



Preparation of areca residue activated carbon composite and its adsorption performance for uranium (VI) in wastewater

Ling-ling Wu^{a,b}, Yan-sen Cao^c, Zhao-peng Li^{a,b}, Lin Hu^{a,b}, Zhi-jun Zhang^{a,b}, Qing Yu^{a,b,*}

^a*School of Resource and Environment and Safety Engineering, University of South China, 421001 Hengyang, China, emails: ckyuqingk@126.com (Q. Yu), wllshmily@foxmail.com (L.-l. Wu), li.z.p@foxmail.com (Z.-p. Li), 175744720@qq.com (L. Hu), zzi181@163.com (Z.-j. Zhang)*

^b*Key Discipline Laboratory for National Defense for Biotechnology in Uranium Mining and Hydrometallurgy, University of South China, 421001 Hengyang, China*

^c*School of Civil and Resource Engineering, University of Science and Technology Beijing, 100083 Beijing, China, email: yansencaoy@126.com*

Received 17 March 2019; Accepted 10 November 2019

ABSTRACT

In this paper, areca residue was used as a new material to prepare activated carbon by microwave. With the iodine adsorption value of wood activated carbon as the main index, the adsorption capacity of activated carbon to uranium was investigated by static adsorption experiment with the different pH value of uranium solution, initial concentration of uranium solution, dosage of areca residue activated carbon and adsorption time. On this basis, the impact of microwave irradiation time, activator concentration and activator immersion time on the production process of activated carbon was analyzed. The structure of the prepared activated carbon from areca residue before and after adsorption treatment was explored by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and Fourier transform infrared spectroscopy. The results showed that the activated carbon prepared by areca residue had the best adsorption effect when the concentration of activator with NaOH was 20%, the soaking time of activator was 36 h, and the microwave irradiation time with power of 700 W was 2 min. It is found that the best percentage removal of uranium from solution was 92.8% under pH value of 7, the dosage of areca residue activated carbon of 8 g/L and the adsorption time of 7 h. The kinetic data followed the pseudo-second-order model. The hydroxyl, carbonyl, carboxyl and C=C groups on the surface of the prepared activated carbon were responsible for adsorption of uranium. Desorption and regeneration processes showed that the activated carbon material prepared by areca residue had the potential of regeneration and reuse.

Keywords: Activated carbon prepared by areca residue; Microwave; Adsorption; Uranium; Wastewater

1. Introduction

Uranium is a major radioactive element as well as nuclear fuel. The development of nuclear power has contributed to the production of a large amount of uranium-containing wastewater [1]. The uranium content in this wastewater is over 100 times of the national allowable discharge

standard [2], and more than one thousand times of that in the natural sea water [3]. The accumulation of uranium elements in the natural environment may result in bad consequences, such as radiation, gene distortion and so on. It will also cause irreversible damage to animals and plants, soil and water sources, and ultimately pose a potential threat to human survival and development [1,4]. Nowadays, the treatment

* Corresponding author.

of uranium-containing wastewater and the enrichment and utilization of uranium in it have attracted more attention of many scholars. Traditionally, corresponding treatment processes include ion exchange method [5], chemical precipitation method [6] and so on. The innovative ones are membrane treatment method, evaporation method, zero-valent iron method, etc. [7].

Activated carbon is a kind of carbonaceous material with rich voids structure and large specific surface area, which possesses good adsorption performance [8,9]. Compared with other adsorption processes, it has the advantages of relatively low cost of raw materials, good performance of repeated use and high adsorption efficiency [10]. For example, Yu et al. [11] found the good adsorption capacity of immobilized activated carbon for uranium. Areca residue refers to the residue of areca food, characterized by easy access, low price and unique fiber hollow structure that is beneficial to the immersing of the activator. Therefore, areca residue can be used as the raw material for preparing activated carbon [12,13]. In addition, the preparation methods of activated carbon mainly include chemical activation method [14] and physical activation method [15]. Among them, activated carbon with good pore structure parameters can be prepared by using NaOH as a chemical activator. Compared with other activators, such as KOH, it has advantages of cost economy, environmental friendliness and less corrosiveness [16]. At the same time, microwave is used as heat source to carbonize areca residue after pretreatment, which has the advantages of fast heating, high thermal efficiency, uniform heating and less pollution [17]. So areca residue was used as raw material to prepare activated carbon with NaOH solution as activator using the method of microwave irradiation in this paper. Then the prepared activated carbon was used to adsorb uranium in aqueous solution. It was expected to explore a new material to treat radioactive wastewater containing uranium.

2. Experiments

2.1. Materials

The residue after chewing of areca food was selected as the raw material for the preparation of activated carbon. The uranium (VI) (1.0 g/L) stock solution was prepared using U_3O_8 powder according to the reference [18]. The prepared stock solution was diluted with ultrapure water and diluted into solutions of different uranium (VI) concentrations for further experiments. All chemicals used in the experiments were of analytical grade.

2.2. Instruments

Microwave Oven (EG720FA5-NS, Midea, China) was used for preparation of the activated carbon. The concentration of uranium (VI) in the solution was measured using an ultraviolet and visible spectrophotometer (T6, Beijing Purkinje General Instrument Co., Ltd., China). The synthesized products were, respectively, subjected to field emission SEM, energy dispersive spectroscopy (FESEM-EDS, Raith ELPHY Quantum Electron Lithography (kit), Raith, Germany) and Fourier transform infrared spectroscopy (FT-IR, Nicole S10,

Thermo Scientific, USA) for morphological characterization and structural evaluation. The pore structure of areca residue powder and activated carbon were analysed by Mercury Porosimeter (AutoPore IV 9500, USA).

2.3. Preparation of activated carbon by areca residue

The activated carbon was prepared using areca as carbon resource. The areca residue came from the market common edible betel nut, as shown in Fig. 1a. The areca residue was soaked in water for 24 h, and then in anhydrous ethanol for another 24 h to remove the impurities such as pectin, sugar, lignin and spice. Then, it was washed by ultrapure water several times, then dried at 100°C in an oven and pulverized to a size of 40 mesh.

