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# Preparation of anion exchange resin by recycling of waste printed circuit boards

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# Abstract

The traditional treatment of the non-metal components of waste printed circuit boards (WPCBs), mainly thermosetting epoxy resins (TEPRs) is very difficult because they are inflexible and insoluble, and thus a new method to convert them into anion exchange resin by chloromethylation and quaternization was studied. The ion exchange capacity (IEC) of the product is  $2.4345 \text{ m} \cdot \text{mol} \cdot \text{g}^{-1}$  and the thermal stability is up to 200°C. The application of the produced anion exchange resin to adsorption of Cr(VI) is studied in detail. The adsorption of Cr(VI) is confirmed by Raman spectrum and the maximum adsorption capacity is  $47.85 \text{ mg} \cdot \text{g}^{-1}$ . As for the isotherms adsorption model, the Langmuir model is more appropriate than Freundlich. The adsorption kinetics is determined and activation energy (Ea) is found to be 3.51KJ·mol<sup>-1</sup>.

**Keywords**: WPCBs, Chloromethylation, Quaternization, Anion exchange resin, Isotherms, Kinetics

# 1. Introduction

Recently waste electric and electronic equipment (WEEE) is increasing sharply due to the increase development of electrical apparatus such as personal computer, mobile phone, and electric vehicle<sup>[1]</sup>. As for the essential part of these electronic equipment, the printed circuit boards (PCBs) are the first to get most attention<sup>[2]</sup> owing to that the purity of precious metals in WPCBs is at least 10 times higher than that of rich-content minerals<sup>[3]</sup>, which makes WPCBs an attractive secondary source

of metals<sup>[4-9]</sup>. Besides these metals, WPCBs usually contains up to 70% non-metals including plastics, resin, glass fibbers, and ceramics<sup>[10-11]</sup> and thermosetting epoxy resins (TEPRs) are the main composition in WPCBs<sup>[12]</sup>.

But because TEPRs are insoluble and infusible, the treatment and recycling of such solid wastes are very difficult. Therefore, after extracting the metals, a large number of TEPRs was sent to landfill sites for disposal or incinerated with other industrial waste to provide energy<sup>[13-14]</sup>. Owing to many additives such as flame retardant containing halogen in TEPRs, the landfill and incineration result in new serious environmental pollution such as emissions of persistent organic pollutant, and thus the eco-friendly recycling gets more and more attention.

It is known that ion exchange resins based on polystyrene are owing to the functional groups introduced to the phenyl rings and the cation exchange resin by introduction of sulfonic acid groups to TEPRs is successfully prepared <sup>[15]</sup>. However the highly acidic environment will result in new pollution and degradation of C-O-C to reduce its performance. Therefore, a new method of recycling the TEPRs into anion exchange resins is studied to introduce chloromethylation and quaternary ammonium.

Chromate, a species of hexavalent chromium Cr(VI), is known to be highly toxic with a strong carcinogenicity and it is commonly used in industrial processes, such as inks, rubber, ceramics, corrosion inhibitors, and pigments for the manufacture of paints. So it is necessary to recycle Cr(VI) from aqueous solutions.

# 2. Experimental

#### 2.1. Materials

The industrial TEPRs powder of WPCBs labeled as aTEPRs was obtained from the Shanghai Solid Waste Management Centre. The simulated TEPRs powder of WPCBs labeled as bTEPRs was manufactured in the lab, 50 wt% E51/polyamide resin was cured at 80 °C and 12 h, grinded into powder of about 1 mm in diameter. The 717 phenylethylene anion exchange resin (717 IER), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, ZnCl<sub>2</sub>, paraformaldehyde, trimethylamine and hydrochloric acid (37 wt. %) were purchased by Sinopharm Chemical Reagent Co., Ltd. (China).

# 2.2.Chloromethylation and quaternization

aTEPR and bTEPR was separately processed, the powder (aTEPR or bTEPR) was dried in a vacuum oven at 110 °C for 24 h. A mixture of 10 g of dried powder, 200 mL of 37% hydrochloric acid, 10 g paraformaldehyde and 20 g ZnCl<sub>2</sub> were stirred magnetically at a fixed temperature and time to conduct chloromethylation reactions. After the reaction, the produced chloromethylated TEPRs (C-TEPRs) was washed with deionized water until the pH about 7 and dried at 60 °C for 12 h. Subsequently the C-TEPRs powders were mixed with some content of trimethylamine to produce quaternary ammonium product (Q-TEPRs) at a set temperature for 12 h. After the quaternization reaction, the Q-TEPRs were filtered and washed with deionized water until the pH about 7 and dried at 60 °C for 24 h. The mechanism of these two steps are shown in Fig. 1 and Fig. 2.



