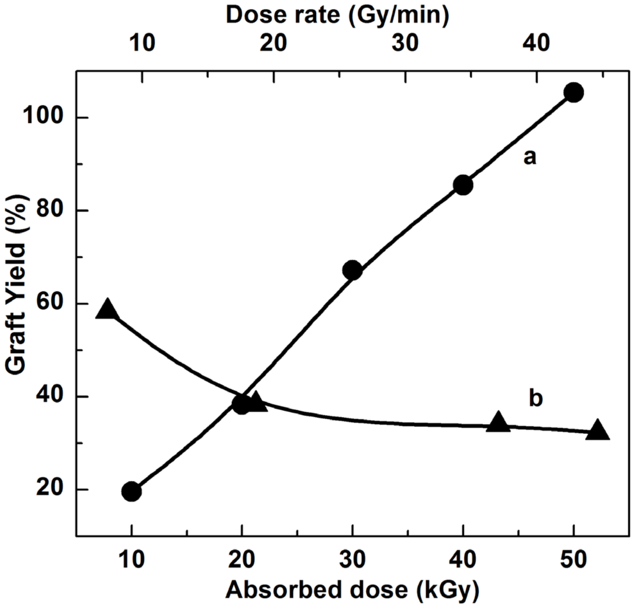

Fig. 4. Effect of dose (a) and dose rate (b) on the GY of 4VP. (MeOH/H_2O = 3:2, monomer concentration: 50 wt%).

Fig. 4b shows the effect of dose rate on the GY of 4VP onto cellulose microspheres. The increase in dose rate resulted in a decreased GY. This can be ascribed to the fact that more radicals would tend to decay by recombination and the grafted poly(4-vinyl pyridine) chains would be subjected to faster termination at a higher dose rate. Therefore, the grafting process was inhibited and GY decreased.

By varying the reaction conditions of the radiation graft polymerization, two adsorbents with different GY (C-VP-I: 36% GY, C-VP-II: 48% GY) were prepared for further adsorption experiments. The nitrogen contents of C-VP-I and C-VP-II were 3.5% and 4.5%, respectively. The average sizes of C-VP-I and C-VP-II were ~299 μm and 324 μm (See supporting information Fig. S1).

3.1.4. Characterization of C-VP

In the IR spectra of cellulose microspheres and C-VP-II (Fig. 5), the absorption peaks are observed at 1556 and 1598 cm^{-1}, corresponding to the stretching vibrations of C=C and C=N bonds of the pyridine molecules [23]. The peak at 1420 cm^{-1} belonged to the C=C bonds of the pyridine ring is also observed [19]. These results can prove the radiation graft polymerization of 4VP onto cellulose microsphere.

3.2. The adsorption of Cr(VI) onto C-VP

3.2.1. Effect of contact time

The effect of contact time on the Cr(VI) uptake of C-VP-I and C-VP-II are shown in Fig. 6. The slopes of the lines joining the data points in the figure reflect the adsorption rates. As shown, the amount of Cr(VI) adsorbed on the adsorbent increased within initial 5 min. Subsequently, the adsorption was improved gradually and reached nearly to equilibrium after 25 min, which is faster than most reported adsorbents [24,25]. The Cr(VI) uptake for C-VP-I and C-VP-II were 59.1 and 73.2 mg g^{-1}, respectively.

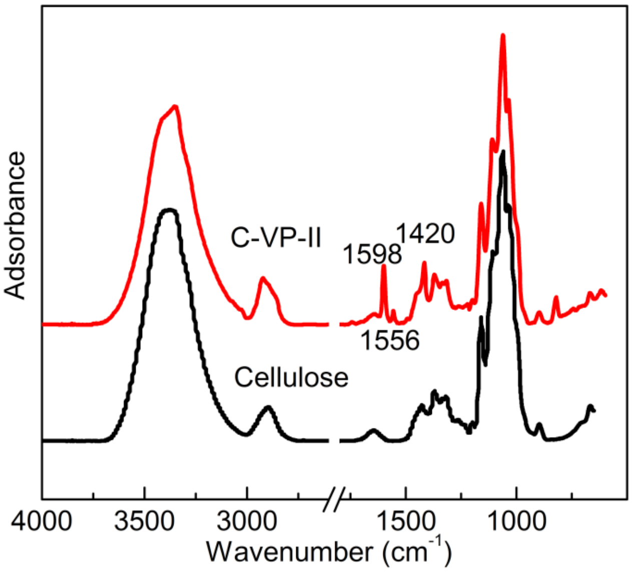

Fig. 5. FT-IR spectra of cellulose and C-VP-II.

