

# Adsorption of cesium from aqueous solution using agricultural residue Walnut shell: Equilibrium, kinetic and thermodynamic modeling studies

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1       **Adsorption of cesium from aqueous solution using agricultural residue - walnut shell:**

2                       **Equilibrium, kinetic and thermodynamic modeling studies**

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15     **Abstract**

16     A novel biosorbent derived from agricultural residue - walnut shell (WS) is reported to remove cesium from aqueous  
17     solution. Nickel hexacyanoferrate (NiHCF) was incorporated into this biosorbent, serving as a high selectivity trap  
18     agent for cesium. Field emission scanning electron microscope (FE-SEM) and thermogravimetric and differential  
19     thermal analysis (TG-DTA) were utilized for the evaluation of the developed biosorbent. Determination of kinetic  
20     parameters for adsorption was carried out using pseudo first-order, pseudo second-order kinetic models and  
21     intra-particle diffusion models. Adsorption equilibrium was examined using Langmuir, Freundlich and  
22     Dubinin-Radushkevich adsorption isotherms. A satisfactory correlation coefficient and relatively low chi-square  
23     analysis parameter  $\chi^2$  between the experimental and predicted values of the Freundlich isotherm demonstrate that  
24     cesium adsorption by NiHCF-WS is a multilayer chemical adsorption. Thermodynamic studies were conducted under

25 different reaction temperatures and results indicate that cesium adsorption by NiHCF-WS is an endothermic ( $\Delta H^\circ > 0$ )  
26 and spontaneous ( $\Delta G^\circ < 0$ ) process.

27 Keywords: Walnut shell; Nickel hexacyanoferrate (NiHCF); Cesium adsorption; Integrated analysis.

## 28 **1. Introduction**

29 Removal of pollutants from industrial wastewater has become one of the most important issues recently for the  
30 increase in industrial activities, especially for heavy metals and radionuclides. Since the big nuclear accident at  
31 Fukushima, Japan in 2011, a large amount of radionuclides were released into water, soil and air, and the hazardous  
32 influence of radioactive wastewater has drawn much attention all over the world. Among radionuclides,  $^{137}\text{Cs}$  is  
33 considered the most abundant and hazardous due to diverse sources and relatively long half-life. Furthermore, it can  
34 be easily incorporated into terrestrial and aquatic organisms because of its similar chemical characteristics with  
35 potassium (Nilchi et al. 2011, Plazinski and Rudzinski 2009). As a result, numerous efforts have been undertaken to  
36 find effective and low cost methods to separate and remove cesium (Cs) from waste solutions (Karamanis and  
37 Assimakopoulos 2007, Lin et al. 2001, Nilchi et al. 2011, Parab and Sudersanan 2010, Volchek et al. 2011).  
38 Generally speaking, the investigated physical-chemical methods for separation and removal of Cs are precipitation,  
39 solvent extraction, adsorption, ion exchange, electrochemical and membrane processes (Avramenko et al. 2011, Chen  
40 et al. , 2013, Delchet et al. 2012, Duhart et al. 2001, Karamanis and Assimakopoulos 2007, Lin et al. 2001). Among  
41 them, solvent extraction, ion exchange and adsorption methods are most widely used. However, due to the high cost  
42 of materials, large-scale application of solvent extraction is limited. In the case of ion exchange process, inorganic ion  
43 exchangers are found to be superior over organic ion exchangers due to their thermal stability, resistance to ionizing  
44 radiation and good compatibility with final waste forms (Nilchi et al. 2002, Plazinski and Rudzinski 2009). Natural  
45 occurring clay minerals such as zeolite, bentonite and montmorillonite are usually used as low cost adsorption  
46 materials for  $\text{Cs}^+$  removal from aqueous solution, however the main disadvantage is the competitive interactions of  
47 other monovalent cations, in particular  $\text{Na}^+$  and  $\text{K}^+$  that can considerably block  $\text{Cs}^+$  adsorption (Borai et al. 2009,  
48 El-Naggar et al. 2008, Goñi et al. 2006, Lehto 1987, Plazinski and Rudzinski 2009).

49 Transition metal hexacyanoferrates, especially nickel hexacyanoferrate (NiHCF) is known as a highly selective  
50 agent for  $\text{Cs}^+$  adsorption (Chen et al. , 2013, Plazinski and Rudzinski 2009). It possesses a special cubic structure with  
51 a channel diameter of about  $3.2\text{\AA}$ , through which only small hydrated ions like  $\text{Cs}^+$  can permeate. Larger hydrated

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ions like  $\text{Na}^+$  get blocked (Plazinski and Rudzinski 2009, Pyrasch et al. 2003). However, the very fine particle size of NiHCF restricts its direct use in practice, thus proper support materials are necessary.

Recently, several kinds of low cost biosorbents have been investigated for the removal of heavy metals (Figueira et al. 2000, Plazinski and Rudzinski 2009, Reddad et al. 2002). Walnut shell, an abundant agricultural residue with good stability has been successfully used in removing heavy metals by adsorption (Altun and Pehlivan 2012, Saadat and Karimi-Jashni 2011, Zabihi et al. 2010). To the best of our knowledge, however, few studies have focused on equilibrium, kinetic and thermodynamic modeling of  $\text{Cs}^+$  adsorption using walnut shell. This study presents the first low cost biosorbent derived from walnut shell (WS) as support material incorporated into NiHCF (NiHCF-WS), fabricated for  $\text{Cs}^+$  adsorption.

## 2. Materials and methods

### 2.1 Materials

Walnut shell used in this study was obtained from Shandong province, China and was immersed and washed with pure water to remove soluble impurities until the water turned clear. The clean WS was completely dried in an oven (EYELA WFO-700, Japan) at  $105^\circ\text{C}$  for more than 24 hours, ground and sieved through No. 8 and 16 size meshes. The granules with diameter between 1~2.36 mm were selected and stored in a desiccator for further use or modification.

### 2.2 Reagents

The chemicals nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) and potassium hexacyanoferrate ( $\text{K}_3[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ ) of A.R. grade were purchased from Wako Pure Chemical Industries Ltd., Japan. Non-radioactive cesium chloride ( $\text{CsCl}$ ) purchased from Tokyo Chemical Industry Co. Ltd., Japan was used as a surrogate for  $^{137}\text{Cs}$  because of its same chemical characteristics. All the other reagents used in this study were purchased from Wako Pure Chemical Industries Ltd., Japan with no purification before use. Pure water generated from a Millipore Elix 3 water purification system (Millipore, USA) equipped with a Progard 2 pre-treatment pack was used throughout the experiments except for ICP-MS analysis.

1.26g  $\text{CsCl}$  was weighed exactly and dissolved into 1L pure water as standard stock  $\text{Cs}^+$  solution ( $1000\text{mg L}^{-1}$ ), which could be diluted to desired concentrations of  $\text{Cs}^+$  solution for further experiments.

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### 78 2.3 Modification of walnut shell

79 The modification of walnut shell contains the following steps. 10 g of clean WS granules were immersed in 100  
80 mL of 50% (v/v%) hydrochloric acid (HCl) for 10 hours at a temperature of 50°C. Then, the WS was dried in an oven  
81 at 105°C overnight after being washed until the eluent pH was almost neutral. The loading of NiCl<sub>2</sub> onto WS and the  
82 treatment of K<sub>3</sub>[Fe(CN)<sub>6</sub>]•3H<sub>2</sub>O with NiCl<sub>2</sub> loaded WS was carried out according to the method reported by Parab  
83 and Sudersanan (Parab and Sudersanan 2010). In brief, 5g of WS was immersed in 20mL of 0.5M NiCl<sub>2</sub>•6H<sub>2</sub>O  
84 solution and placed in a double shaker (Taitec NR-30, Japan) at 200 rpm and room temperature (25±1°C) for 24  
85 hours followed by filtration and washing with pure water to remove excess NiCl<sub>2</sub>•6H<sub>2</sub>O. Next, the NiCl<sub>2</sub> loaded WS  
86 was added to 10mL of 5% (wt%) K<sub>3</sub>[Fe(CN)<sub>6</sub>]•3H<sub>2</sub>O solution and placed into a water bath (SANSYO SWR-281D,  
87 Japan) at 30°C for 24 hours. The resultant NiHCF loaded WS was separated by filtration, washed with pure water  
88 and dried at 60°C. The entire procedure was repeated three times to ensure the incorporation of NiHCF onto the WS.  
89 This NiHCF-WS material was used for further characterization as well as Cs<sup>+</sup> adsorption studies.

### 90 2.4 Kinetic studies

91 4g of NiHCF-WS was mixed with 200mL Cs<sup>+</sup> solution (adsorbent dosage of 20g L<sup>-1</sup>) in a 200mL-glass flask  
92 (AS ONE, Japan) under initial Cs<sup>+</sup> concentration of 10mg L<sup>-1</sup>, and the flask was shaken by a double shaker (TAITEC  
93 NR-30, Japan) at 200 rpm for 48 hours. Supernatants (about 1mL for each) including the initial solution (as the zero  
94 min point) were withdrawn at predetermined time intervals prior to the Cs<sup>+</sup> concentration determination.