Fig. 1 Mechanism of chloromethylation



Fig. 2 Mechanism of quaternization

# 2.3. Ion exchange capacity (IEC)

IEC (m·mol·g<sup>-1</sup>) was determined by silver nitrate–base titration<sup>[16]</sup>. Cl<sup>-</sup> of resins was washed with aqueous Na<sub>2</sub>SO<sub>4</sub> in the ion exchange column, converting the resins into SO<sub>4</sub><sup>2-</sup> type. Then the SO<sub>4</sub><sup>2-</sup> resins were titrated and IEC was calculated. Dilute silver nitrate was used to titrate aqueous Na<sub>2</sub>SO<sub>4</sub> that had been partially removed by Cl<sup>-</sup> type resins. Eq. (1) was used to calculate IEC.

$$IEC = \frac{(V_2 - V_1)c_1}{m}$$
(1)

 $V_2$  and  $V_1$  are and volume of the standard solutions that used to titrate the aqueous  $Na_2SO_4$  and the blank, respectively,  $c_1$  is the molar concentration of the aqueous silver nitrate ,while m is the weight of the products (Cl<sup>-</sup> type).

# 2.4. Characterization

FTIR spectra were obtained on an Avatar 370 FTIR spectrometer, with powders dispersed in KBr powder. TGA–DTG was obtained on a Netzsch STA 409 PC

instrument at a rate of 10 °C  $\cdot$  min<sup>-1</sup> under a nitrogen atmosphere up to 800 °C.

Raman spectra were performed on a LABHR-UV. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi (Thermo Fisher Scientific China Ltd). Elemental analysis was performed on a Vario Micro cube (Elementar Analysensteme GMBH).

# **2.5.** Adsorption of Cr(VI)

Cr(VI) solutions were prepared by dissolving  $K_2Cr_2O_7$  in deionised water and adsorption were carried out under batch mode. The concentration of Cr(VI) was determined by UV-visible spectroscopy (Agilent 8453) using 1,5-diphenylcarbazide as the complexing agent at the wavelength of 540 nm. Solutions of 0.01 M NaOH and HCl were used for adjustment of pH <sup>[17]</sup>. To obtain the ion exchange isotherms and kinetics of Q-bTEPRs, the resins were washed with HCl, converted to the Cl<sup>-</sup> form and dried in an oven at 60 °C to a constant weight.

# 3. Results and discussion

# **3.1.** Ion exchange capacity

The most important parameter of ion exchange resins is IEC and Table 1 shows the IEC and SD which was calculated from Eq. (2)<sup>[18]</sup>

$$SD = \frac{G_s - G_d}{G_d} \times 100\% \qquad (2)$$

Where Gs is the weight of swollen powder and Gd is the weight of dry powder.

Table 1 The adsorption properties of 717 IER, Q-aTEPRs and Q-bTEPRs.

Sample	$IEC(mmol \cdot g^{-1})$	SD (%)
Q-aTEPRs	2.4345	19.57

Q-bTEPRs	2.7124	25.76
717 IER	3.1546	29.47

The IEC of Q-bTEPRs and Q-aTEPRs were 2.7124 and 2.4345  $m \cdot mol \cdot g^{-1}$  and they are 77.17% and 85.98% for a value of 717 IER, respectively. The SD of Q-aTEPRs is lower than that of Q-bTEPRs and 717 IER, which may because of the impurities e.g. glass fibres and residual metals. Obviously, Q-aTEPRs have good exchange capacity.

# **3.2.** Characteristics of the products

The typical photographs of TEPRs are shown in Fig. 3.