Next, the NaOH solution and the crushed areca residue were first mixed at a liquid to solid ratio of 10:1 (mass to mass ratio) and then reacted at 303.15 K for a certain time. Afterwards, the areca residue was dried at 353.15 K for 4 h. The dried areca residue with a weight of 3 g was placed in 30 mL of alundum crucible and placed in a microwave oven. Since the energy absorbed by areca residue is mainly related to microwave power and irradiation time in the process of microwave carbonization. The higher the microwave power, the shorter the irradiation time when the energy required for carbonization is satisfied. And the optimum irradiation time tends to be stable when the power is constant. Meanwhile, the power condition of 700 W can be met easily, which is convenient to operate. So the microwave carbonization process of areca residue was performed with the microwave power of 700 W and anaerobic environment for 1–3 min. After microwave irradiation, the activated carbon sample was boiled in a hydrochloric acid solution with a mass fraction of 20% and pickled for 5 h. Then the sample was rinsed with 353.15 K hot ultrapure water until the pH value was close to neutrality. Then, it was dried at 383.15 K for 4 h, and then ground and passed through a 200 mesh sieve. Finally, the activated carbon product was obtained, as shown in Fig. 1b. The main criterion for the adsorption capacity of the prepared activated carbon was determined by the national standard [19]. The Iodine value was calculated by the following equation:

$$A = \frac{5(10c_1 - 1.2c_2v) \times 127}{m} \times D \quad (1)$$

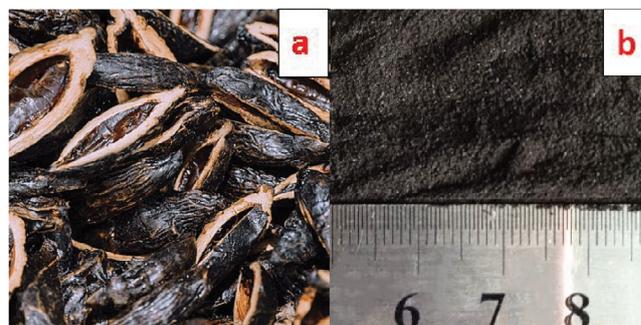


Fig. 1. Betel nut raw materials on the market (a) and prepared betel nut slag activated carbon (b).

where A is adsorption value of iodine on activated carbon (mg g^{-1}); c_1 is concentration of iodine standard solution (mol L^{-1}); c_2 is concentration of sodium thiosulfate standard solution (mol L^{-1}); v is amount of sodium thiosulfate solution consumed (mL); m is quality of activated carbon (mg); D is the correction factor of the iodine value experiment; the constant factor 127 is the molar mass of iodine (g mol^{-1}).

The parameters of the whole preparation process are shown in Table 1.

2.4. Adsorption experiments

The adsorption experiments were carried out to investigate the effects of pH value, initial uranium concentration, amount of adsorbent and contact time on the adsorption of uranium (VI). The areca residue activated carbon prepared under the optimal conditions was placed in an Erlenmeyer flask and mixed with 50 mL of uranium (VI) ion solution. After adsorption for a certain time in a shaker at a temperature of 303.15 K and a speed of 140 rpm, the supernatant liquid was filtered to determine the uranium (VI) concentration, and the percentage removal and adsorption capacity of uranium (VI) were calculated by the following equations:

$$R_t = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)$$

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (3)$$

where C_0 and C_t are the concentration of uranium (VI) (mg/L) at initial time and time t (min), respectively; V is the volume of testing solution (L); and m is the amount of the adsorbent (g).

The determination method of uranium concentration refers to the national standard EJ267.4-1984. The concentration of uranium in solution was determined by spectrophotometry. When the pH was 7.8, uranium (VI) formed a stable purple-red complex with 2-(5-bromo-2-pyridylazo)-5-diethylphenol and fluoride ions in the water-acetone medium. The complex was maximally absorbed at 578 nm, thereby performing colorimetric determination. First, the standard

curve was drawn, and then the uranium concentration in the solution to be measured was calculated according to the standard curve. In 25 mL volumetric flask, 0, 0.5, 1, 2, 3 and 5 mg/L uranium standard solutions of 10 mL were added, respectively, and 5 mL mixed masking agent solution was added; a drop of phenolphthalein indicator (0.1%) was added, respectively, and then a drop of ammonia solution was added to make the solution red; a drop of hydrochloric acid was added to adjust the solution to colorless; 2 mL buffer solution, 6 mL acetone and 1 mL Br-PADAP ethanol solution were added, respectively. It was necessary to ensure that each reagent was shaken evenly after dropping. Finally, the distilled water was used to calibrate the calibration line. After shaking, the reagent was left undisturbed for 45 min. Referring to the reagent blank, the absorbance of each reagent was measured with a 1 cm colorimetric dish at 578 nm on the ultraviolet-visible spectrophotometer, and the standard curve was drawn as shown in Fig. 2.

2.5. Studies of desorption and regeneration

0.2 g of residue activated carbon after adsorption of uranium was placed in a 200 mL Erlenmeyer flask. Then added 50 mL of 0.1 mol/L hydrochloric acid solution, kept the temperature at 303.15 K, and desorbed for 4 h, took the supernatant liquid and filter to determine the uranium concentration. The desorbed adsorbent was washed, dried to constant weight, and subjected to adsorption experiments again.

3. Results and discussion

3.1. Characterization

3.1.1. Porosity

The characterization results of the pores of the samples are shown in Table 2. Samples 1 and 2 are, respectively, areca residue powder below 200 mesh screen and areca residue activated carbon powder carbonized by microwave. And the relationship between pore size diameter and cumulative pore

Table 1
Preparation parameters of activated carbon by areca residue

Group	Microwave irradiation time (s)	NaOH dipping time (h)	NaOH mass fraction (%)
1	110	24	20
2	120	24	20
3	130	24	20
4	120	12	20
5	120	24	20
6	120	36	20
7	120	24	10
8	120	24	20
9	120	24	30

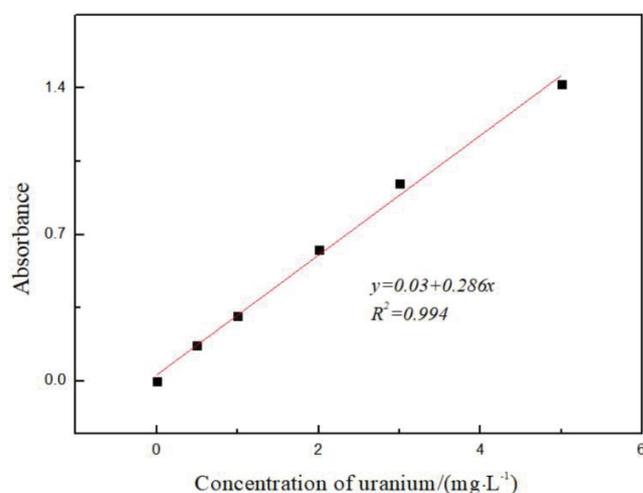


Fig. 2. Standard curve for determination of uranium concentration.

Table 2

Porosity, total pore area and specific surface area ratio of each pore diameter section of the sample

Sample	Porosity, %	Total pore area, m ² g ⁻¹	Specific surface area ratio of each aperture section, %		
			<10 nm	10–100 nm	>100 nm
Sample 1	62.0468	2.229	4.49	89.73	5.78
Sample 2	54.7283	10.226	1.96	5.87	92.17

area before and after carbonization of areca residue powder by microwave is shown in Fig. 3.