In the order to investigate the mechanism of adsorption, the obtained kinetic adsorption data were evaluated by pseudo-first-order equation [Eq. (3)] [26] and pseudo-second-order equation [Eq. (4)] [27], respectively.

The pseudo-first-order equation is expressed as:

$$q_t = q_e(1 - \mathrm{e}^{-k_1 t}) \tag{3}$$

The pseudo-second-order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where k_1 and k_2 is the pseudo-first-order and pseudo-second-order rate constants of adsorption, q_t and q_e is the Cr(VI) uptake at time t and at equilibrium, respectively.

The values of different parameters calculated by the pseudo-first-order and pseudo-second-order kinetic model along with these corresponding correlation coefficients are given in Table 1. The theoretical values of q_e are well in agreement with the experimental values in the case of pseudo-second-order model. Meanwhile, the correlation coefficients R_2^2 for the pseudo-second-order kinetic model are nearly equal to 1. The q_e values calculated from the first-order kinetic mode give significantly different values compared to experimental values, and the correlation coefficients R_1^2 are also found to be slightly lower. Thus, the adsorption kinetics fitted well with the pseudo-second-order model, confirming that the adsorption process of Cr(VI) on C-VP-I and C-VP-II were mainly controlled by a chemisorption mechanism [28].

3.2.2. Effect of adsorption feed

The effect of the adsorption feed on the Cr(VI) removal from solution was also studied by changing the dose between 0.2 and 1.0 g L^{-1} fixed initial Cr(VI) concentration of 100 mg L^{-1}. It is evident from Fig. 7 that the Cr(VI) recovery of C-VP-II increased from 16.2 to 73.5% as the dose increased from 0.2 to 1.0 g L^{-1}, which could be attributed to the increase in the number of active sites available for adsorption.

3.2.3. Effect of temperature

The temperature plays a very important role in the adsorption of Cr(VI). The effect of temperature on Cr(VI) removal by C-VP-II is shown in Fig. 8. The Cr(VI) uptakes at various temperatures increased with the increase of temperature, which could be attributed to the accelerated diffu-

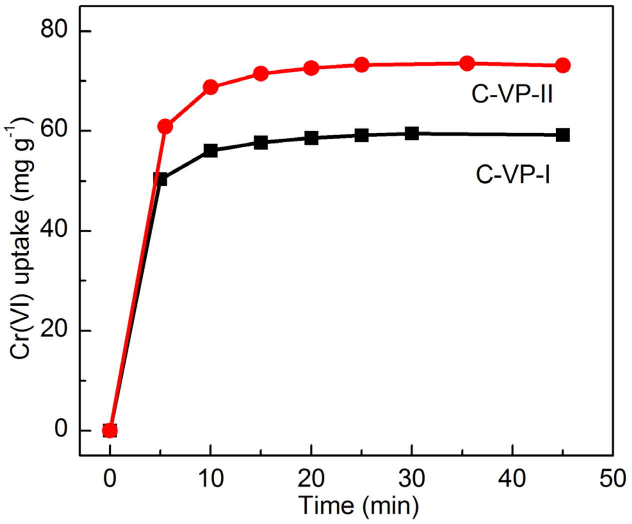

Fig. 6. Dynamics of Cr(VI) removal by C-VP-I and C-VP-II in 50 mL 100 mg L^{-1} solution.. (Adsorbent feed: 1.0 g L^{-1}; pH: 4.68; Cr(VI) concentration: 100 mg L^{-1}).