Fig. 3 Photographs of a (aTEPRs), b (C-aTEPRs), c (Q-aTEPRs), d (bTEPRs), e (C-bTEPRs), f (Q-bTEPRs)

It can be observed that the light yellow colour of aTEPRs turns brown after chloromethylation and the colour turns even darker when treated with trimethylamine. The transparent bTEPRs powder turns light yellow after chloromethylation and then turns yellow after quarternization. This may be due to the chloromethyl groups and quaternary ammonium groups that are introduced to the product respectively .

The FTIR spectra are shown in Fig.4.



Fig. 4 FTIR spectra of bTEPRs, C-bTEPRs and Q-bTEPRs

In the spectrum of bTEPRs, the vibration at 3434 cm<sup>-1</sup> is assigned to hydroxyl groups (-OH). Aromatic cyclic groups are observed by the band intensity at 1623 cm<sup>-1</sup>, and the band at 1238 cm<sup>-1</sup> is associated with the vibration of aromatic ethers (Ar-O).

After chloromethylation, there are obvious differences in the spectrum. The presence of a new peak at 732 cm<sup>-1</sup> is assigned to the symmetric and asymmetric stretching vibrations of C-Cl in C-bTEPRs.

After quaternization, two peaks at 1262 and 1219 cm<sup>-1</sup> are observed which are assigned to quantenary ammonium groups and the vibration of C-Cl at 732 cm<sup>-1</sup> decreases. These results indicate that the C-Cl is replaced by C-N and quantenary ammonium groups have been introduced to the C-bTEPRs.

Elemental analysis is shown in table 2. There is a weight loss of C and H in

C-bTEPRs compared with bTEPRs, which is due to the introduction of the chloromethyl groups. As for Q-bTEPRs, when compared with C-bTEPRs, the weight of N and H also have a great increase, indicating that quaternary ammonium groups were introduced to the product.

Table 2. Elemental Composition of TEPRs

TEPRs	N Area	C Area	H Area
bTEPRs	2894 (3.62%)	39829 (69.13%)	12620 (6.92%)
C-bTEPRs	2441 (3.25%)	33132 (60.98%)	11272 (6.616%)
Q-bTEPRs	5037 (3.84%)	64553 (68.70%)	22001 (7.11%)

XPS measurement of bTEPRs, C-bTEPRs and Q-bTEPRs were carried out and the XPS wide scan spectra are shown in Fig. 5.



Fig. 5 The XPS wide scan spectra of bTEPRs, C-bTEPRs and Q-bTEPRs.

As for the bTEPRs sample, strong peaks at about 285 eV (related to C, 1s), 533 eV (related to O, 1s) and weak peaks at about 400 eV (corresponding to N, 1 s) were observed. After chloromethylation, a new peak for chlorine (Cl, 2p, 200eV) was observed, indicating the successful chloromethylation of bTEPRs. The binding energies and element compositions are summarized in Table 3.

Samples	C1 s (285eV)	O 1s (533eV)	N 1s (400eV)	Cl 2p (200eV)
bTEPRs	80.74	16.49	2.77	_
C-bTEPRs	75.91	15.52	2.48	6.09
Q-bTEPRs	74.98	18.65	3.81	2.56

Table 3. XPS elemental compositions and atomic ratios

The content of N in Q-bTEPRs is 3.81%, higher than that in bTEPRs and C-bTEPRs, which is due to the introduction of quaternary ammonium groups.

The XPS narrow scan N 1s scan spectra for bTEPRs, along with the XPS narrow scan N 1s and curve fit for Q-bTEPRs are shown in Fig. 6.



Fig.6 The XPS narrow scan spectra of N 1s for bTEPRs and curve fitting of N 1s for the Q -bTEPRs.

Comparing the N 1s curve of bTEPRs with Q-bTEPRs, there is one new peak at about 402.2 eV, which is attributed to the  $R_4N^{+[19]}$ . The result indicates that quaternary ammonium groups are introduced.

The thermal analysis of ion exchange resins is studied to know the thermal properties of the resin<sup>[20-21]</sup> and Fig. 7 and 8 show the TG-DTG curves of bTEPRs and Q-bTEPRs, respectively.