95 In order to investigate the mechanism of adsorption, non-linearized Lagergren pseudo first-order kinetic model  
96 (Karamanis and Assimakopoulos 2007) and pseudo second-order kinetic model (Parab and Sudersanan 2010) were  
97 applied to analyze the adsorption process, which were expressed as follows:

98 Lagergren pseudo first-order kinetic model:

$$99 \quad q_t = q_e (1 - e^{-k_1 t}) \quad (1)$$

100 pseudo second-order kinetic model:

$$101 \quad q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (2)$$

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102 where  $t$  (min) is the contact time,  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) are the adsorption rate constants;  $q_e$  and  $q_t$  ( $\text{mg g}^{-1}$ )  
103 represent the uptake amount of ion by the adsorbent at equilibrium and time  $t$ , respectively.

104 In addition, the determination of the limiting step of the adsorption process is necessary by predicting the  
105 diffusion coefficient using a diffusion based model. The possibility of intra-particle diffusion resistance affecting the  
106 adsorption was explored in this study by using the intra-particle diffusion equation (Delchet et al. 2012) as follows:

$$107 \quad q_t = k_p t^{1/2} + C \quad (3)$$

108 where  $t$  (min) is the contact time,  $q_t$  ( $\text{mg g}^{-1}$ ) is the  $\text{Cs}^+$  uptake amount at time  $t$ ,  $k_p$  ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) is the intra-particle  
109 diffusion rate constant determined from the slopes of the linear plots.  $C$  is the constant, which indicates the thickness  
110 of the boundary layer, i.e., the larger the value of  $C$  the greater is the boundary layer effect.

## 111 **2.5 Equilibrium studies**

112 A fixed amount of NiHCF-WS was mixed with 20mL  $\text{Cs}^+$  solution in a 50mL-polypropylene tube (VIOLAMO,  
113 Japan) at a shaking speed of 200rpm. Resultant supernatants were withdrawn after 24 hours prior to the  $\text{Cs}^+$   
114 concentration determination.

### 115 **2.5.1 Adsorption isotherms**

116 To optimize the design of a adsorption system, it is important to establish the most appropriate correlation for  
117 equilibrium conditions (Parab and Sudersanan 2010). According to different adsorption mechanisms, there are  
118 currently several different adsorption isotherms used for fitting experimental adsorption results. Among these,  
119 Langmuir (Langmuir 1918), Freundlich (Freundlich 1907) and Dubinin-Radushkevich (D-R) (Dubinin et al. 1947)  
120 isotherms are widely used and therefore are applied in this study. The nonlinear forms of these isotherms are given as  
121 follows:

$$122 \quad \text{Langmuir isotherm: } q_e = \frac{q_m b C_e}{1 + b C_e} \quad (4)$$

$$123 \quad \text{Freundlich isotherm: } q_e = k_f C_e^n \quad (5)$$

$$124 \quad \text{D-R isotherm: } q_e = q_m \exp(-\beta \varepsilon^2) \quad (6)$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

125 where,  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of  $\text{Cs}^+$  adsorbed at equilibrium,  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration of  $\text{Cs}^+$ .  $b$   
 126 ( $\text{L mg}^{-1}$ ) is a constant related to the free energy or net enthalpy of adsorption ( $b \propto e^{-\Delta G/RT}$ ) (Mohan and Singh 2002),  
 127 and  $q_m$  ( $\text{mg g}^{-1}$ ) is the adsorption capacity at the isotherm temperature.  $k_f$  and  $n$  are equilibrium constants indicative of  
 128 adsorption capacity and adsorption intensity respectively.  $\beta$  ( $\text{mol}^2/\text{kJ}^2$ ) is the constant related to the adsorption energy,  
 129  $R$  ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) is the gas constant and  $T$  (K) is the absolute temperature of the aqueous solution.

### 131 2.5.2 Role of ion exchange

132 In the case of anionic metal hexacyanoferrate complexes, it is assumed that there is a true exchange between  $\text{K}^+$   
 133 and  $\text{Cs}^+$  (Haas 1993, Lehto 1987). Therefore, an attempt was made to link the  $\text{Cs}^+$  adsorption to its likely ion  
 134 exchange reaction with  $\text{K}^+$  through equilibrium studies. In addition to the batch experiments, a blank experiment was  
 135 carried out by adding a corresponding amount of adsorbent into the same volume of pure water instead of  $\text{Cs}^+$   
 136 solutions. The  $\text{Cs}^+$  adsorbed and  $\text{K}^+$  released was calculated according to mass balance using the equations below:

$$A_{\text{Cs}^+} = \frac{(C_0 - C_e)V}{133} \times 1000 \quad (8)$$

137 where  $A_{\text{Cs}^+}$  ( $\mu\text{mol}$ ) is the amount of  $\text{Cs}^+$  adsorbed by NiHCF-WS,  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial concentration of  $\text{Cs}^+$ ,  $C_e$   
 138 ( $\text{mg L}^{-1}$ ) is the equilibrium concentration of  $\text{Cs}^+$ ,  $V$  (L) is the volume of solution and 133 is the molar mass of Cs.

$$R_{\text{K}^+} = \frac{(C_e - C_b)V}{39} \times 1000 \quad (9)$$

140 where  $R_{\text{K}^+}$  ( $\mu\text{mol}$ ) is the amount of  $\text{K}^+$  released into solution,  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration of  $\text{K}^+$ ,  $C_b$   
 141 ( $\text{mg L}^{-1}$ ) is the concentration of  $\text{K}^+$  in the blank solution,  $V$  (L) is the volume of solution and 39 is the molar mass of  
 142 K.

### 144 2.6 Thermodynamic studies

145 In order to obtain the thermodynamic nature of the adsorption process, 0.2g NiHCF-WS was added into 20mL  
 146  $\text{Cs}^+$  solutions with an initial concentration of  $10 \text{ mg L}^{-1}$  (adsorbent dosage of  $10 \text{ g L}^{-1}$ ) at different temperatures (298,  
 147 308 and 318K) for 24h. Thermodynamic parameters, namely, standard Gibbs free energy ( $\Delta G^\circ$ ), standard enthalpy  
 148 ( $\Delta H^\circ$ ) and standard entropy ( $\Delta S^\circ$ ) changes were also determined in order to obtain the thermodynamic nature of the

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149 adsorption process. The amounts of  $\Delta H^\circ$  and  $\Delta S^\circ$  could be calculated from the slope and intercept of the straight line  
150 obtained from plotting  $\ln Kd$  versus  $1/T$ , respectively using the following equation (Nilchi et al. 2011, Tsai et al.  
151 2009):

$$\ln Kd = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

153 where  $Kd$  ( $\text{mL g}^{-1}$ ) is the distribution coefficient,  $R$  ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) is the gas constant and  $T$  (K) is the absolute  
154 temperature of the aqueous solution.

155 After obtaining  $\Delta H^\circ$  and  $\Delta S^\circ$  values of the adsorption,  $\Delta G^\circ$  of each temperature was calculated by the  
156 well-known equation as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

## 158 2.7 Analysis

159 All of the samples were collected by filtering supernatants through  $0.22\mu\text{m}$  mixed cellulose ester membrane  
160 (Millipore, Ireland) and diluted with pure water to a proper extent (below  $1\text{mg L}^{-1}$ ) into 15mL-polypropylene tubes  
161 (VIOLAMO, Japan) prior to inductively coupled plasma-mass spectrometry (ICP-MS) (Perkin Elmer ELAN DRC-e,  
162 USA) analysis.

163 In order to evaluate the probable differences in structure between raw and modified walnut shell, field emission  
164 scanning electron microscope (FE-SEM) analysis was performed using a JEOL JSM-6330F type microscope. A  
165 thermogravimetric and differential thermal analysis (TG-DTA) of WS and NiHCF-WS was carried out using a  
166 thermal analyzer (EXSTAR TG/DTA 7300, Japan) equipped with an AS-3 auto sampler. About 7.5mg of each  
167 sample was prepared into an aluminum-PAN, heated up to  $500^\circ\text{C}$  at a constant rate of  $10^\circ\text{C min}^{-1}$  in normal  
168 atmosphere for thermal analysis using an open-Al-pan as reference. The whole procedure is shown in Fig.S1 (see  
169 Electronic Supplementary Material) during which the air flow rate was kept at  $200\text{mL min}^{-1}$ .

170 The concentrations of  $\text{Cs}^+$  and  $\text{K}^+$  in aqueous samples were analyzed by a fully quantitative analytical method on  
171 a Perkin Elmer ELAN DRC-e ICP-MS in standard mode. Each sample was analyzed 5 times and the average was  
172 taken. The relative standard deviation (RSD) of multiple measurements was less than 2% and in most cases, less than  
173 1.5%.