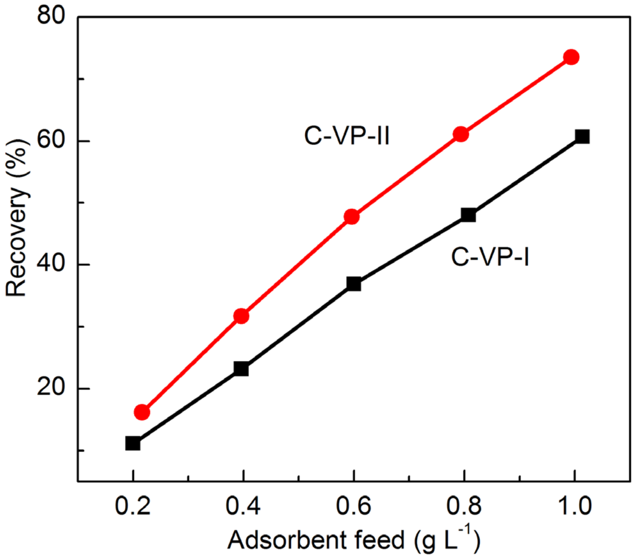

Fig. 7. The effect of adsorbent dose on the removal of Cr(VI) by the C-VP-I and C-VP-II.(Cr(VI) concentration:100 mg L^{-1}; pH: 4.68).

Table 1
Kinetic parameters for the adsorption of Cr(VI) onto C-VP-I and C-VP-II

	q_{exp} (mg g^{-1})	Pseudo-first-order model			Pseudo-second-order model		
		q_e (mg g^{-1})	k_1 (min^{-1})	R_1^2	q_e (mg g^{-1})	k_2(g mg^{-1} min^{-1})	R_2^2
C-VP-II	73.2	72.6	0.323	0.974	73.6	0.032	0.999
C-VP-I	59.1	58.7	0.379	0.932	59.5	0.043	0.999

q_{exp} (mg g^{-1}) is the experimental values of Cr(VI) uptake.

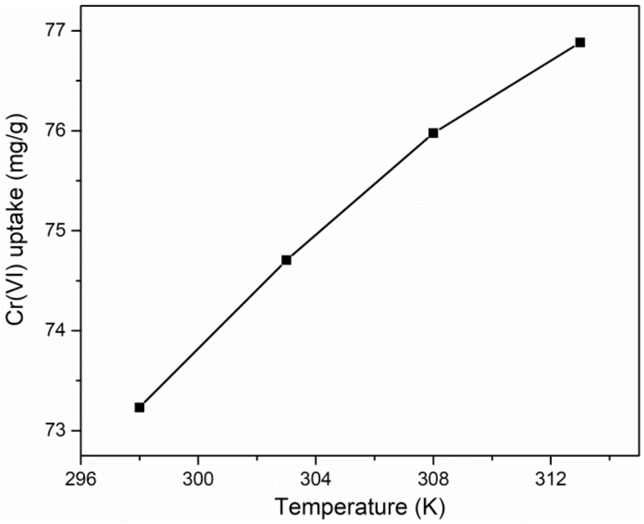

Fig. 8. The effect of temperature on the removal of Cr(VI) by the C-VP-II. (Cr(VI) concentration: 100 mg L^{-1}; adsorbent feed: 1.0 g L^{-1}, pH: 4.68).

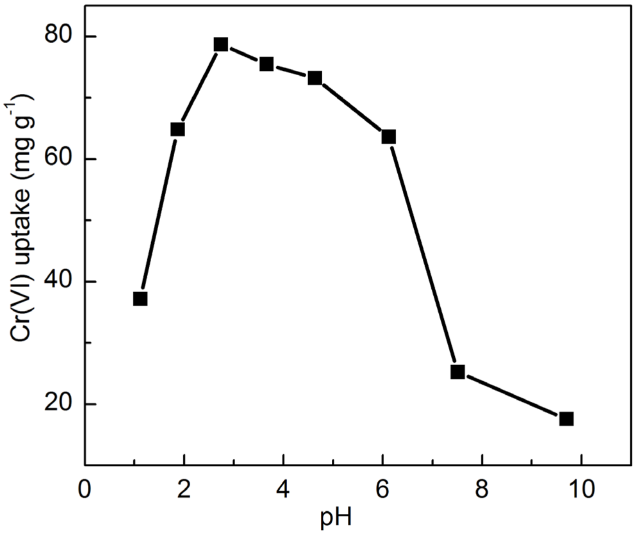

Fig. 9. The effect of pH on Cr(VI) adsorption by C-VP-II. (Cr(VI) concentration: 100 mg L^{-1}; adsorbent feed: 1.0 g L^{-1}).

sivity of Cr(VI) ions from the external layer into the micro pores of the C-VP-II with the increasing temperature. The temperature had little effect on the adsorption capacity and low temperature was more energy efficient. Taking all these factors into consideration, these experiments were carried out at 298 K.