The characterization results showed that the porosity of areca residue powder was 62.0468%, the total pore area was 2.229 m²/g, and the specific surface area of the micro pore segment accounted for the largest proportion (94.22%) before carbonization by microwave. And the porosity of areca residue activated carbon powder was 54.7283%, the total pore area was increased to 10.226 m²/g, and the specific surface area of the mesoporous and above pore segments accounted for the largest proportion (92.17%) after carbonization by microwave.

It was found that the porosity of areca residue after carbonization decreased slightly compared with that before carbonization by microwave, the total pore area increased greatly, the ratio of specific surface area of the micro pore segment decreased significantly, and the ratio of specific surface area of the mesoporous and above pore segments increased significantly.

It is concluded that the surface and internal pore structure of areca residue powder changed greatly before and after carbonization by microwave. On the one hand, due to the effect of microwave heating, a part of its internal closed pores are forced to release under the action of air pressure, and a part of the combined water is lost, which makes the internal structure of areca residue powder shrink and the pores decrease. On the other hand, microwave can effectively promote the development of pore structure, which makes the unconnected pores previously expand and connect, and makes the pore diameter expand and the pore spacing decrease; thus leading to the increase of the total pore area. It may be the result of the above two effects for the small decrease of porosity after carbonization by microwave.

3.1.2. SEM and EDS

SEM was used to observe morphologies of the prepared activated carbon before and after adsorbing uranium to compare their differences. Figs. 4a and c present many loose porous structures and irregular protrusions on the surface of activated carbon before uranium adsorption, which increases its specific surface area and contributes to the adsorption of uranium by the prepared activated carbon. In Figs. 4b and d, the surface morphology of the activated carbon experienced a great change after the adsorption of uranium on the areca residue activated carbon, such as the disappearing of the pore volume and the dense activated carbon, indicating that the voids on the surface of the activated carbon were filled with uranium. The chemical compositions of the activated carbon before (a) and after (b) adsorbing uranium were obtained by the EDS analysis, as shown in Fig. 5. It can be seen from Fig. 5a that areca residue activated carbon had no uranium element before it adsorbed uranium. It could be seen from Fig. 5b that after the adsorption of uranium by activated carbon, the uranium content reached 0.39%, indicating that a certain amount of uranium was adsorbed in the voids of the areca residue activated carbon.

3.1.3. Fourier transform infrared spectroscopy

The FT-IR of the prepared activated carbon materials before adsorption (a) and after adsorption (b) is shown in Fig. 6. FTIR spectrum of activated carbon showed the band at around 3,163 cm⁻¹ due to –OH stretching vibration of hydroxyl groups. The bands at about 1,700 cm⁻¹ were attributed to the carboxyl group. In addition, FTIR spectrum

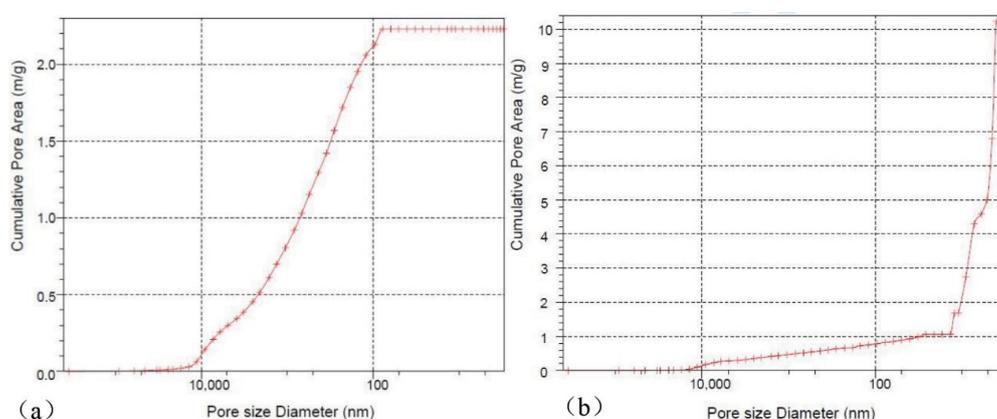


Fig. 3. Relationship between pore size diameter and cumulative pore area before (a) and after (b) carbonization of areca residue powder by microwave.

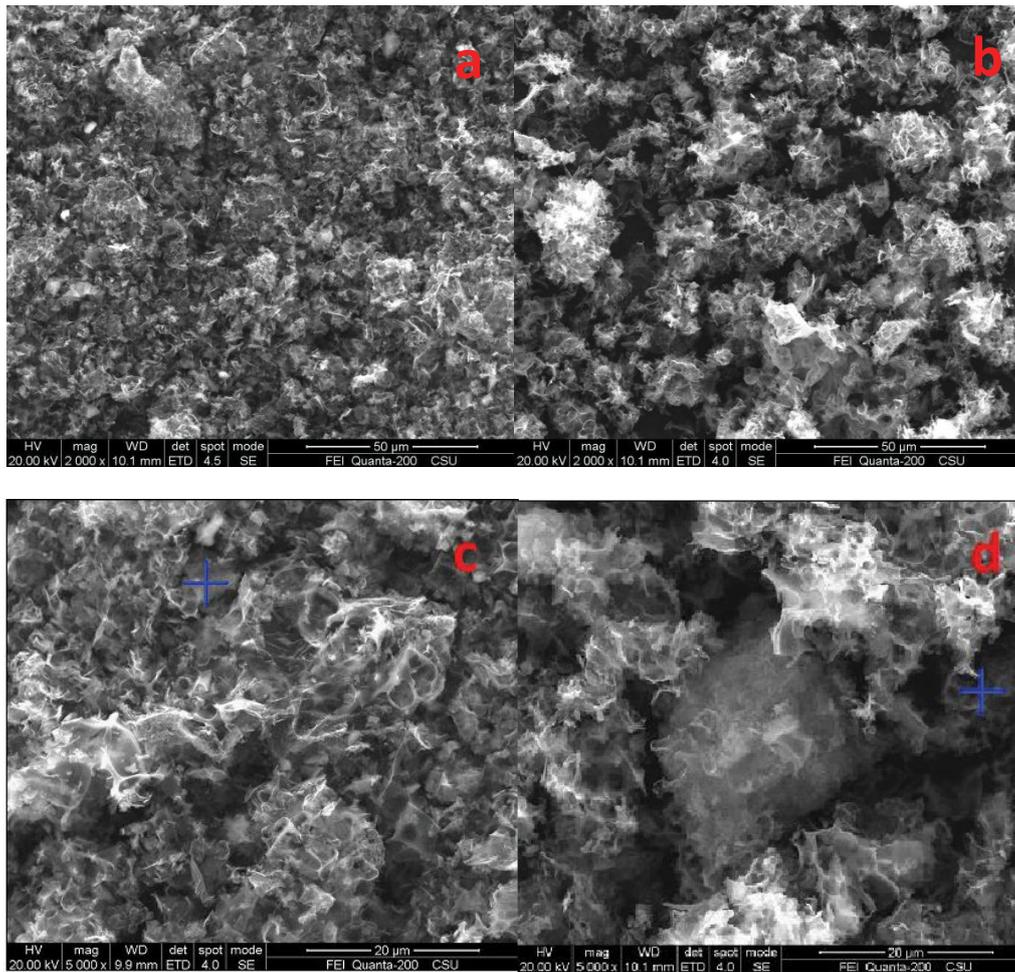


Fig. 4. SEM images of the prepared activated carbon before (a, c) and after (b, d) adsorption.