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## 174 2.8 Calculation

175 The Cs<sup>+</sup> adsorption results are given as uptake amount ( $q$ ) and distribution coefficient ( $Kd$ ). The Cs<sup>+</sup> uptake  
176 amount  $q$  (mg g<sup>-1</sup>) was calculated from the mass balance as follows:

$$177 \quad q = \frac{(C_0 - C_t)V}{1000M} \quad (12)$$

178 Distribution coefficient  $Kd$  (mL g<sup>-1</sup>), which is mass-weighted partition coefficient between solid phase and liquid  
179 supernatant phase reflecting the selectivity for objective metal ions, was calculated according to the formula:

$$180 \quad Kd = \frac{C_0 - C_t}{C_t} \times \frac{V}{M} \quad (13)$$

181 where,  $C_0$  and  $C_t$  (mg L<sup>-1</sup>) are the concentrations of Cs<sup>+</sup> at contact time of 0 (initial concentration) and  $t$  determined  
182 by ICP-MS,  $V$  (mL) is the volume of Cs<sup>+</sup> solution and  $M$  (g) is the mass of adsorbent used.

## 183 2.9 Quality assurance and quality control

184 In order to ensure reliability and improve accuracy of the experimental data in this study, kinetic and equilibrium  
185 studies on Cs<sup>+</sup> adsorption were conducted in duplicate with a mean  $\pm$ SD being reported. All of the figures and the  
186 kinetic fitting displayed in this paper were accomplished using the Origin 7.5 program (OriginLab, USA).

## 187 3. Results and discussion

### 188 3.1 Characterization of biosorbent

#### 189 3.1.1 Field emission scanning electron microscope (FE-SEM)

190 The FE-SEM images of walnut shell before and after modification are shown in Fig.1. It can be seen that the raw  
191 walnut shell has a complex and multilayer structure including the obvious fibrous lignocellulosic (Fig.1a). After  
192 modification, there is a remarkable difference in the surface structure of walnut shell with NiHCF particles attached  
193 on the surface of walnut shell, as depicted by the arrows in Fig.1b.

#### 194 3.1.2 Thermogravimetric and differential thermal analysis (TG-DTA)

195 A large number of reactions occur during the thermal degradation of lignocellulosic materials. Therefore, a  
196 thermal degradation pre-study conducted on the biomass material, is very important in terms of the efficient design of

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197 thermochemical processes for the conversion of biomass into energy and products (Damartzis et al. 2011). The  
198 TG-DTA curves, which display the thermal degradation characteristics for the WS and NiHCF-WS, were recorded as  
199 a function of time (Fig.2). Based on the TG curves, it can be said that the major mass loss occurred in the thermal  
200 degradation of WS (98.2%) and NiHCF-WS (96.4%), respectively. Their TG curves can be divided into three parts;  
201 representing loss of water, volatilization of hemicellulose like contents, and decomposition of cellulose and lignin  
202 components (Kar 2011). Compared with WS, the second and last parts of the TG curves obtained from the  
203 NiHCF-WS were obviously different with shorter time needed. It can be seen that approximately 37.4% of TG loss  
204 occurred during the second part and finished at a time of about 28 minute for the NiHCF-WS. However, the positive  
205 peak of the DTA curve was more obvious than that of WS, which might be due to the loss of impurities with lower  
206 calorific value than hemicellulose during the modification. Another great difference, the third part began at time of 30  
207 minutes and temperature of about 350°C, much lower than WS, indicating the decomposition temperature greatly  
208 decreased after modification. During this step, approximately 52.3% of TG was lost, higher than that of WS.

209 Through comparing the TG-DTA results of WS and NiHCF-WS, it can be concluded that the modification  
210 process didn't alter the thermal stability of WS and therefore NiHCF-WS can be used as a thermally stable adsorbent.

### 211 **3.2 Effect of contact time and kinetic study**

212 Fig.3 shows the effect of contact time on the Cs<sup>+</sup> adsorption and application of kinetic models to Cs<sup>+</sup> adsorption  
213 by WS and NiHCF-WS. Table 1 lists the sorption rate constants associated with pseudo first and second order kinetic  
214 models. It can be seen from Fig.3 that Cs<sup>+</sup> adsorption is a rapid process, about 2h is needed to reach equilibrium for  
215 the NiHCF-WS. The equilibrium uptake amount of Cs<sup>+</sup> was greater than 0.5mg g<sup>-1</sup>. In addition, the adsorption  
216 process on only-WS is complicated and not efficient with an equilibrium uptake amount of approximately 0.1mg g<sup>-1</sup>.  
217 It is clearly indicated that the NiHCF-WS has a much better adsorption performance for Cs<sup>+</sup> than only-WS.

218 Compared to the first-order model, the pseudo second-order kinetic model had a higher correlation coefficient  
219 for NiHCF-WS, suggesting that the Cs<sup>+</sup> adsorption process is a chemisorption rather than physisorption.

220 Fig.4 shows the amount of adsorbed Cs<sup>+</sup>,  $q_t$  (mg g<sup>-1</sup>), versus the square root of time for NiHCF-WS. The  
221 presence of three linear regions on the curve is possibly due to the presence of three steps during the adsorption  
222 process (Damartzis et al. 2011): an external mass transfer step such as the boundary layer diffusion occurred first,  
223 then an intra-particle diffusion step for the second and lastly a saturation step. In this study, the first linear region with

224 a high slope signaled a rapid external diffusion stage depicting macro-pore or inter-particle diffusion, which is  
225 different from the second step, gradual adsorption stage controlled by intra-particle (micro-pore) diffusion, and the  
226 last step (saturation stage). This observation can also be linked with adsorption mechanisms mainly involving the  
227 surface layers of crystallites (Ramaswamy 1999).

### 228 3.3 Equilibrium studies

#### 229 3.3.1 Cesium adsorption isotherms

230 In order to obtain the equilibrium isotherm, the initial Cs<sup>+</sup> concentration varied from 5-400 mg L<sup>-1</sup> (5, 10, 20, 50,  
231 75, 100, 200, 400) while maintaining an adsorbent dosage of 20g L<sup>-1</sup>, and the amount of adsorbed Cs<sup>+</sup> was  
232 investigated.

233 Fig.5 shows the application of nonlinear Langmuir, Freundlich and D-R isotherms to the Cs<sup>+</sup> adsorption on  
234 NiHCF-WS. In this study, chi-square analysis was applied to estimate the degree of difference ( $\chi^2$ ) between the  
235 experimental data and the isotherm data, which is calculated by the following equation (Mirmohseni et al. 2012):

$$236 \quad \chi^2 = \sum \frac{(q_e^{\text{exp}} - q_e^{\text{cal}})^2}{q_e^{\text{cal}}} \quad (12)$$

237 where  $q_e^{\text{cal}}$  (mg g<sup>-1</sup>) is the equilibrium uptake amount calculated from the isotherm and  $q_e^{\text{exp}}$  (mg g<sup>-1</sup>) is the  
238 experimental equilibrium uptake amount. A smaller  $\chi^2$  value indicates a better fitting isotherm.

239 In addition, the values of normalized standard deviation (NSD (%)) were also calculated to validate the fitness of  
240 isotherm to experimental data (Karamanis and Assimakopoulos 2007), which is defined as:

$$241 \quad \text{NSD}(\%) = 100 \times \sqrt{\frac{\sum [(q_e^{\text{exp}} - q_e^{\text{cal}}) / q_e^{\text{exp}}]^2}{N - 1}} \quad (13)$$

242 where  $N$  is the number of measurements. Similarly, a smaller NSD (%) value indicates a better fitting isotherm.

243 The results of  $\chi^2$  and NSD (%) are given in Table 2 and indicate the three adsorption isotherms match the  
244 experimental data ( $R^2 > 0.9$ ). Although the  $R^2$  value of the Freundlich isotherm is similar with that of the Langmuir or  
245 D-R isotherm, the  $\chi^2$  and NSD (%) values of the Freundlich isotherm are much smaller, implying that the adsorption  
246 of Cs<sup>+</sup> on NiHCF-WS is a multilayer adsorption rather than monolayer adsorption. Furthermore, the value of  $n$  is less  
247 than 1, suggesting this adsorption process is favorable (Parab and Sudersanan 2010).

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248 As another important function, the Langmuir isotherm could give us the estimated maximum adsorption capacity  
249 ( $q_m$ ) of NiHCF-WS,  $4.94\pm 0.5\text{mg g}^{-1}$ , which is similar to that provided by D-R isotherm. In conclusion, the adsorption  
250 isotherms demonstrated that the  $\text{Cs}^+$  adsorption onto NiHCF-WS is a multilayer chemical ion exchange process.