3.2.4. Effect of solution pH

Solution pH is another factor because pH affects not only the degree of ionization and speciation of adsorbate but also the surface charge of adsorbent during reaction. The result of pH affecting the Cr(VI) removal by C-VP-II is shown in Fig. 9. The Cr(VI) uptake increased from 37.2 mg g^{-1} to 76.7 mg g^{-1} as the initial solution pH increased from 1.12 to 2.74. The Cr(VI) uptake subsequently decreased steadily to 63.6 mg g^{-1} when pH increased from 2.74 to 6.12, and decreased further to 0.6 mg g^{-1} as pH increased to 11.85 . Cr(VI) can exist in various ionic forms in the solution phase, such as CrO_4^{2-}, $Cr_2O_7^{2-}$, $HCrO_4^-$, and H_2CrO_4, and their concentrations vary as a function of pH and chromium concentration [29]. In the pH range of 2 to 6, the predominant species existed as $HCrO_4^-$. The surface of adsorbent was positively charged because of the protonation of surface nitrogen containing groups. Therefore, the higher Cr(VI) adsorption could occur in low pH because of the electrostatic attraction between anionic $HCrO_4^-$ and positively charged a mine groups of absorbent. When pH was less than 2.0, the $HCrO_4^-$ species converted to $H_2Cr_2O_7$, which unfavorably interacted with the protonated amine groups. When pH > 6, $Cr_2O_4^{2-}$ was dominant and the deprotonation process occurred with increasing pH, which lead to a decrease in the number of adsorption sites. Besides, the increasing competition between OH^- and Cr(VI) species hindered the Cr(VI) adsorption. Accordingly, pH value at 2.74 was an ideal parameter for the adsorbent.

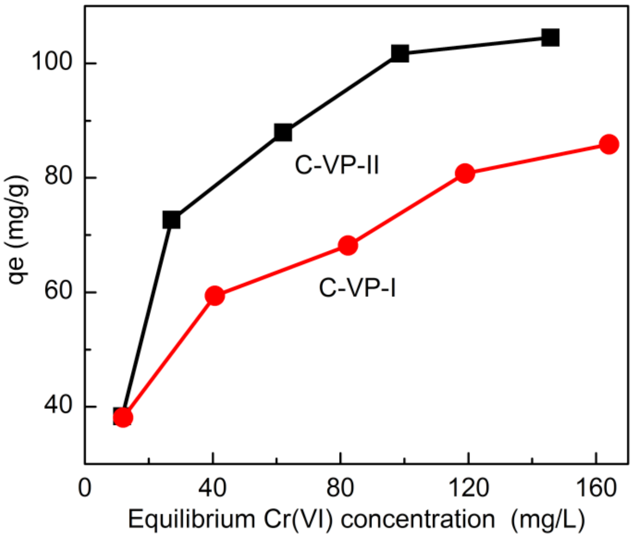

Fig. 10. Adsorption isotherms of Cr(VI) on C-VP-I and C-VP-II. (Adsorbent feed: 1.0 g L^{-1}; pH: 4.68).

3.2.5. Capacity of the adsorbent

The adsorption isotherms of Cr(VI) on C-VP-I and C-VP-II are shown in Fig. 10. To investigate the relationship between Cr(VI) species and the adsorbent and to elaborate the capacity of the adsorbent, the experimental data were analyzed by the Langmuir [30] and Freundlich isotherm model [31], which could be expressed as Eqs. (5) and (6):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \tag{5}$$

where q_m (mg g^{-1}) is the maximum adsorption capacity at monolayer, q_e (mg g^{-1}) is the amount of Cr(VI) adsorbed at equilibrium, C_e (mg L^{-1}) is the equilibrium concentration

Table 2
The isotherm model constants and correlation coefficients of Cr(VI) adsorption