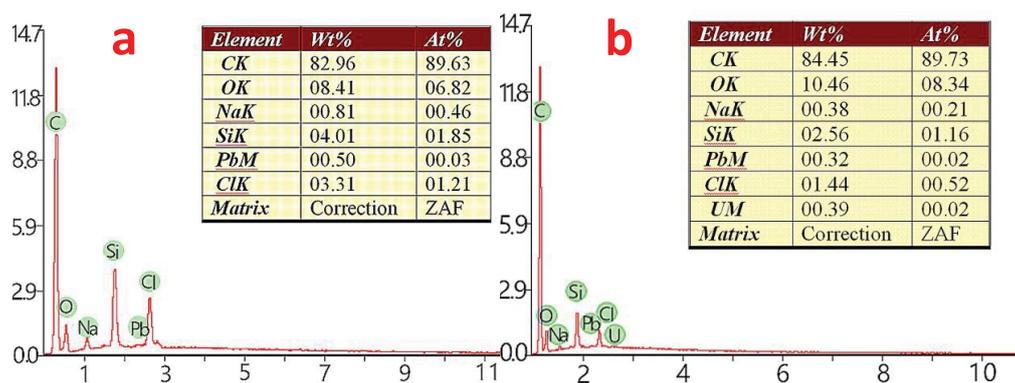


Fig. 5. EDS spectra of the prepared activated carbon before (a) and after (b) adsorption treatment.

of activated carbon exhibited characteristic absorption C=C bond appearing at around $1,585\text{ cm}^{-1}$ and C–O stretching vibrations at $1,585\text{ cm}^{-1}$. The characteristic peaks of hydroxyl, carbonyl, C–O and C=C shifts after adsorption of uranium can be observed, which may result from the participation of the above functional groups.

3.2. Influential factors of microwave preparation of activated carbon by areca residue

The variation of iodine adsorption value with microwave irradiation time was studied. As shown in Fig. 7, when the irradiation time was less than 2 min, the adsorption capacity

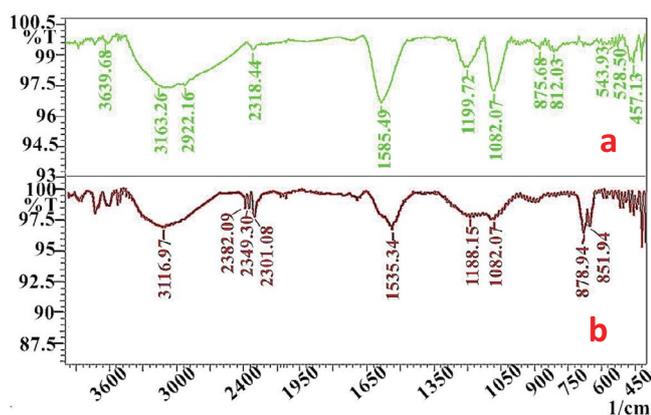


Fig. 6. FT-IR spectra of areca residue activated carbon before (a) and after (b) adsorption treatment.

of the prepared activated carbon to iodine increases with the rise of the irradiation time and reached its maximum when the irradiation time was 2 min. However, the iodine adsorption value of activated carbon decreased when the irradiation time was extended to 2 min 10 s. This may be attributed to the increase of the carbonization temperature for the areca residue and the generation of a large number of micropores when lengthening the irradiation time. With the continuous growth of the irradiation time, the temperature also rose rapidly, and the previously generated micropores were gradually destroyed. The generation of new micropores was at a lower rate than the destroy process of previous ones. Meanwhile, the surface structure was also damaged, thus the adsorption of activated carbon to iodine was reduced. In summary, the optimal irradiation time was determined as 2 min, at which the iodine adsorption value reached 620.41 mg/g.

3.2.2. Impact of activator soak time

In this paper, sodium hydroxide was used as an activator for the preparation of activated carbon. As displayed in Fig. 8, with the increasing soak time of the sodium hydroxide activator, the adsorption effect of the prepared activated carbon was gradually enhanced, but it showed a gentle trend when the soak time was greater than 24 h. The possible explanations are given below. When the soak time was less than 24 h, the activator did not fully enter the areca residue and hence played a minor role in the activation process. With the increase of soak time, the activator gradually penetrated into the structure of areca residue, thus promoting the generation of voids in the areca residue during charring. When a certain time was reached, the areca residue was saturated with the activator and the activation process was completed. The continued extension of the soak time posed no longer significantly impact. Therefore, the optimum soak time of areca residue was about 36 h, at which the iodine adsorption value reached 615.41 mg/g.

3.2.3. Impact of activator concentration

As shown in Fig. 9, with the increase of activator concentration, the adsorption capacity of activated carbon to iodine

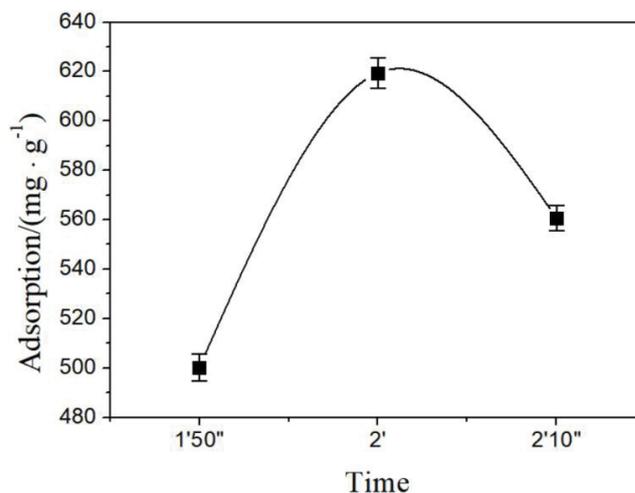


Fig. 7. Adsorption of iodine on activated carbon prepared at different microwave irradiation times.