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Fig. 7 TG-DTG curves of bTEPRs (10 °C·mn<sup>-1</sup>, N<sub>2</sub>: 50 ml·min<sup>-1</sup>)



Fig. 8 TG-DTG curves of Q-bTEPRs (10 °C·mn<sup>-1</sup>, N<sub>2</sub>: 50 ml·min<sup>-1</sup>)

There is one major weight loss at 423 °C of bTEPRs, however, the significant weight loss of Q-bTEPRs presents at 325, 405 and 527 °C, indicating the process of decomposition is different from the bTEPRs. The Q-bTEPRs has three main weight loss steps. The first weight-loss step beginning around 50 °C and up to 207.2 °C is mainly due to the loss of water<sup>[22]</sup>, The second step is the decomposition of functional

groups such as quaternary ammonium or chloromethyl groups<sup>[23]</sup>. The third step of the temperature higher than 682.3 °C corresponds to the polymer backbone degradation<sup>[24]</sup>. The TG curve demonstrates that the Q-bTEPRs have a good thermal stability and high degradation temperature.

## 3.3. Adsorption of Cr(VI)

Cr(VI) is toxic material and it is quite soluble in the aqueous phase almost over the entire pH range and mobile in the natural environment<sup>[18]</sup>. Therefore, the prepared anion exchange resin is studied to adsorb Cr(VI).

Raman spectra of Cr(VI) solution, Q-bTEPRs and Cr(VI)-loaded Q-bTEPRs are shown in Fig. 9.



Fig. 9 Raman spectra of Cr(VI) solution, Q-bTEPRs and Cr(VI)-loaded Q-bTEPRs

The vibrations of the bands at 640.9, 825.3, 1116.3 and 1188.5 cm<sup>-1</sup> are the characteristic peaks of Q-bTEPRs. After the adsorption of Cr(VI), a new peak is observed at 900.5 cm<sup>-1</sup> indicating that Cr(VI) ions have been introduced to the structure of Q-bTEPRs. Yue  $Min^{[25]}$  also observed a Cr(VI) peak at 854.2 cm<sup>-1</sup> for

absorbed Cr(VI) on amine surfactant modified peanut shell, which was attributed to the surface interaction species. The Cr(VI) solution (5 g·L<sup>-1</sup>) has a characteristic peak at 908.4 cm<sup>-1</sup>, which is consistent with Xu's result<sup>[26]</sup> that Cr(VI) ion in a 0.5 mol·L<sup>-1</sup> of potassium dichromate solution has a characteristic peak at 903.3 cm<sup>-1</sup>. However, it is observed that the characteristic peak of Cr(VI) solution (908.4 cm<sup>-1</sup>) is shifted to a new peak (900.5 cm<sup>-1</sup>) after the sorption of Cr(VI) into Q-bTEPRs. This indicates that the bonding environment between Cr(VI) and Q-bTEPRs is quite different from that of free Cr(VI) ions in solution and confirms that the Cr(VI) can be adsorption with the prepared anion exchange resin.

# 3.3.1. Effect of pH

The pH value of solution is one of the most important parameters for the adsorption of Cr(VI) whose speciation is governed by the solution acidity. Some experiments were carried out to examine the effect of initial pH on the adsorption of Cr(VI) with 100 mg $\cdot$ L<sup>-1</sup> solutions and 0.1g resin at 298 K under 120 r·min<sup>-1</sup> agitation for 150 min.

Fig. 10 shows the effect of pH on the Cr(VI) adsorption. A major drop is observed in removal extent as pH value increases from 1.0 to 8.0.



Fig. 10 Effect of pH on adsorption quantity

The adsorption capacity of Cr(VI) sharply reduces from 44.25 mg·g<sup>-1</sup> to 28.22 mg·g<sup>-1</sup> as the pH value increases from 4.0 to 7.0.That's because the chromate may be represented in various forms in the solution phase as a function of pH. When the pH value is in the range of 1.0-3.0, there exists a mixture of Cr(VI) speciation, including HCrO<sub>4</sub><sup>-</sup>, HCr<sub>2</sub>O<sub>7</sub><sup>-</sup>, Cr<sub>3</sub>O<sub>10</sub><sup>2-</sup> and Cr<sub>4</sub>O<sub>13</sub><sup>2-</sup> and decreasing the pH value results in the formation of more polymerized chromium oxide species<sup>[27]</sup>. Fewer active sites on Q-bTERs are needed to complete the ion exchange with more polymerized chromium oxide species with the same electric charge, leading to a high level of Cr(VI) ion uptake. In the pH value range of 3.0-6.0, the speciation of Cr(VI) is stable at HCrO<sub>4</sub><sup>-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2- [28]</sup>, which needs one active site to finish on corresponding Cr(VI) removal. The decrease of adsorption at higher pH value (pH>6) could be explained by the dual competition caused by the increasing of OH<sup>-[29]</sup>.