Model		Langmuir			Freundlich		
	q_{exp} (mg g^{-1})	q_m (mg g^{-1})	b (L mg^{-1})	R^2	K_F (mg^{1-n} L g^{-1})	n	R^2
C-VP-I	85.9	96.5	0.041	0.990	17.97	3.227	0.985
C-VP-II	104.5	121.6	0.045	0.997	16.97	2.589	0.872

q_{exp} (mg g^{-1}) is the experimental values of Cr(VI) uptake.

of Cr(VI) in solution, b (L mg^{-1}) is the Langmuir constant related to the affinity of binding sites, which is a measure of the energy of adsorption, The slope and the intercept of the linear plot of C_e/q_e vs. C_e enable the constants of Langmuir adsorption isotherm to be determined,

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

where K_F (L mg^{-1}) is the Freundlich constant related to the adsorption capacity of the adsorbent and η is the heterogeneity factor which can indicate the adsorption intensity of the adsorbent.

Simulated isotherm parameters and correlation coefficients (R^2) are listed in Table 2. A comparison of R^2 for the two isotherm models revealed that the Langmuir model could be better described the adsorption process than Freundlich model. These results suggested the adsorption of Cr(VI) onto C-VP was monolayer, and the surface of C-VP was homogeneous. The Langmuir constant b was related to the affinity of binding sites, which could be considered as a measure of the energy of adsorption. The essential characteristic of the Langmuir isotherm can be expressed using RL, which is a dimensionless constant equal to $1/(1+bC_0)$. C_0 is the initial Cr(VI) concentration. The RL values calculated were between 0 and 1, indicating the adsorption of Cr(VI) on the C-VP is a favorable one. The maximum adsorption uptake q_m of C-VP-I and II determined from the Langmuir model was 96.5 mg g^{-1} and 121.6 mg g^{-1}, which were higher than the experimental values. It might be attributed to the incomplete contact of Cr(VI) and the adsorbent. The maximum adsorption uptake of C-VP-II was higher than most reported adsorbents [32–34], demonstrating that C-VP was a promising material for Cr(VI) removal.

3.2.6. Desorption and regeneration

The regeneration ability is very important for its practical application. For the regeneration, the Cr(VI)-adsorbed C-VP-II are eluted with 100 mL NaOH solution (0.1 M) for 1 h and more than 95% of the adsorbed Cr(VI) anions were desorbed from C-VP-II. The C-VP-II was subsequently protonated in 1 mol L^{-1} HCl solution. The adsorption–desorption experiments are repeated for five cycles, and the results are shown in Fig. 11. The adsorption capacity was 73.4 mg g^{-1} at the first cycle and then slightly deceased to 66.2 mg g^{-1} at the fifth cycle. The results indicate that the obtained adsorbents have good regeneration ability.

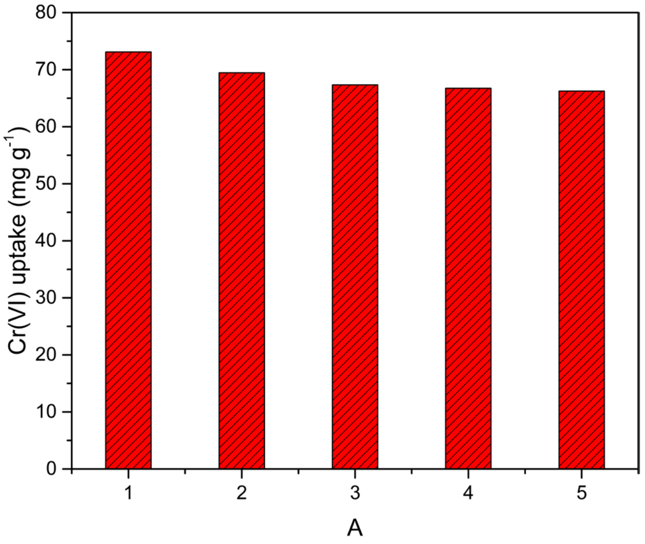

Fig. 11. Cr(VI) uptake of C-VP-II in five successive cycles of desorption–adsorption (pH: 4.68; adsorbent feed: 1.0 g L^{-1}).