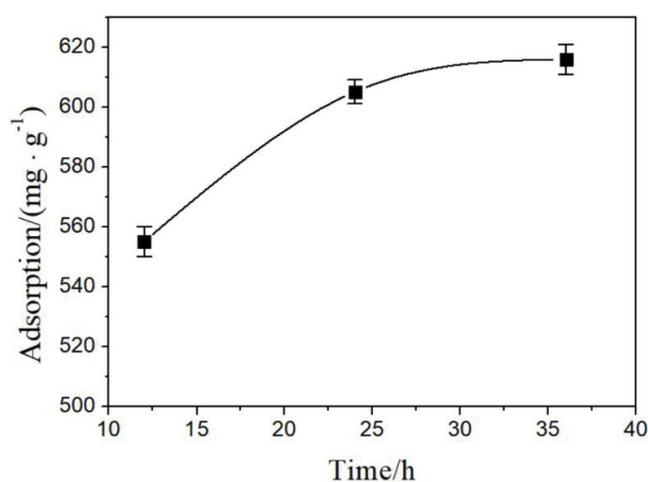


Fig. 8. Adsorption value of iodine on activated carbon prepared.

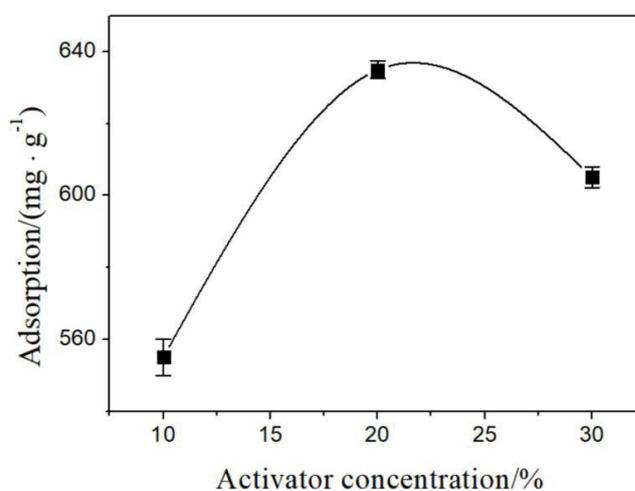


Fig. 9. Adsorption value of iodine on activated carbon prepared by areca residue at different activator concentration.

first increased and then decreased when the concentration was greater than 20%. With the increase in concentration, activator entered the areca residue to occupy more active sites, thereby promoting the decomposition and cross-linking of the areca residue. The activation speeded up, and a great number of micropores formed during the increase of carbonization. When the concentration reached over 20%, excessive erosion of areca residue occurred when the betel nut slag was carbonized, resulting in a larger pore size of the micropore and smaller specific surface area. It was then concluded that the optimum concentration of activator was 20%, at which the iodine adsorption value reached 635.49 mg/g.

3.3. Uranium (VI) adsorption performance

3.3.1. Impact of adsorbent dosage

Under the condition that the initial concentration of uranium (VI) was 20 mg/L, the adsorption time was 24 h, the initial pH of uranium (VI) solution was 7 and the adsorption temperature was 303.15 K, the influence of the dosage of activated carbon prepared by areca residue was investigated. As shown in Fig. 10, as the amount of charcoal slag activated carbon increased, the specific surface area of activated carbon and the number of adsorption sites increased. So the percentage removal of uranium increased. However, since the initial concentration of the uranium solution was constant, the unit adsorption amount decreased as the amount of activated carbon increased. When the dosage was 8 g/L, the percentage removal was 92.03% and the adsorption amount was 2.30 mg/g. As the amount of the injection continued to increase, the changes in the adsorption amount and the percentage removal were not significant. Therefore, it could be determined that the optimum amount of activated carbon was 8 g/L.

3.3.2. Impact of contact time

The impact of contact time (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, and 24 h) on the adsorption of uranium ions onto the

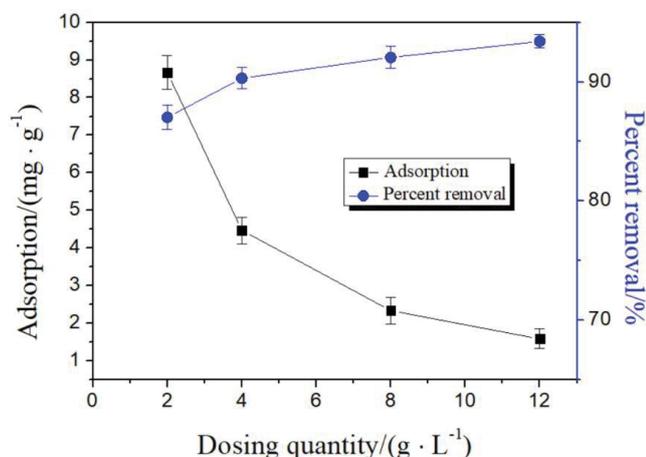


Fig. 10. Effects of uranium percentage removal and adsorption capacity of the adsorbent dosage ($V = 50$ mL, $C_0 = 20$ mg/L, $\text{pH} = 7 \pm 0.1$, $t = 24$ h, $T = 303.15$ K).

prepared activated carbon was investigated using 20 mg/mL initial uranium concentration at respective $\text{pH} = 7.0 \pm 0.1$ and 303.15 K. The results are shown in Fig. 11. It can be seen from Fig. 11 that in the initial stage of adsorption, the percent removal and adsorption capacity of the prepared activated carbon for uranium increased rapidly with the increase of adsorption time. When the adsorption time was more than 7 h, the percentage removal and adsorption capacity of the prepared activated carbon on uranium increased slowly and tended to be gentle with the increase of adsorption time. This was because that there were many adsorption sites on the activated carbon and the adsorption speed was faster at the initial stage of adsorption. Then, with the increase of time, the exposed adsorption sites decreased, and the percentage removal and adsorption amount increased slowly until it stabilized. Therefore, the contact time of 7 h was deemed sufficient to establish sorption equilibrium, at which the percentage removal of 90.73% and the adsorption capacity of 2.27 mg/g were obtained.

3.3.3. Impact of initial uranium concentration

The initial concentration provides a major driving force to overcome all mass transfer resistance of uranium between the aqueous and solid phases. The experiment on adsorption of uranium (VI) by the prepared activated carbon was carried out under various concentrations with the temperature of 303.15 K and the contact time of 24 h. This ensured that the adsorption of uranium reached equilibrium. As shown in Fig. 12, it can be seen that with the increase of the initial concentration of uranium, the unit adsorption capacity of areca residue activated carbon for uranium gradually increased, and the percentage removal decreased slightly. The reason may be that as the initial concentration of uranium increased, the uranyl ion in the solution can be more fully attached to the surface of the activated carbon, and thus the amount of adsorption increased. However, the increase of concentration led to an increase in the number of uranyl ion groups. After the adsorption of activated carbon reached saturation, the uranyl ions those were not adsorbed were freed around the activated carbon, resulting in a small decrease in

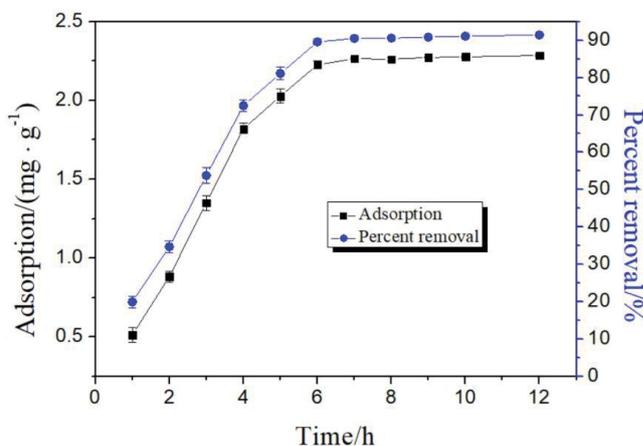


Fig. 11. Impact of contact time on adsorption of uranium ($V = 50$ mL, $C_0 = 20$ mg/L, $m = 0.4$ g, $\text{pH} = 7 \pm 0.1$, $T = 303.15$ K).

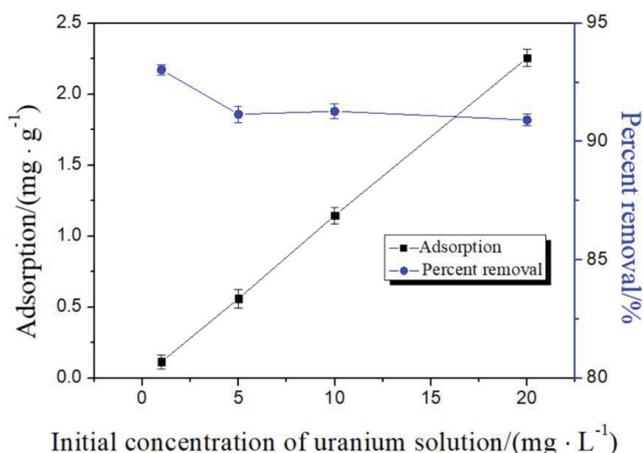


Fig. 12. Effect of initial uranium concentration on adsorption capacity of uranium (VI) ($V = 50$ mL, $m = 0.4$ g, $\text{pH} = 7 \pm 0.1$, $t = 24$ h, $T = 303.15$ K).

the percentage removal. When the initial concentration of uranium was 5 mg/L, the adsorption efficiency of areca residue activated carbon was 91.31%, and the adsorption amount was 0.571 mg/g. After that, as the initial concentration of uranium continued to increase, the adsorption capacity continued to increase, but the change in percentage removal was not obvious at the same time. Therefore, the optimum initial concentration of uranium can be determined to be 5 mg/L. It was indicated that areca residue activated carbon was suitable for treating low concentration uranium-containing wastewater.

3.3.4. Impact of initial pH

In order to completely simulate the acid–base environment of the uranium solution, the pH of the solution was adjusted to different pH degrees by HCl and NaOH before the adsorption experiment. When the initial concentration of uranium (VI) was 20 mg/L, the dosage of areca residue activated carbon was 8 g/L, the adsorption time was 24 h, and the adsorption temperature was 303.15 K, the initial pH of the solution was investigated for the effect on uranium adsorption efficiency. The result is shown in Fig. 13. It can be seen that pH had a great influence on the adsorption effect of areca residue activated carbon. With the increase of the initial pH of the solution, the percentage removal and adsorption capacity of the prepared activated carbon for uranium increased first and then decreased. When pH was 7, the percentage removal and adsorption amount reached the highest value, the corresponding percentage removal was 92.8% and the adsorption amount was 2.32 mg/g. When the pH value was low, the uranium hydrolyzed ion exists in the form of UO_2^{2+} , and the concentration of H^+ in the solution was higher. The uranyl ion competed with the hydrogen ion to adhere to the active site on the activated carbon surface, resulting in a smaller adsorption amount of activated carbon to UO_2^{2+} . When the pH of the solution was around 7, the uranium was present in the aqueous solution in the form of $(\text{UO}_2)_3(\text{OH})_5^+$. When the pH of the solution was greater than 8, it mainly existed in the form of $\text{UO}_2(\text{OH})_3^-$, the negative

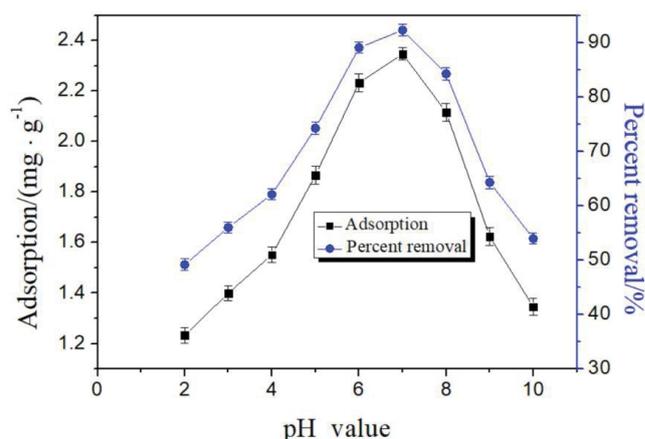


Fig. 13. Impact of initial pH for uranium adsorption on the prepared activated carbon ($V = 50$ mL, $m = 0.4$ g, $C_0 = 20$ mg/L, $t = 24$ h, $T = 303.15$ K).

charge of uranyl ion increased, and the adsorption capacity of activated carbon for uranium decreased. Therefore, it can be inferred that uranium was mainly adsorbed on activated carbon in the form of $(\text{UO}_2)_3(\text{OH})_5^+$. Therefore, the optimum pH of the optimum solution for the adsorption of uranium by areca residue activated carbon was 7.

3.3.5. Desorption and regeneration

An effective adsorbent should possess not only good selective adsorption properties but also excellent desorption and regeneration. The latter are of significance to evaluate the economic performance of adsorbents in actual applications. The results showed that the desorption rate was 73.9% and after the second adsorption, the percentage removal reached 90.9%. This indicated the potential of regeneration and reuse for the activated carbon material prepared by areca residue, thus improving the economy of the adsorption process to some extent.

3.4. Adsorption isotherm model

In the study of adsorption equilibrium, Langmuir and Freundlich formulas are commonly used to describe the isothermal adsorption process. Langmuir isothermal equation assumes that adsorption of sorbent to solute is single-layer adsorption, and due to the limitation of specific surface area of sorbent, its adsorption capacity has a maximum value, which is called adsorption capacity. Its linear expression is:

$$\frac{\rho_e}{q_e} = \frac{\rho_e}{q_m} + \frac{1}{bq_m} \quad (4)$$

where q_e (mg/g) is the mass of adsorbent adsorbed per unit mass, ρ_e (mg/L) denotes the mass concentration of adsorbents in adsorption equilibrium, q_m (mg/g) is the maximum adsorption capacity of adsorbent monolayer, and b is constant.

The linear expression of Freundlich adsorption isotherm is Eq. (5):

$$\lg q_e = \frac{1}{n} \lg \rho_e + \lg K_f \tag{5}$$

where q_e (mg/g) is the mass of adsorbent adsorbed per unit mass, ρ_e (mg/L) denotes the mass concentration of adsorbents in adsorption equilibrium, K_f is the adsorption coefficient, and n is constant. The larger the value of n is, the smaller the value of $1/n$ is, and the better the adsorption performance is. It is generally believed that adsorbent is easy to adsorb adsorbents when $1/n$ is between 0.1 and 0.5. And it is difficult for adsorbent to adsorb when $1/n$ is greater than 2.

Experimental data were fitted according to Langmuir formula and Freundlich formula, and the obtained curves are shown in Fig. 14. Isothermal adsorption data parameters are listed in Table 3. Results showed that the Langmuir equation of correlation coefficient (r^2) is 0.9999, the Freundlich equation of the correlation coefficient (r^2) is 0.9725, and the Langmuir adsorption curve was better fitted than the Freundlich adsorption curve. So Langmuir equation is better than Freundlich equation in describing the adsorption of U(VI) on activated carbon prepared by areca residue. Also, it is better than the multi-layer covering mode for the single-layer adsorption mode with uniform adsorption for the adsorption process, and the activated carbon prepared by areca residue is easier to adsorb U(VI) in solution.

3.5. Adsorption kinetics

To study the adsorption kinetics of uranium (VI) on the prepared activated carbon in aqueous solutions, pseudo-first-order and pseudo-second-order kinetic models were adopted to investigate the kinetic mechanism of adsorption processes between adsorbent and adsorbate.

The pseudo-first-order kinetic model is expressed as

$$\ln(Q_e - Q_t) = \ln Q_e - \frac{k_1}{2,303} t \tag{6}$$

The pseudo-second-order kinetic model is expressed as follows:

$$\frac{1}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{7}$$

where Q_e (mg/g) and Q_t (mg/g) are the adsorption capacities at equilibrium and time t (h), respectively; k_1 (h^{-1}) and k_2 (h^{-1}) are the rate constants of pseudo-first-order and pseudo-second-order models for the adsorption of uranium (VI), respectively. The kinetic parameters, such as k_1 , k_2 , Q_e and correlation coefficient (R^2) were calculated based on the linear form of models in Figs. 15a and b. As the results are shown in Table 4, the values of Q_e and R^2 for the pseudo-second-order kinetics are higher than those for the pseudo-first-order kinetics. And the amount adsorbed at equilibrium calculated according to pseudo-second-order kinetic model was 2.40 mg/g for activated carbon, which was close to the values of experiment (2.27 mg/g).

As a result, the kinetic behavior of uranium adsorption onto areca residue activated carbon can be described by the pseudo-second-order kinetic model.

4. Conclusions

- The activated carbon prepared by areca residue was developed based on microwave method for highly efficient extraction of uranium from wastewater. The adsorption of the prepared activated carbon reached the best when the concentration of activator with NaOH was 20%, the soaking time of activator was 36 h, and the microwave irradiation time with power of 700 W was 2 min. The porosity of areca residue after carbonization decreased slightly compared with that before carbonization by microwave, the total pore area increased greatly, the ratio of specific surface area of the micro pore segment decreased significantly, and the ratio of specific surface area of the mesoporous and above pore segments increased significantly.
- In addition, the uranium adsorption was characterized by SEM-EDS and FT-IR. SEM images showed that after

Table 3
Isotherm parameters for U(VI) adsorption on activated carbon prepared by areca residue

Langmuir			Freundlich		
q_m	b	r^2	K_f	n	r^2
2.2761	-0.0104	0.9999	$10^{-10.24}$	0.0949	0.9725

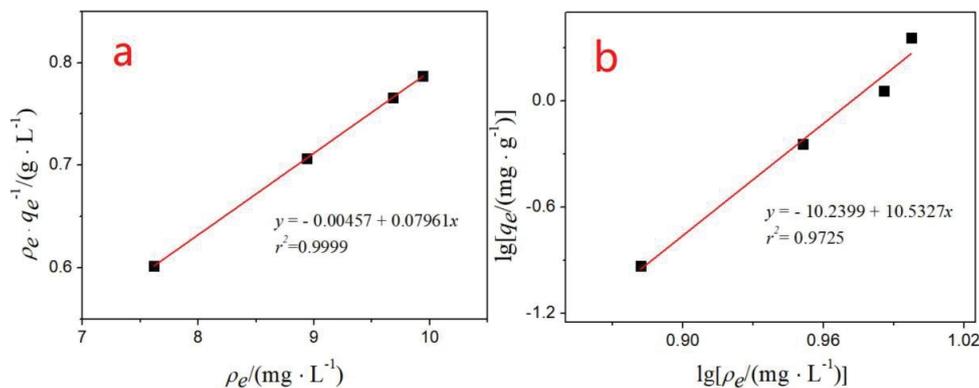


Fig. 14. Langmuir (a) and Freundlich (b) adsorption isotherms.

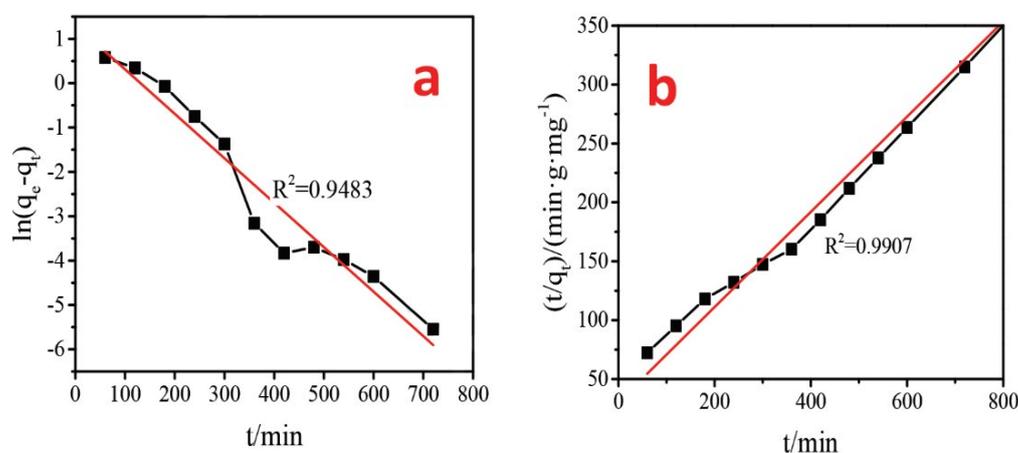


Fig. 15. Pseudo-first-order (a) and pseudo-second-order (b) kinetic models.

Table 4

Kinetic constants for adsorption of uranium on the activated carbon prepared by areca residue

Pseudo-first-order model			Pseudo-second-order model		
K_1 (min^{-1})	Q_e (mg/g)	R_1^2	K_2 (g/mg)	Q_e (mg/g)	R_2^2
0.01	2.29	0.94254	0.0535	2.402	0.99065

the adsorption of uranium on the areca residue activated carbon, the pore volume disappeared and the activated carbon was dense. This exhibited that the voids on the surface of the activated carbon were filled with uranium. The results of EDS demonstrated that uranium ion was adsorbed on the surface of activated carbon after adsorption. The results of FT-IR presented the possible involvement by the functional groups of hydroxyl, carbonyl, C–O and C=C in the adsorption of uranium.

- Based on the adsorption experiment, the optimum adsorption conditions for the adsorption of uranium by areca residue activated carbon: the pH of uranium solution was 7, the dosage of areca residue activated carbon was 8 g/L, the adsorption time was 7 h, the optimum percentage removal was 92.8%, and the adsorption amount was 2.32 mg g^{-1} . Langmuir equation was better than Freundlich equation in describing the adsorption of U (VI) on activated carbon prepared by areca residue. The kinetic behavior of areca residue activated carbon adsorption of uranium was more in line with the quasi-second-order kinetic equation.
- The desorption efficiency of areca residue activated carbon after adsorption of uranium reached 73.9%, and the adsorption efficiency reached 90.9% after the second repeated adsorption. It indicated that areca residue activated carbon had reusable performance and was an efficient and cheap adsorbent for treating low concentration uranium-containing wastewater.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

This study was supported by the National Natural Science Foundation of China (No. 51804164, No. 51774187), Natural Science Foundation of Hunan Province (No. 2019JJ50498, No. 2017JJ3274, No. 2018JJ2329, No. 2018JJ3448), the Research Foundation of Education Bureau of Hunan Province (No. 18B276, No. 18B266, No. 17A184, and No. 18A247), and State Key Laboratory of Safety and Health for Metal Mines (No. 2018-JSKSSYS-007).

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

- [1] S.T. Zhuang, R. Chen, M. Kang, J.L. Wang, Kinetic and equilibrium of U(vi) adsorption onto magnetic amidoxime-functionalized chitosan beads, *J. Clean. Prod.*, 188 (2018) 655–661.
- [2] J. Yu, X.G. Luo, B. Liu, J. Zhou, J. Feng, W.K. Zhu, S.L. Wang, Y.D. Zhang, X.Y. Lin, P. Chen, Bayberry tannin immobilized bovine serum albumin nanospheres: characterization, irradiation stability and selective removal of uranyl ions from radioactive wastewater, *J. Mater. Chem. A*, 6 (2018) 15359–15370.
- [3] Z.B. Zhang, X.F. Yu, X.H. Cao, R. Hua, M. Li, Y.H. Liu, Adsorption of U(VI) from aqueous solution by sulfonated ordered mesoporous carbon, *J. Radioanal. Nucl. Chem.*, 301 (2014) 821–830.
- [4] Q. Yu, D.X. Ding, D.K. Li, Y.P. Yu, Y. Luo, Q.F. Wang, N. Hu, Adsorption mechanism of uranium of immobilizing *Aspergillus niger* activated carbon, *Chin. J. Nonferrous Met.*, 26 (2016) 936–945.

- [5] Karan, Rajan, Sreenivas, Studies on lowering of uranium from mine water by static bed ion exchange process, *Sep. Sci. Technol.*, 54 (2019) 1607–1609.
- [6] N. Sen, M. Darekar, P. Sirsat, K.K. Singh, S. Mukhopadhyay, S.R. Shirsath, K.T. Shenoy, Recovery of uranium from lean streams by extraction and direct precipitation in microchannels, *Sep. Purif. Technol.*, S1383–5866 (2019) 30140–30146.
- [7] T.A. Saleh, Naeemullah, M. Tuzen, A. Sari, Polyethylenimine modified activated carbon as novel magnetic adsorbent for the removal of uranium from aqueous solution, *Chem. Eng. Res. Des.*, 117 (2017) 218–227.
- [8] M.M. Johns, W.E. Marshall, C.A. Toles, Agricultural by-products as granular activated carbons for adsorbing dissolved metals and organics, *J. Chem. Technol. Biotechnol.*, 71 (2015) 131–140.
- [9] W.W. Tang, X.X. Wang, G.M. Zeng, J. Liang, X.D. Li, W.L. Xing, D. He, L. Tang, Z.F. Liu, Electro-assisted adsorption of Zn(II) on activated carbon cloth in batch-flow mode: experimental and theoretical investigations, *Environ. Sci. Technol.*, 53 (2019) 2670–2678.
- [10] Q.S. Liu, T. Zheng, P. Wang, L. Guo, Preparation and characterization of activated carbon from bamboo by microwave-induced phosphoric acid activation, *Ind. Crop. Prod.*, 31 (2010) 233–238.
- [11] Q. Yu, D.X. Ding, D.K. Li, Y.P. Yu, Y. Luo, Q.F. Wang, Adsorption mechanism of uranium of immobilizing activated carbon, *Metal Mine*, 2 (2016) 172–175.
- [12] Y.B. Tang, L. Qiang, F.Y. Chen, Preparation and characterization of activated carbon from waste ramulus mori, *Chem. Eng. J.*, 203 (2012) 19–24.
- [13] M. Danish, T. Ahmad, R. Hashim, N. Said, M.N. Akhtar, J.M. Saleh, O. Sulaiman, Comparison of surface properties of wood biomass activated carbons and their application against rhodamine B and methylene blue dye, *Surf. Interfaces*, 11 (2018) 1–13.
- [14] M. Danish, R. Hashim, M.N.M. Ibrahim, M. Rafatullah, T. Ahmad, O. Sulaiman, Characterization of Acacia mangium wood based activated carbons prepared in the presence of basic activating agents, *Bioresources*, 6 (2011) 3019–3033.
- [15] L.M. Sun, L.P. Zhang, J.H. Xue, B.Z. Li, Research progress on preparation methods and applications of activated carbon, *Chem. Bioeng.*, 33 (2016) 5–8.
- [16] C.Y. Ma, Y. Mao, P.F. Xu, J.Q. Liu, X.S. Song, Preparation and characterization of high specific area activated carbon by KOH/NaOH activation from abandoned capsicum straw, *J. Funct. Mater.*, 44 (2013) 704–708.
- [17] C. Wang, Preparing high quality activated carbon from Eupatorium adenophorum by microwave irradiation and its mechanism analysis, *Technol. Mkt.*, 23 (2016) 86–88.
- [18] J.Y. Zeng, H. Zhang, Y. Sui, N. Hu, D.X. Ding, F. Wang, J.H. Xue, Y.D. Wang, New amidoxime based material TMP-g-AO for uranium adsorption under seawater conditions, *Ind. Eng. Chem. Res.*, 56 (2017) 5021–5032.
- [19] Standard Test Method for Determination of Iodine Number of Activated Carbon, ASTM D4607–2014 [S].