# 3.3.2. Effect of time and temperature

Experiments were carried out at 298 K with 100 mg $\cdot$ L<sup>-1</sup> solutions and 0.1 g resin under 120 r $\cdot$ min<sup>-1</sup> agitation at pH 2. The results in Fig. 11 shows that the adsorption of

Cr(VI) almost finished within 120 min. With increasing temperature, the adsorption of Cr(VI) increased.



Fig. 11 Effect of time and temperature on adsorption

#### 3.4. Ion exchange isotherms and kinetics

# 3.4.1. Ion-exchange isotherms

The most powerful tools for the analysis of adsorption processes are isotherms.The Langmuir and Freundlich isotherm models are widely used to study adsorption.

The Langmuir isotherm is expressed as <sup>[30]</sup>:

$$\frac{C_{e}}{q_{e}} = \frac{C_{e}}{Q_{0}} + \frac{1}{Q_{0}b} \qquad (3)$$

Where Ce is the equilibrium concentration  $(mg \cdot L^{-1})$ ,  $q_e$  is the solid-phase adsorbate concentration at equilibrium  $(mg \cdot g^{-1})$ ,  $Q_0$  is theoretical monolayer adsorption capacity  $(mg \cdot g^{-1})$  and b is related to the energy of adsorption  $(L \cdot mg^{-1})$ .

The Freundlich isotherm model is expressed as <sup>[31]</sup>:

$$\log q_e = \log k_f + (1/n) \log C_e \quad (4)$$

Where  $k_f$  is adsorption capacity and *n* is related to the intensity of adsorption.

The Langmuir isotherm describes adsorption on a homogenous surface and the model is derived from several assumptions, such asthe uniform energies of the adsorption site and no transmigration of adsorbates on the surface of materials. The Freundlich isotherm is appreciable to heterogeneous surfaces and multilayer adsorption<sup>[31]</sup>.

Fig. 12 shows a study of the maximum adsorption of Cr(VI) from its solution (100 mg·L<sup>-1</sup>) by 0.1 g of resin was done at pH 2 by varying the concentration of Cr(VI), the mixture was agitated at 120 r·min<sup>-1</sup> at 298 K until the adsorption equilibrium.



Fig. 12 Sorption isotherm of Cr(VI) by 0.1g resin at pH 2

Figs. 13 and 14 show linearized Langmuir and Freundlich adsorption of Cr(VI).



Fig. 13 Langmuir isotherm for ion exchange of Cr(VI) on Q-bTEPRs (pH2.0; vibration frequency,  $120r \cdot min^{-1}$ ; initial metal concentration,  $100mg \cdot L^{-1}$ )



Fig. 14 Freundlich isotherm for ion exchangeofCr(VI) on Q-bTEPRs (pH, 2.0; vibration frequency,  $120r \cdot min^{-1}$ ; initial metal concentration,  $100 \text{ mg} \cdot \text{L}^{-1}$ )

The Langmuir and Freundlich adsorption constants, evaluated from isotherms, and correlation coefficients are presented in Table 4.

Table 4 Parameters of Langmuir and Freundlich isotherms for the ion exchange of metals on Q-bTEPRs.

	Langmuir constants		Freundlich constants			
	$Q_{\theta}(\mathrm{mg}\cdot\mathrm{g}^{-1})$	$b(L \cdot mg^{-1})$	$R^2$	$k_f$	п	$R^2$
Cr(VI)	47.847	0.175	0.9986	14.904	3.679	0.8149

The correlation coefficients of Cr(VI) were 0.9986 and 0.8149, respectively. The Langmuir isotherm model is a better fit to the equilibrium adsorption data.

# 3.4.2. Adsorption kinetics

According to Helfferich's theory <sup>[32]</sup>, there are three equations to determine the controlling step of ion exchange.