4. Conclusion

A novel cellulose-based microspheres adsorbent for Cr(VI) removal was synthesized successfully by radiation grafting of 4VP onto cellulose microspheres. The structure of adsorbent was verified with FT-IR analysis. The adsorption equilibrium can be achieved with 25 min due to the strong electrostatic interaction between the adsorbent and $HCrO_4^-$. The optimum adsorption was observed at pH 2.74 for initial Cr(VI) concentration of 100 mg L^{-1}. The Cr(VI) adsorption followed pseudo-second order mode. The adsorption experimental data fitted Langmuir isotherm with maximum theoretical Cr(VI) uptake of 121.6 mg g^{-1}. Also, it was observed that C-VP can be used several times with only slight loss in adsorption capacity. Based on the experiment results, the prepared C-VP is a promising adsorbent for Cr(VI) removal with high efficiency.

Acknowledgments

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Supporting information

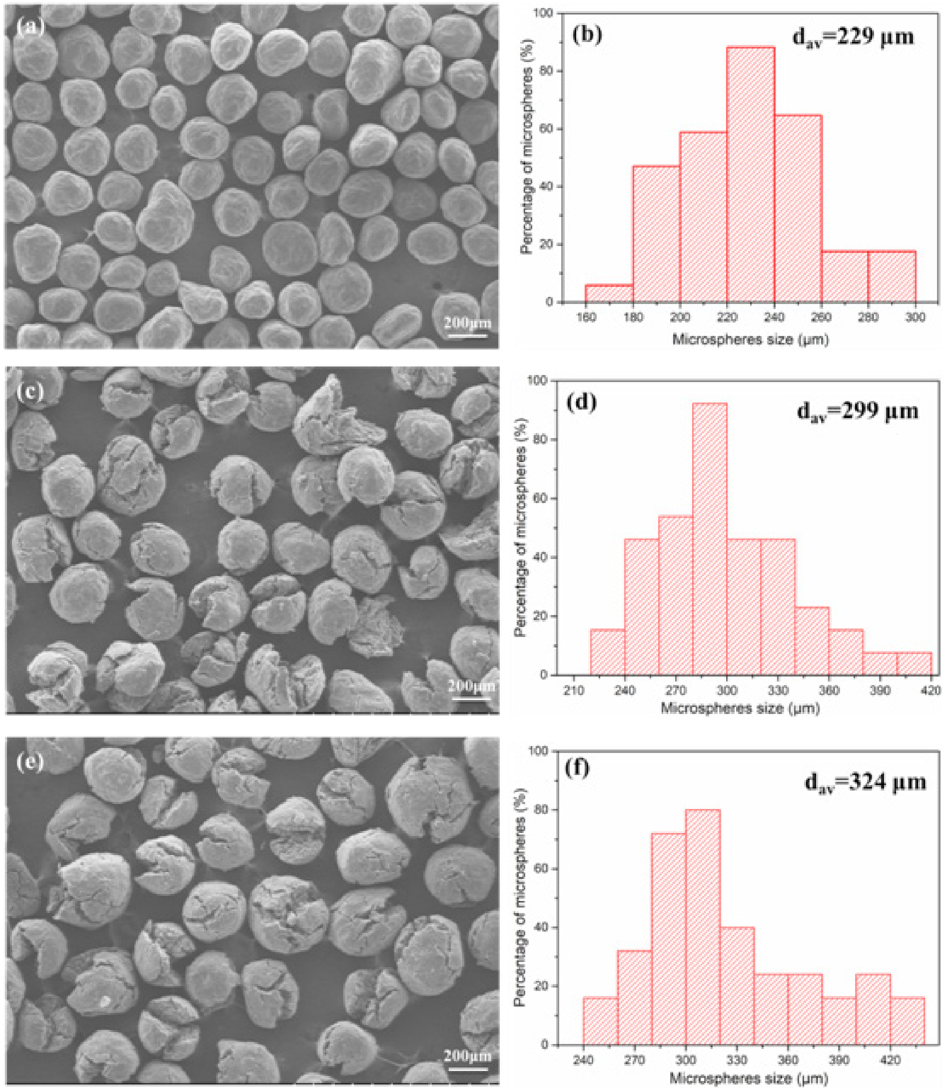

Fig. S1. SEM images of the cellulose microspheres (a), C-VP-I (c) and C-VP-II (e); microspheres size histograms of the cellulose microspheres (b), C-VP-I (d) and C-VP-II (f). (100 microspheres counted for every sample).