### 251 **3.3.2 Role of ion exchange with $\text{K}^+$**

252 It is hypothesized that if adsorption is mainly caused by ion exchange reaction, then the quantity of the released  
253 cations (in gram-equivalent) would be close to that of the adsorbed target ions. Table 3 shows the relationship  
254 between the  $\text{Cs}^+$  adsorbed and  $\text{K}^+$  released during the  $\text{Cs}^+$  adsorption process and two significant phenomena are  
255 observed. With the increase in dosage (No.1-4) and initial  $\text{Cs}^+$  concentration (No.4-7), both  $\text{Cs}^+$  adsorbed and  $\text{K}^+$   
256 released increase, demonstrating affinity between them. On the other hand, the test results reveal that the amount of  
257  $\text{K}^+$  released into solutions are greater than that of  $\text{Cs}^+$  adsorbed except for the dosage of  $5\text{g L}^{-1}$  (probably caused by  
258 experimental error). In other words, the released  $\text{K}^+$  from the adsorbent is not completely exchanged by  $\text{Cs}^+$   
259 (Avramenko et al. 2011, Loos-Neskovic et al. 2004), which is also in agreement with the relationship between  $\text{Ca}^{2+}$   
260 released and  $\text{Cs}^+$  adsorbed reported by Miah (Miah et al. 2010). This indicates that the amount of  $\text{K}^+$  released into the  
261 solution is partly through dissolution other than ion exchange with  $\text{Cs}^+$ . However, it is not clearly demonstrated the  
262 existence of chemical ion exchange process between  $\text{Cs}^+$  and  $\text{K}^+$  from the data reported in this table. Basing on the  
263 above conclusion that the existence of dissolution of  $\text{K}^+$ , as a result, the variations between adsorbed  $\text{Cs}^+$  and released  
264  $\text{K}^+$  at the same dosage ( $20\text{g L}^{-1}$ ) and different initial  $\text{Cs}^+$  concentrations are compared in order to determine the  
265 possible equal relationship between them. As a comparison between No.4 and 5, the variation of adsorbed  $\text{Cs}^+$  is  
266  $8.94\pm 0.07\mu\text{mol}$ , which is similar with the variation of released  $\text{K}^+$  ( $8.72\pm 0.03\mu\text{mol}$ ). In addition, the variation of  
267 adsorbed  $\text{Cs}^+$  between No.5 and 6 is  $2.01\pm 0.08\mu\text{mol}$ , which is also similar with the variation of released  $\text{K}^+$   
268 ( $3.31\pm 0.17\mu\text{mol}$ ). When the initial  $\text{Cs}^+$  concentration is increased from 200 to  $400\text{mg L}^{-1}$  (No.6 and 7), the variation  
269 of adsorbed  $\text{Cs}^+$  ( $2.21\pm 0.11\mu\text{mol}$ ) is similar with released  $\text{K}^+$  ( $2.91\pm 0.09\mu\text{mol}$ ). Through the above comparisons, it is  
270 consequently concluded that there is indeed an exchange process between  $\text{Cs}^+$  and  $\text{K}^+$ . The  $\text{K}^+$  in the NiHCF-WS  
271 plays an important role in the  $\text{Cs}^+$  adsorption process as the ion exchanger.

### 272 **3.4 Thermodynamic study**

273 The distribution coefficient  $Kd$  was calculated using Eq. (13). The plotting of  $\ln Kd$  versus  $1/T$  gave a straight  
274 line with a correlation coefficient ( $R^2$ ) of 0.99 (see Fig.S2 in Electronic Supplementary Material), from which the  
275  $\Delta H^\circ$  and  $\Delta S^\circ$  was determined using Eq. (10). Furthermore, the standard Gibbs free energy at each temperature was

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276 calculated using Eq. (11) and the results are listed in Table 4.

277 As shown in Table 4, the distribution coefficient of  $\text{Cs}^+$  adsorption by NiHCF-WS increased remarkably with the  
278 increase in temperature, implying that high temperature was favorable for  $\text{Cs}^+$  adsorption. The same phenomenon was  
279 observed by Nilchi et al. (Nilchi et al. 2011), who used copper hexacyanoferrate to adsorb  $\text{Cs}^+$  from aqueous solution.  
280 The negative amounts of  $\Delta G^\circ$  at different temperatures and the positive amount of  $\Delta H^\circ$  revealed that the chemical ion  
281 exchange process was a spontaneous and endothermic adsorption reaction in this study.

## 282 **4. Conclusion**

283 Walnut shell, an agricultural residue, was reused as a support material for effective cesium adsorption from  
284 aqueous solution and the integrated analysis of adsorption of cesium from aqueous solution using NiHCF-WS was  
285 carried out. The rapid adsorption process fitted well with the pseudo second-order kinetic model with the equilibrium  
286 cesium uptake amount above  $0.5\text{mg g}^{-1}$ . The good correlation coefficient (0.93), low  $\chi^2$  and NSD values suggest that  
287 cesium adsorption on NiHCF-WS could be best described by the Freundlich adsorption isotherm. Results showed that  
288 the NiHCF-WS was an effective adsorbent for cesium adsorption and the adsorption process was endothermic and  
289 spontaneous. In addition, the incorporation of walnut shell and NiHCF overcame the difficulty of separation of  
290 NiHCF nano-particles from solution. Basing on the conclusions in this study, more effective modification will be  
291 carried out to improve the performance of this material and thereafter the evaluation will be performed for the  
292 application of this material into treating real radioactive wastewater in future studies.

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375



**Graphic abstract:**

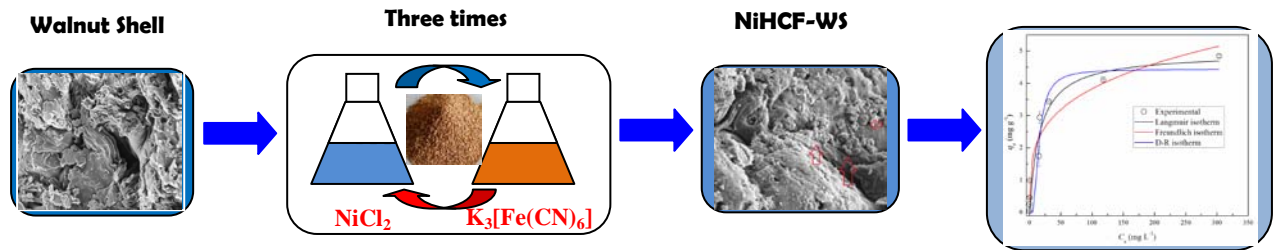


Fig. 1

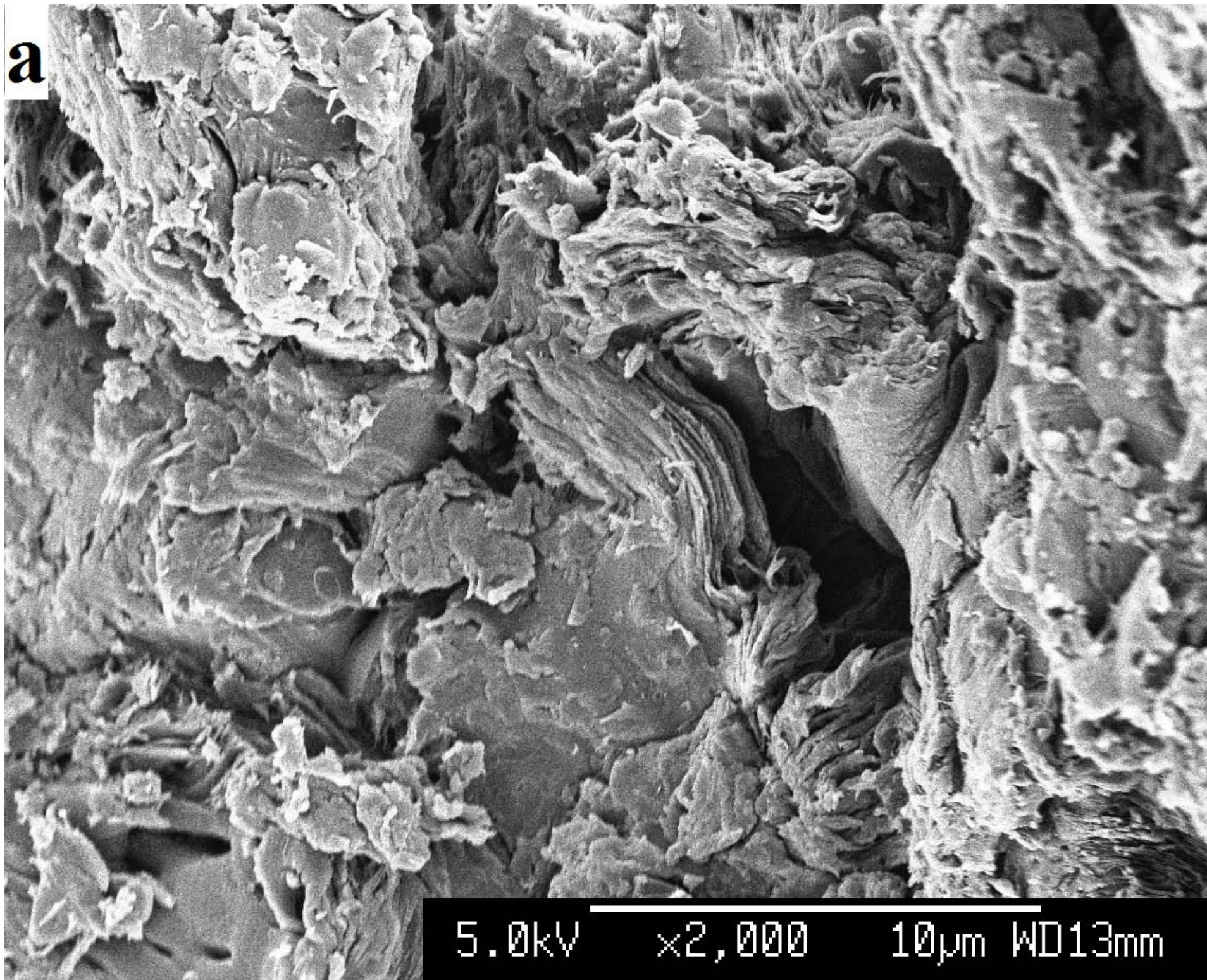


Fig. 1

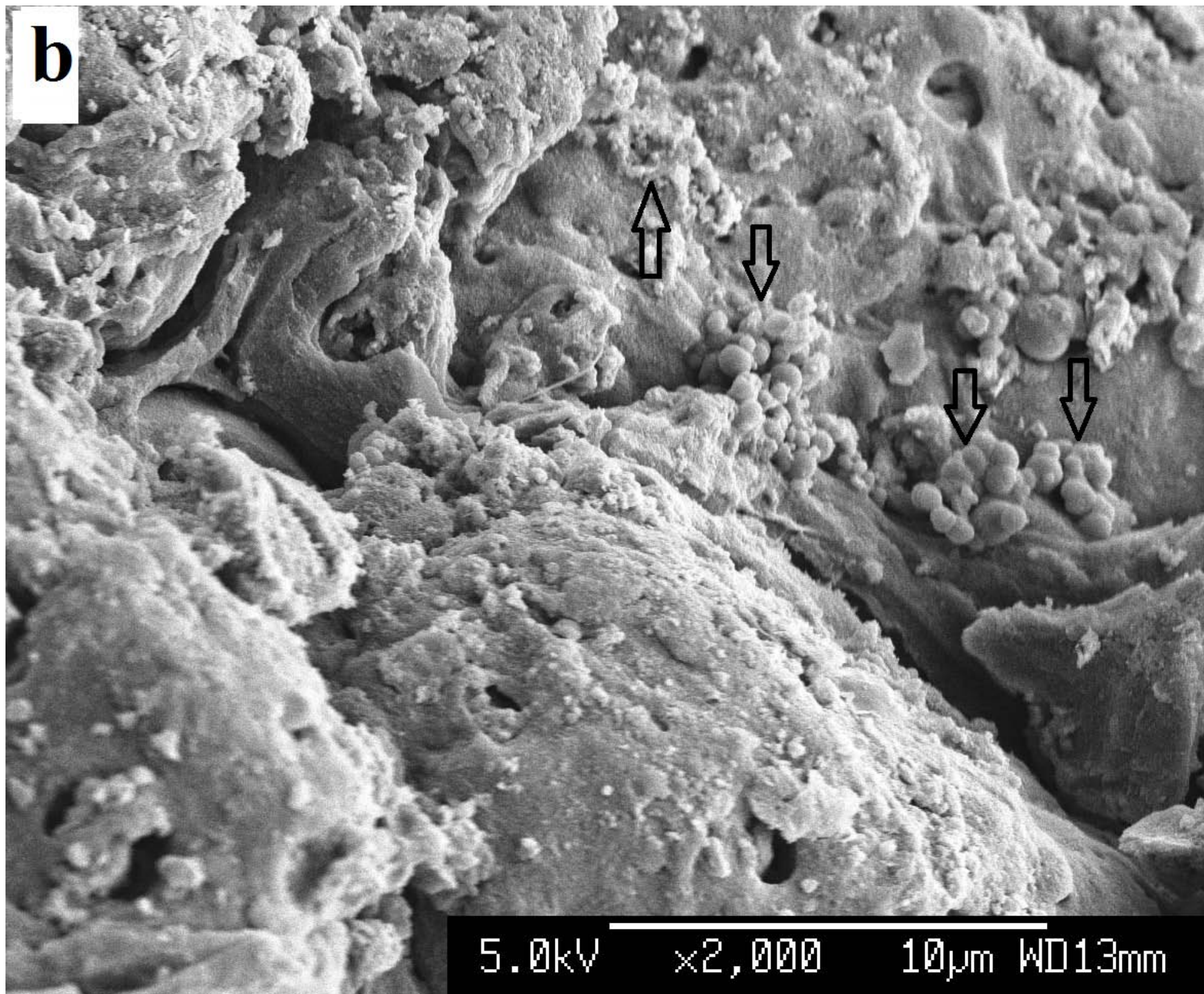


Fig. 2(1)

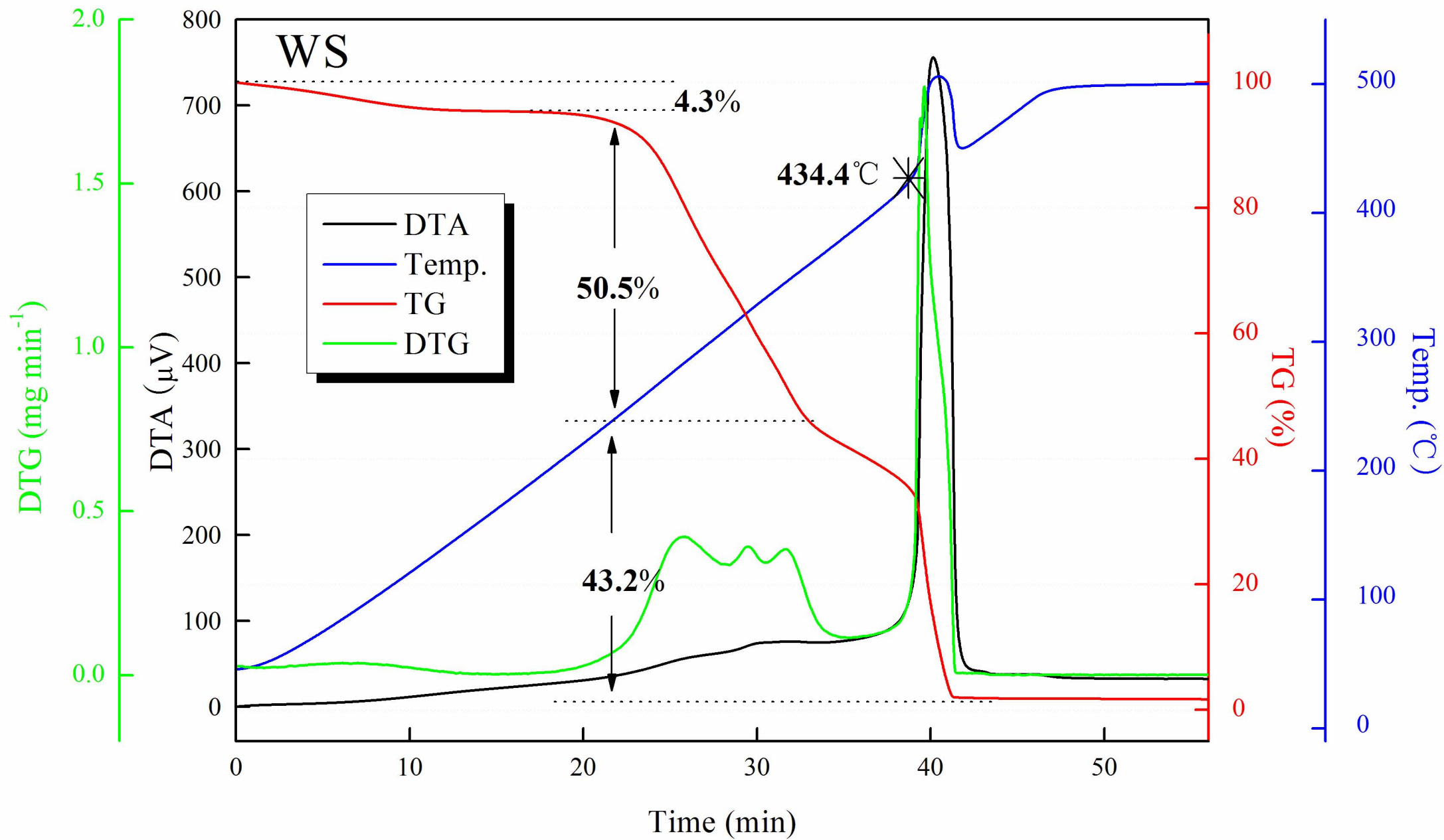


Fig. 2(2)

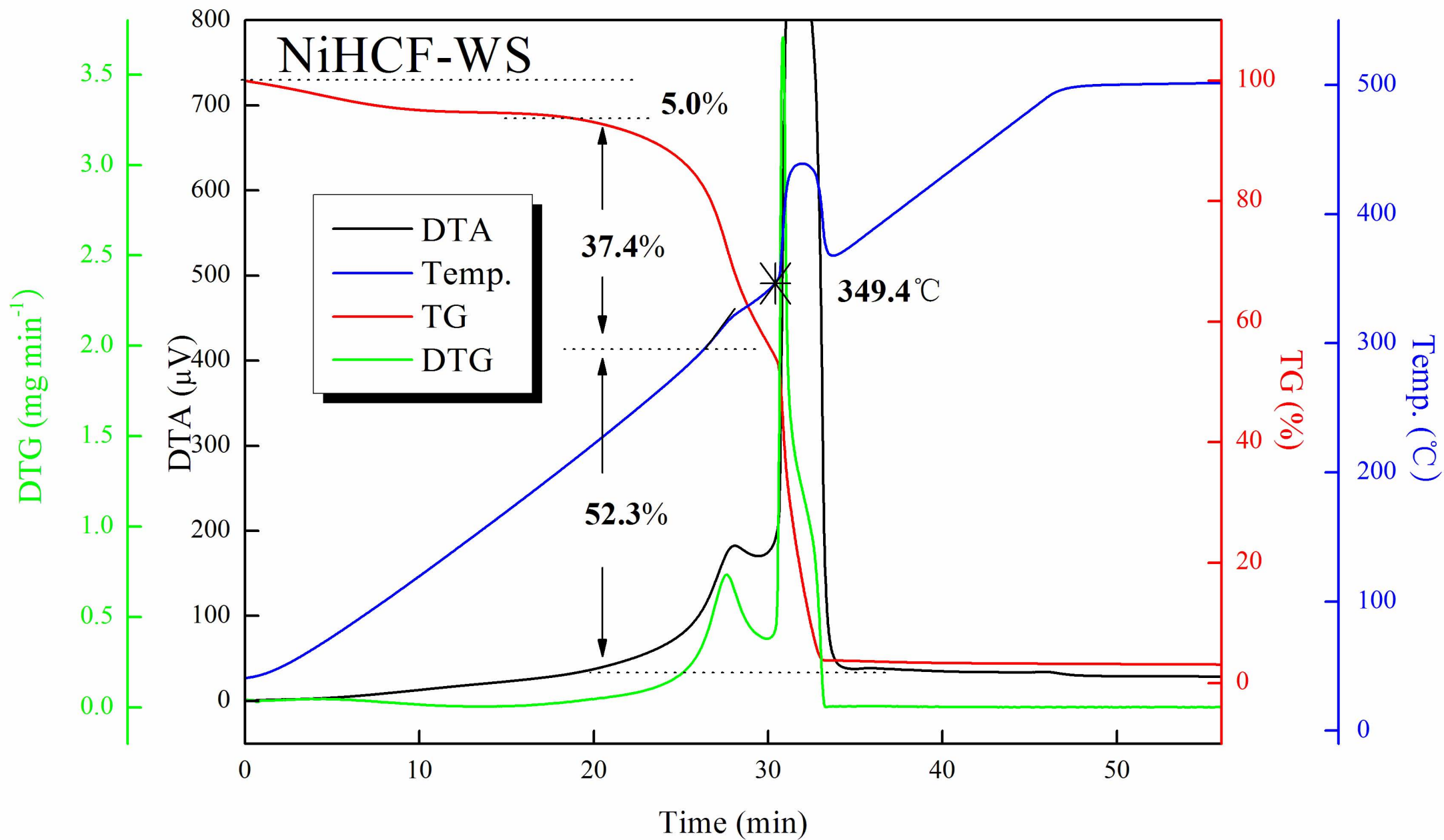


Fig. 3

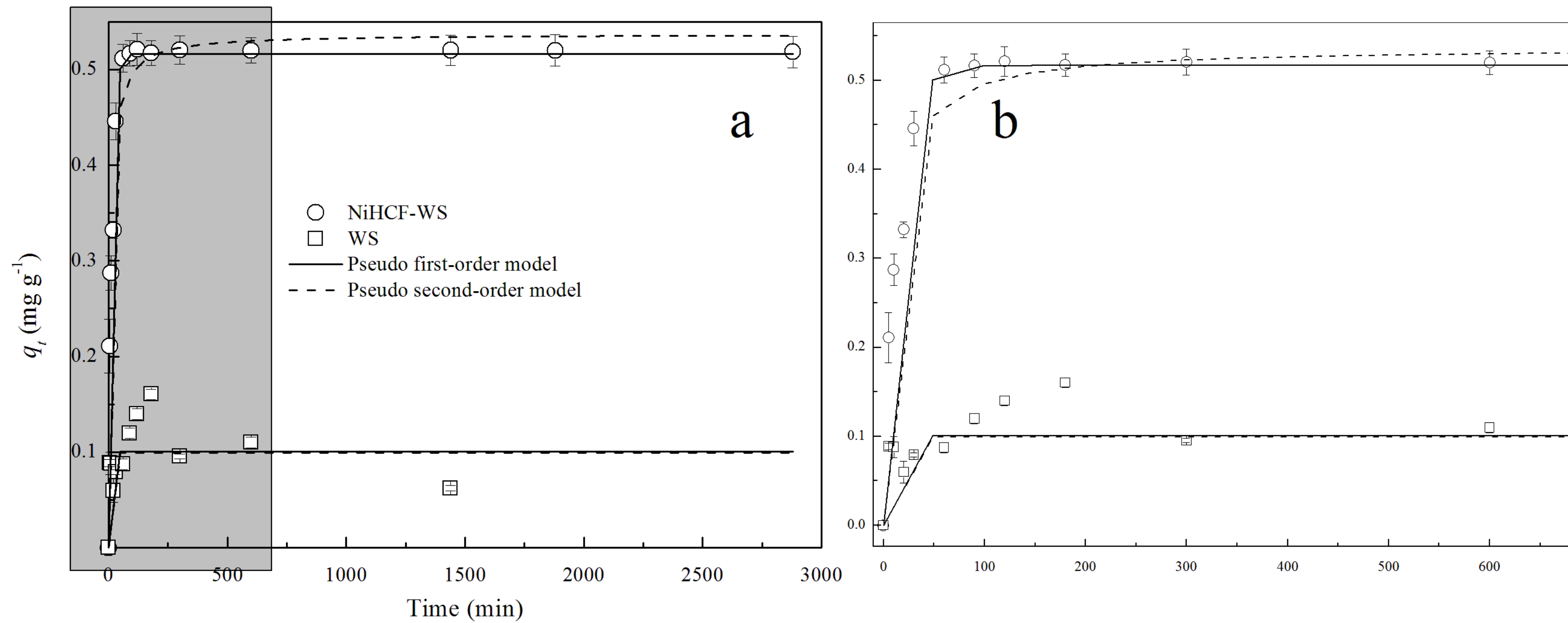


Fig. 4

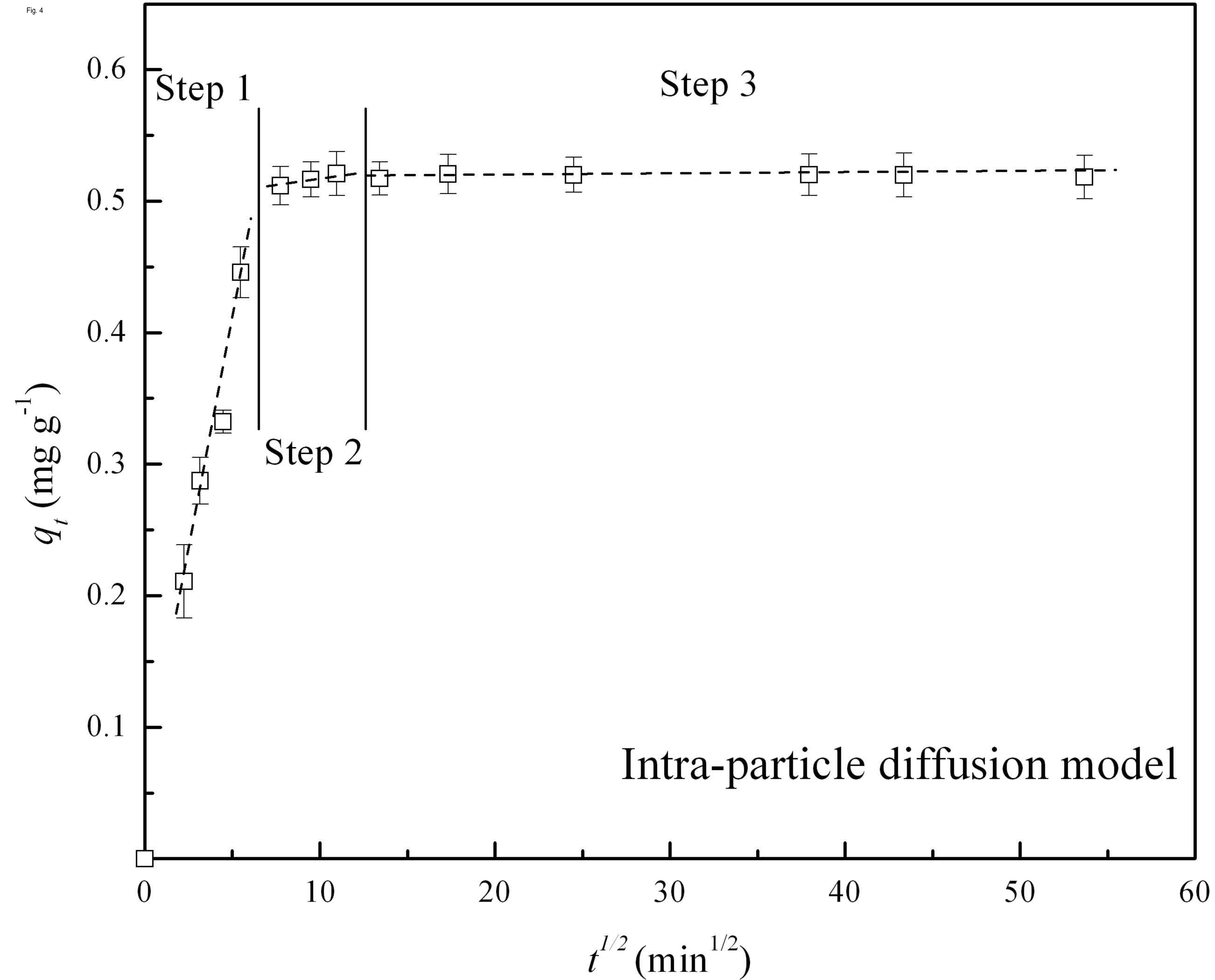


Fig. 5

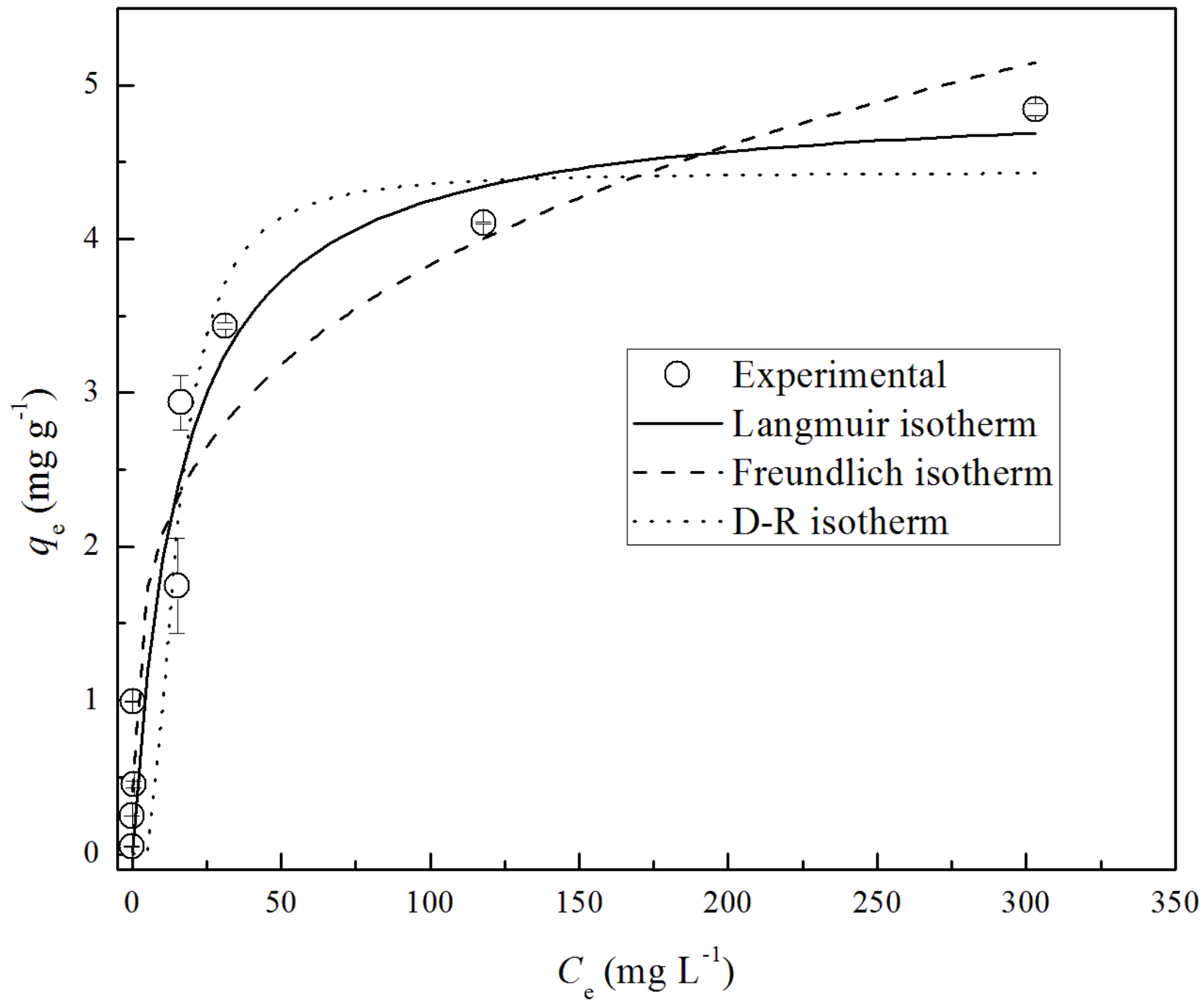




Fig. S1

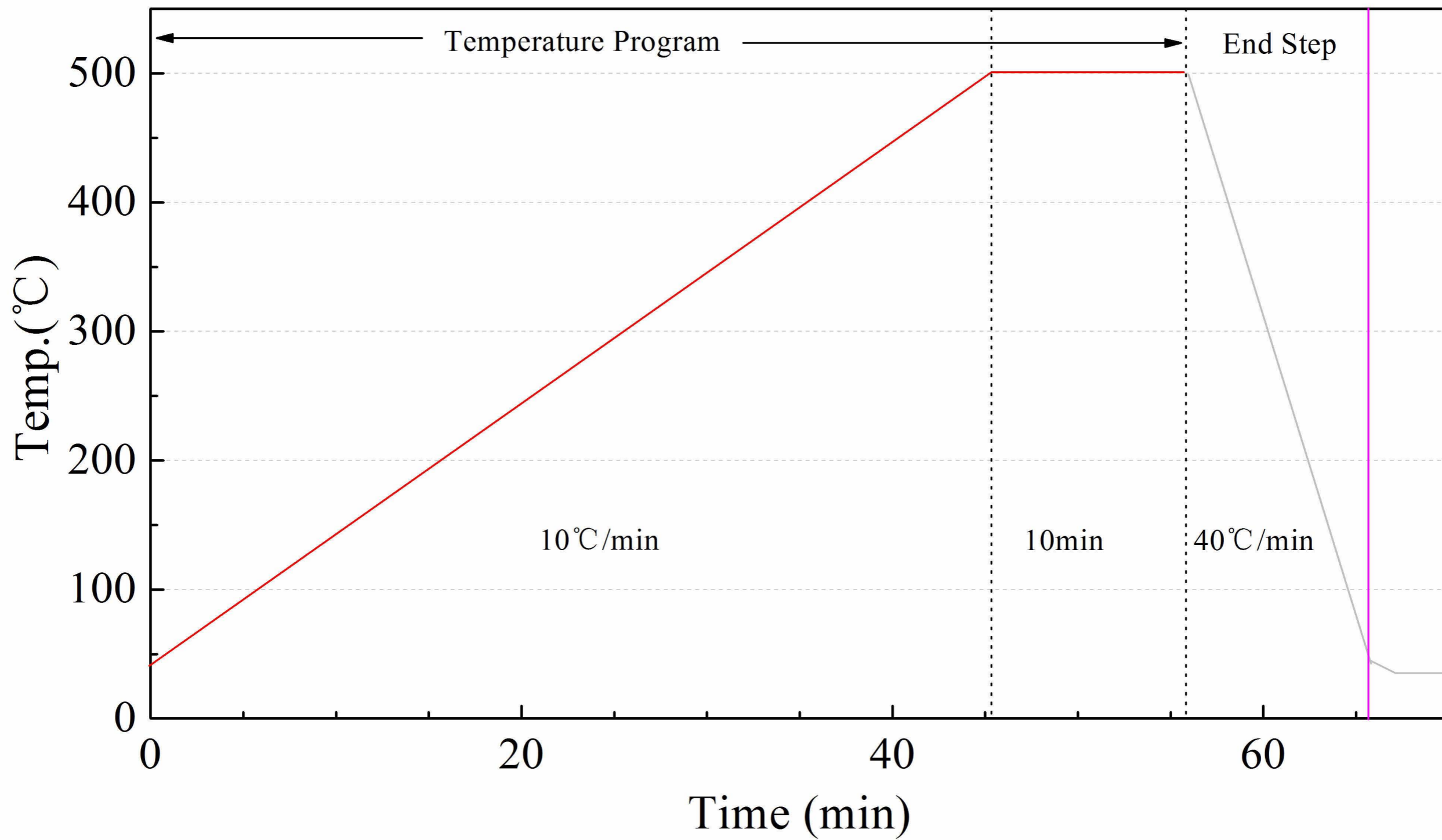
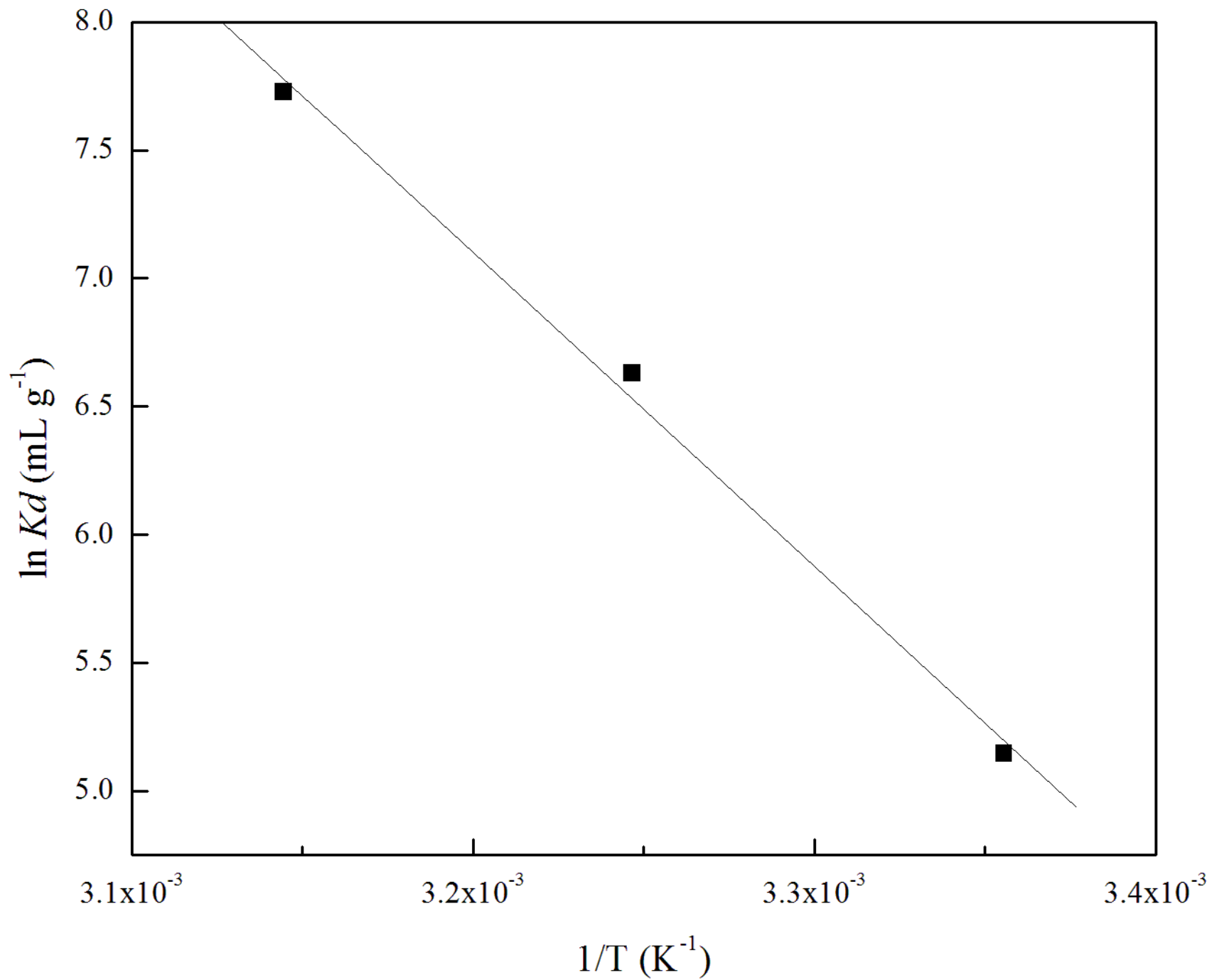


Fig. S2



**Figure captions:**

**Fig.1** – Typical scanning electron microscope images of walnut shell before (a) and after (b) modification. (Acceleration voltage of 5.0kV and 2000× magnification, arrows show the nickel hexacyanoferrate particles)

**Fig.2** – TG-DTA results of walnut shell and nickel hexacyanoferrate incorporated walnut shell obtained at the heating rate of  $10^{\circ}\text{C min}^{-1}$  in air atmosphere. (Pan: Al-Pan; Reference: Open-Al-Pan; Upper limit temperature:  $550^{\circ}\text{C}$ ; Gas flow rate:  $200\text{mL min}^{-1}$ )

**Fig.3** – Application of non-linearized pseudo first (solid line) and second (dash line) order kinetic models for cesium ( $10\text{mg L}^{-1}$ ) adsorption by walnut shell (square) and nickel hexacyanoferrate incorporated walnut shell (circle) at  $25^{\circ}\text{C}$  ( $20\text{g L}^{-1}$ ). (Fig.(b) shows the enlarged dark part in Fig.(a).)

**Fig.4** – Intra-particle diffusion model of cesium ( $10\text{mg L}^{-1}$ ) adsorption by nickel hexacyanoferrate incorporated walnut shell ( $20\text{g L}^{-1}$ ) at  $25^{\circ}\text{C}$  (Symbols represent the experimental data.)

**Fig.5** – Nonlinear Langmuir (solid line), Freundlich (dash line) and D-R (dot line) isotherms of cesium adsorption on nickel hexacyanoferrate incorporated walnut shell at  $25^{\circ}\text{C}$ . (Symbols represent the experimental data, whereas the lines represent the simulated data fitted using the adsorption isotherms.)

**Fig. S1** – Temperature program of TG-DTA analysis. (Red line represents the temperature program and only during this period the experimental data are recorded. Gray line shows the end step with a speed of  $40^{\circ}\text{C min}^{-1}$  and as said, the experimental data are not recorded during this step.)

**Fig. S2** – Effect of solution temperature on the distribution coefficient of cesium ( $10\text{mg L}^{-1}$ ) adsorption by NiHCF-WS ( $10\text{g L}^{-1}$ ) ( $R^2=0.99$ ).

Table 1

	Pseudo first-order kinetic model		Pseudo second-order kinetic model		
	WS	NiHCF-WS	WS	NiHCF-WS	
$q_{eexp}^a$ (mg g <sup>-1</sup> )	0.11±0.04	0.52±0.004	$q_{eexp}$ (mg g <sup>-1</sup> )	0.11±0.04	0.52±0.004
$k_1$ (min <sup>-1</sup> )	0.37±0.39	0.071±0.006	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	(-3.8±4.0)×10 <sup>45</sup>	0.23±0.03
$q_{ecal}^b$ (mg g <sup>-1</sup> )	0.10±0.01	0.52±0.009	$q_{ecal}$ (mg g <sup>-1</sup> )	0.099±0.01	0.54±0.01
$R^2$	0.492	0.946	$R^2$	0.483	0.981

<sup>a</sup> means the equilibrium sorption capacity estimated from the experimental data.

<sup>b</sup> means the equilibrium sorption capacity calculated from the kinetic model.

Table 2

Langmuir isotherm		Freundlich isotherm		D-R isotherm	
$q_m$ (mg g <sup>-1</sup> )	4.94±0.5	$k_f$ (mg g <sup>-1</sup> L <sup>1/n</sup> mg <sup>-1/n</sup> )	1.12±0.2	$q_m$ (mg g <sup>-1</sup> )	4.43±0.4
$b$ (L mg <sup>-1</sup> )	0.06±0.02	$n$	0.27±0.04	$\beta$ (mol <sup>2</sup> /kJ <sup>2</sup> )	(3±0.8)×10 <sup>-5</sup>
$R^2$	0.93	$R^2$	0.93	$R^2$	0.92
$\chi^2$	21.1	$\chi^2$	0.96	$\chi^2$	1.3×10 <sup>281</sup>
NSD (%)	57.3	NSD (%)	60.7	NSD (%)	310.2

Table 3<sup>a</sup>

No.	Dosage (g L <sup>-1</sup> )	Initial Cs <sup>+</sup> concentration (mg L <sup>-1</sup> )	Cs <sup>+</sup> adsorbed (μmol)	K <sup>+</sup> released (μmol)
1	5	10	0.5±0.02	0.1±0.0
2	10	10	0.9±0.002	1.5±0.06
3	15	10	1.4±0.001	4.6±0.3
4	20	10	1.4±0.001	4.7±0.2
5	20	100	10.3±0.07	13.4±0.2
6	20	200	12.3±0.01	16.7±0.02
7	20	400	14.6±0.1	19.6±0.1

<sup>a</sup> Samples were tested in 50mL polypropylene tubes with 20mL Cs<sup>+</sup> solutions at room temperature and 200rpm for 24h.

Table 4

Temp. (K)	$Kd$ (mL g <sup>-1</sup> )	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (kJ K <sup>-1</sup> mol <sup>-1</sup> )
298	171.4	-12.9		
308	757.1	-16.8	101.8	0.385
318	2264.3	-20.6		