Film diffusion	$\mathbf{F} = \frac{3c_0 k_m}{aQr} t \tag{5}$
Particle diffusion	$1 - 3(1 - F)^{\frac{2}{3}} + 2(1 - F) = \frac{6\overline{D}c_0}{aQr^2}t \qquad (6)$
Chemical reaction	$1 - (1 - F)^{1/3} = \frac{k_c c_0}{r} t \tag{7}$

Where  $c_0$  is the initial concentration of Cr(VI),  $k_m$  is film diffusion coefficient, a is stoichiometric coefficient, Q is ion exchange capacity, r is particle radius,  $\overline{D}$  is effective coefficients of the solid phase,  $k_c$  is the rate constant of chemical reaction. As for the different equations, the results show in Fig. 15.



Fig. 15 Fitting curves for the controlling step estimation of ion-exchange kinetics

Based on linear fitting, obviously F and t have the best linear relationship and thus film diffusion is the rate controlling step<sup>[33]</sup>.

As the temperature increases the slope of the curves increase, the results are shown in Fig. 16



Fig. 16 Fitting curves of the adsorption kinetics at various temperatures

The adsorption rate constants K obtained from the slope is shown in Table 5.

T (K)	$k x 10^{-3} (g \cdot mg^{-1} \cdot min^{-1})$	$R^2$
298	2.3	0.9942
303	2.5	0.9964
308	2.6	0.9903
313	2.7	0.9950

Table 5 Adsorption rate constants and R<sup>2</sup> at different temperature

The  $R^2$  at different temperature are 0.9942, 0.9964, 0.9903 and 0.9950 respectively that further proved the dominant procedure is film diffusion control.

The rate constant K can be expressed in Arrhenius form of  $\ln K = \frac{-Ea}{RT} + A$ , where R (8.314 J·mol<sup>-1</sup>·k<sup>-1</sup>) is the universal gas constant, T is the temperature (K), A is the pre-exponential factor and Ea is the activation energy (J·mol<sup>-1</sup>). The plot of lnK versus T<sup>-1</sup> is shown in Fig. 17.



Fig. 17 Relationship between apparent rate constant and temperature

According to the Arrhenius equation, the apparent adsorption activation energy is  $3.51 \text{ kJ} \cdot \text{mol}^{-1}$ , thus the adsorption kinetic equations is shown as eqn (8).

$$K = 0.2968 \times \exp(\frac{-3.51 \times 10^3}{8.314 \times T})$$
(8)

The positive value of Ea indicates that the adsorption is endothermic and that higher temperature favours adsorption.

# 4. Conclusions

Thermosetting epoxy resins (aTEPRs), non-metal materials from WPCBs, were recycled into anion exchange materials by chloromethylation and quarternization and the method is a low cost method to produce a high-value product. The maximal IEC was 2.4345 m·mol·g<sup>-1</sup> and it can be used safely up to 200 °C.

The prepared anion exchange materials is an effective adsorbent for the removal of Cr(VI) and the optimal pH for adsorption of Cr(VI) is 2.0. The Langmuir and Freundlich isotherm models were studied to fit the experimental data and the Langmuir isotherm is more appropriate. The adsorption capacity for Cr(VI) were calculated from the Langmuir model of 47.847 mg·g<sup>-1</sup>. Using the Arrhenius Equation, the activation energy of adsorption was calculated, and the activation energy is 3.15 kJ·mol<sup>-1</sup>, indicating that the adsorption processes are endothermic.

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# Preparation of anion exchange resin by recycling of waste printed circuit boards

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# Abstract

The traditional treatment of the non-metal components of waste printed circuit boards (WPCBs), mainly thermosetting epoxy resins (TEPRs) is very difficult because they are inflexible and insoluble, and thus a new method to convert them into anion exchange resin by chloromethylation and quaternization was studied. The ion exchange capacity (IEC) of the product is 2.4345 mmol·g<sup>-1</sup> and the thermal stability is up to 200°C. The application of the produced anion exchange resin to adsorption of

Cr(VI) is studied in detail. The adsorption of Cr(VI) is confirmed by Raman spectrum and the maximum adsorption capacity is 47.85 mg·g<sup>-1</sup>. As for the isotherms adsorption model, the Langmuir model is more appropriate than Freundlich. The adsorption kinetics is determined and activation energy (Ea) is found to be 3.51 KJ·mol<sup>-1</sup>.

The graphic abstract is as below:

