*Korean J. Chem. Eng.*, 37(5), 776-783 (2020)
DOI: 10.1007/s11814-020-0492-7

pISSN: 0256-1115
eISSN: 1975-7220

# Removal of U(VI) from aqueous solution using carboxymethyl cellulose-modified Ca-rectorite hybrid composites

**Xinghao Liu*,**,***, Shuheng Hu**,†, Di Xu****,†, and Dadong Shao***,†**

*Center for Environment and Water Resource, College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P. R. China
**School of Resources & Environmental Engineering, Hefei University of Technology, Hefei 230009, Anhui, P. R. China
***Jiangsu Key Laboratory of Chemical Pollution Control and Resources Reuse, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China
****State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China
(*Received 27 October 2019 • accepted 12 January 2020*)

**Abstract**−Uranium (VI), as a toxic contaminant, is a potential detriment to human health and environmental safety. In this experiment, carboxymethyl cellulose/Ca-rectorite composite material (Ca-REC/CMC) was prepared by cross-linking reaction to remove U(VI) from the liquid. The crystal structure was detected by X-ray diffraction (XRD) and surface structure and morphology of the materials were investigated by scanning electron microscopy (SEM). The surface functional groups of prepared materials were detected by Fourier transform infrared spectroscopy (FT-IR). The adsorption capacity of Ca-REC/CMC improved obviously after being modified by CMC. The adsorption capacity of Ca-REC/CMC was closely related to ionic strength and pH. According to thermodynamic parameter calculation, the adsorption process was endothermic and spontaneous. Adsorption isotherms could be depicted perfectly by the Langmuir model. Ca-REC/CMC maintained stability and regeneration after recycling six times. The adsorption mechanism, including electrostatic interactions and ionic interaction, was investigated by the X-ray photoelectron spectroscopy (XPS). Ca-REC/CMC is considered as remarkable potential material for removing U(VI) from the water environment.

Keywords: Ca-REC Hybrid Composites, Carboxymethyl Cellulose (CMC), U(VI), Adsorption Mechanism

## INTRODUCTION

Pollution from heavy metals has attracted worldwide attention. According to an International Energy Agency (IEA) investigation, more than 40% of the energy will come from the global nuclear industry by 2030, which will cause a rising demand for consumption of U(VI) with long lifetime ($t_{1/2}$=4.51×10$^9$ years for U-238) [1]. At the same time, nuclear waste will inevitably be released into the natural environment, bringing about various problems, including radiation and high toxicity to human health (kidney and liver damage, and death eventually) and other species (such as in the Fukushima nuclear leak) [2-4]. Therefore, U(VI) is necessarily to be separated and recovered from aqueous solutions before getting into the environment, which is not only beneficial to the nuclear power development, but also is propitious to human health and environmental security [5]. Different techniques containing chemical precipitation, membrane filtration, adsorption, and ion exchange have been used in enriching U(VI) from the water environment and radioactive wastewater [6-9]. Amongst the techniques, adsorption is the most extensive and efficient method to remove U(VI) from aqueous solution. It has high efficiency of adsorption, ease of operation, wide range of materials sources at low prices, environmental friendliness, and large scale application [10,11].

Clay, as a major environmental media, has been taken into U(VI) enrichment from radioactive wastewater. However, natural clay usually does not have excellent adsorption efficiency. For examples Wang et al. [12] used natural bentonite to adsorb U(VI) from aqueous ($q_m$=4.15-21.4 mg/g at 298-338 K). In recent years, clay minerals have been modified by some techniques to improve adsorption efficiency, which has become popular. Liu et al. [13] investigated the performance of bentonite modified by polyaniline for adsorption of U(VI) with $q_m$=14.1-17.5 mg/g at 293-333 K. Ca-rectorite (Ca-REC), as a rare layered clay mineral, has expansiveness, large surface area and high cation exchange capacity. Ca-REC as substrate material could effectively adsorb Cr(VI) from aqueous solution [14]. Wu et al. [15] reported that the Na-REC was modified by chitin and chitosan (CS) to get a composite material with large specific surface area, which was beneficial to adsorbing target pollutions. CS with large quantity of amino and hydroxyl functional groups is good for interaction with heavy metals.

An ideal adsorbent must possess high selectivity, adsorption capacity, charming price, strong stability and reusability. In this article, Ca-REC/CMC with high enrichment ability for U(VI) was prepared by cross-linking reaction between Ca-REC and CMC. The crystal form, surface morphology and the surface functional groups

†To whom correspondence should be addressed.
E-mail: shuheng.hu@163.com, dxu@niglas.ac.cn, shaodadong@126.com
Copyright by The Korean Institute of Chemical Engineers.

of Ca-REC/CMC were investigated by the XRD, SEM and FT-IR. According to the adsorption tests with batch techniques, Ca-REC/CMC had an exceptional performance for U(VI) adsorption from simulated aqueous solutions. Furthermore, the adsorption mechanism, including electrostatic interactions and ionic interaction, was investigated by XPS.

## MATERIAL AND METHODS

### 1. Materials

Ca-REC is native to Zhongxiang, Hubei Province, PR China. Carboxymethyl cellulose sodium and γ-Propyl silane (KH-560) (purity >99%) were obtained from Aladdin. All other chemicals were reagent grade.

### 2. Preparation of Ca-REC/CMC

There are two steps to prepare Ca-REC/CMC. Hydroxylation of Ca-REC: 25 mL $H_2O_2$, 5.0 g Ca-REC, and 50 mL deionized water were added into 250 mL flask, the pH of solution was adjusted to 10 using $Na_2SiO_3$. After stirring 500 rpm/min for 7 h at 50 °C, the suspension was filtrated and washed to neutral by deionized water, then dried at 80 °C. Thus, hydroxylated Ca-REC was obtained. Synthesis of Ca-REC/CMC: 0.1 g CMC was dissolved in 4 mL 1 mol/L NaOH solution and stirred 500 rpm/min for 1 h, then 1 mL KH-560 was added. The suspension was further stirred at the same speed for 4 h and ultra-sounded for 30 min. At the end, 0.4 g hydroxylated Ca-REC was added and the suspension was stirred at 500 rpm/min for 6 h. The composites were percolated and washed to neutral by deionized water, then dried at 80 °C.

### 3. Characterization

To characterize the hydroxylated Ca-REC and synthesized Ca-REC/CMC, the lattice shapes and surface functional groups of materials were investigated by X-ray diffraction (XRD) analysis with Cu K$\alpha$ radiation and Fourier transform infrared spectroscopy (FT-IR) with Mattson 1000, Unicam infrared spectrophotometer at room temperature, respectively. The morphology of materials was analyzed by the ZEISS Gemini 500 SEM microscope. The Brunner-Emmet-Teller (BET) surface area was investigated by TriStar II 3flex equipment using $N_2$ adsorption/desorption isotherm. The content and interaction of surface functional groups were detected by X-ray photoelectron spectroscopy (XPS) with the peak energy corrected with C 1s peak at 284.6 eV. The surface charge characteristics of materials were obtained by the Malvern Zeta sizer Nano ZS (England).

### 4. Batch Experiments

To investigate the property of enrichment of U(VI) by Ca-REC/CMC, batch experiments were performed with various volumes of 0.5 g/L Ca-REC/CMC and 20 mg/L U(VI), which were mixed in 10 mL centrifuge tubes in the presence of 0.1 M NaCl solution at T=293 K. Before solution containing U(VI) was added, the bulk suspensions of Ca-REC/CMC and 0.1 M NaCl were blended for 24 h to achieve pre-equilibrium of salt with solid. The pH of solution was adjusted to 5 by adding small volume of HCl or NaOH (0.01 or 0.1 mol/L). The reaction of solution was placed into oscillators to achieve adsorption equilibrium for 24 h at the same controlled temperature as the adsorption experiments. The adsorbents and solution were separated by centrifugal machine (BECKMAN COULTER 64R, USA). UV-vis spectrophotometry (UV-2550, Shimadzu) was applied to measure the concentration of U(VI) with Arsenazo-III method. All the experiments were repeated three times.

The calculation formula of adsorption efficiency and adsorption amounts are listed in the supply information (S1-2).

## RESULTS AND DISCUSSION

### 1. Characterization

The XRD patterns of Ca-REC and Ca-REC/CMC are shown in Fig. 1(a). The characteristic peaks of Ca-REC were as follows: 2$\theta$= 4.06°, 8.08°, 11.63°, 17.64°, 20.75°, 24-30°, 35.01° and 62.59° [16,17]. CMC, as an amorphous structure, exhibited a wide diffraction peak at 2$\theta$=20.2° [18]. The intensity of two peaks (2$\theta$=4.06°, 8.08°) was significantly weakened and the positons of peaks were slightly skewed after combining with CMC, which could be explained that the original structure was destroyed by CMC modification. Besides, the Ca-REC/CMC and pure Ca-REC had the similar peaks, while no characteristic peak at about 20° of CMC came out in the Ca-REC/CMC, which indicated that the quantity of CMC was little and uniformly dispersed in Ca-REC/CMC [19].

FT-IR can be used to analyze surface functional groups of biopolymers and determine molecular interactions. The FT-IR spectrum of Ca-REC and Ca-REC/CMC is shown in Fig. 1(b). The peak at 3,645 $cm^{-1}$ was attributed to the hydroxyl stretching of Al-OH. And the peak at 850 $cm^{-1}$ was caused by anisomerous stretch-

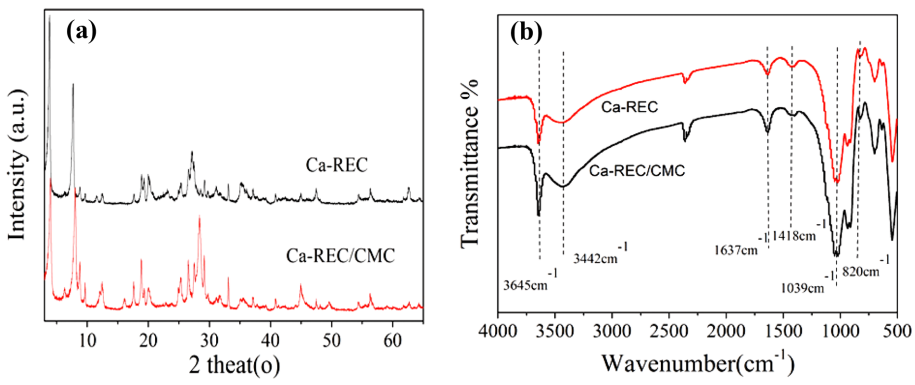



**Fig. 1. (a) XRD and (b) pattern of Ca-REC and Ca-REC/CMC.**

ing vibration of Al-O-Al. The vibration intensity of these two bonds was enhanced due to the reactions of hydroxyl groups between CMC with Al [20]. The intensity of Si-O stretching vibration at 1,039 $cm^{-1}$ was weakened, which might be the interaction of hydroxyl groups on the surface of Ca-REC with hydroxyl, ether bond and carbonyl groups in CMC molecule to form associated hydrogen bonds [21]. The less pronounced broad peak at 3,442 $cm^{-1}$ was assigned to -OH stretching and bending in the H-O-H group. And the peaks at 1,637 $cm^{-1}$ and 1,478 $cm^{-1}$ were caused by stretching vibration and bending vibration of carboxyl groups [22], which demonstrated that carboxymethyl cellulose was loaded onto the substrate of Ca-REC.

The SEM images of the Ca-REC (A), (B) and Ca-REC/CMC (C), (D) composite are shown in Fig. 2. The Ca-REC possessed a typical layer-by-layer structure, at the edges of Ca-REC, platy and folded aggregates of compact parallel layers were either continuously stacked or thinly curled. In addition, the surface of Ca-REC was smooth [22]. After being modified by the CMC, its morphology changed obviously, the surface of Ca-REC/CMC had a rough morphology. A few particles of CMC attached to the surface compared with pure Ca-REC. The $N_2$ adsorption/desorption isotherm including surface areas of Ca-REC and Ca-REC/CMC is listed in Fig. S1. The Ca-REC value of specific areas increased from 9.7 $m^2$/g to 18.3 $m^2$/g after CMC modification. It proved that CMC was loaded successfully on the surface of Ca-REC.

**2. Adsorption Performance**

2-1. Adsorption Kinetics

Adsorption kinetics is a significant standard for evaluating the

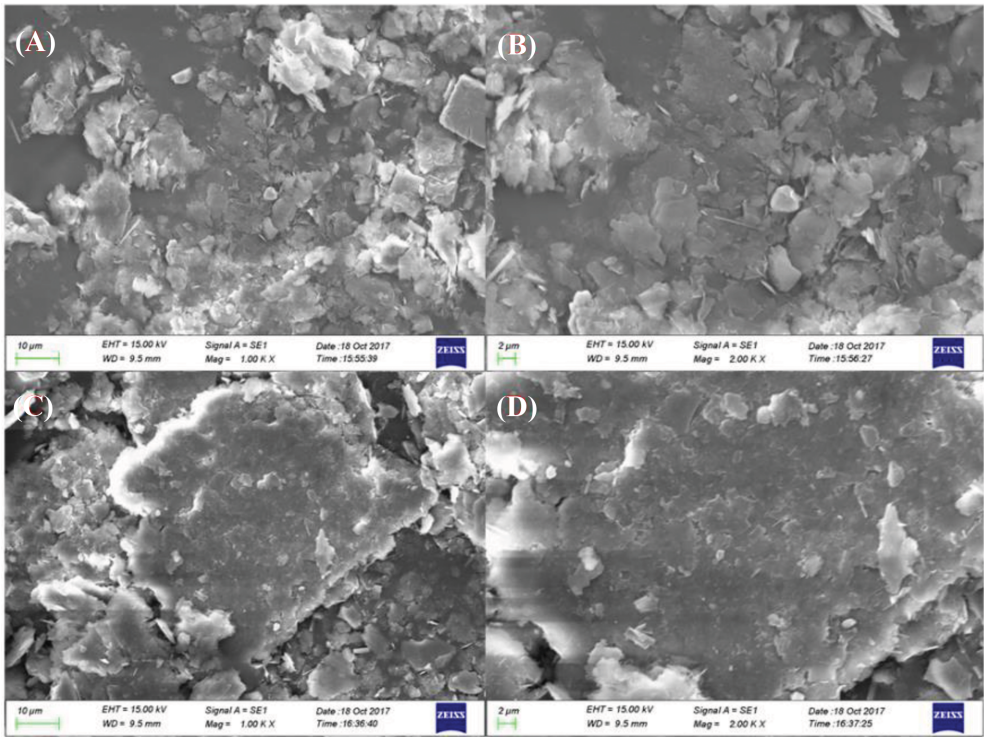



**Fig. 2. The SEM of (A), (B) Ca-REC and (C), (D) Ca-REC/CMC.**

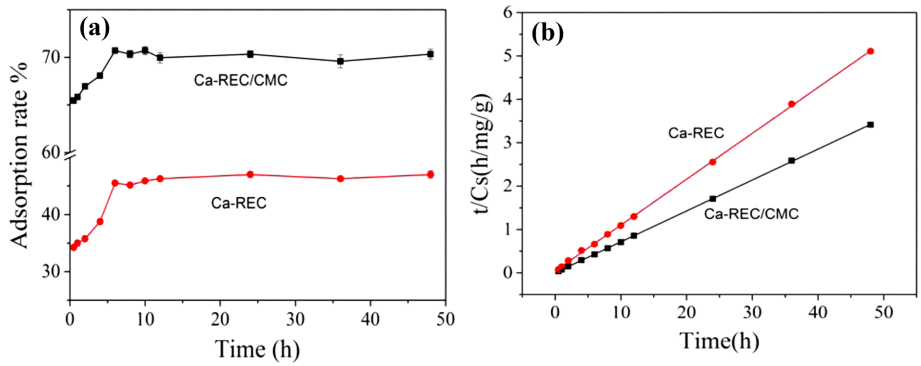



**Fig. 3. (a) Adsorption kinetics and (b) pseudo-second-order kinetic model of Ca-REC Ca-REC/CMC. pH=5.0±0.1, T=293 K, m/V=0.5 g/L, C[U(VI)]$_{initial}$=20 mg/L, I=0.1 mol/L NaCl.**

performance of adsorbents. The result is shown in Fig. 3(a), which indicates that the adsorption of U(VI) onto Ca-REC/CMC and Ca-REC increased at the first 4 h, followed by a slow increase, the adsorption capacity attained adsorption equilibrium after 6 h. The results also displayed that the efficiency of removal U(VI) using Ca-REC/CMC (almost 75%) was much higher than pure Ca-REC (over 45%). Because the carboxymethyl cellulose in the outer layer of the adsorbent was a strong hydrophilic polymer, its affinity with water could make it swell rapidly [23]. Two kinetic models (the pseudo-first-order and pseudo-second-order kinetic) were applied to investigate the possible mechanism of the adsorption process [13]. The kinetic reaction equations are listed in the supply information (S3-4).

As shown in Fig. 3(b), the adsorption of U(VI) on Ca-REC/CMC and Ca-REC could be appropriate for the pseudo-second-order kinetics ($R^2$>0.999). Adsorption quickly reached equilibrium of U(VI) onto Ca-REC/CMC and Ca-REC, which could explain that the process of adsorption was a major ion exchange and chemical adsorption [24]. At the first stage, the active sites on the surface of material interacted with U(VI). But, at the second stage, the remaining little active sites could not easily react with U(VI). Because, the electrostatic repulsion of adsorbent molecules was enlarged with increasing adsorption time [25].

2-2. Effect of Solid Content

For cutting down the cost in practical application, the influence of solid content should be taken into account. Fig. 4(a) shows the influence of adsorbent content on the adsorption of U(VI) onto Ca-REC/CMC. The equation of $K_d$ is listed in the supply information (S5).

In Fig. 4(a), the adsorption ability of Ca-REC/CMC for U(VI) increased rapidly with the content of adsorbents increasing. The adsorption ability of U(VI) increased from 33.7% to 66.8% with adding the quantity of Ca-REC/CMC from 0.2 to 0.8 g/L, which could be explained that the active sites and functional groups increased for the surface complexation on Ca-REC/CMC. When the solid/liquid ratio was larger than 0.8, the relative available surface area of adsorbents was decreased and most energy sites were occupied by a "solid effect", which could lead to a slight increase of adsorption capacity [26]. However, the $K_d$ value slightly decreased with increasing solid content. When the solid content was low, the competition among the solid particles could be ignored, which was in agreement with physico-chemical properties of $K_d$ values [27].

2-3. Effect of Water Chemistries

The pH value and ion strength (IS) are significant factors for removing U(VI) in solution. They can change the surface charge and influence active sites of adsorbing materials [10]. The adsorption ability of Ca-REC/CMC in 0.001, 0.01 and 0.1 mol/L NaCl solution was examined from pH 2 to 10. Fig. 4(b) shows that the pH values had a great effect of removing U(VI) from the solution. It can be seen that, for the three concentrations of IS, the adsorption ability of Ca-REC/CMC for U(VI) increased sharply with increasing pH from 2 to 7, and then maintained at a high level. Whereas, an obvious decrease of the adsorption ability of Ca-REC/CMC was observed at pH>7.0, which clearly suggested that

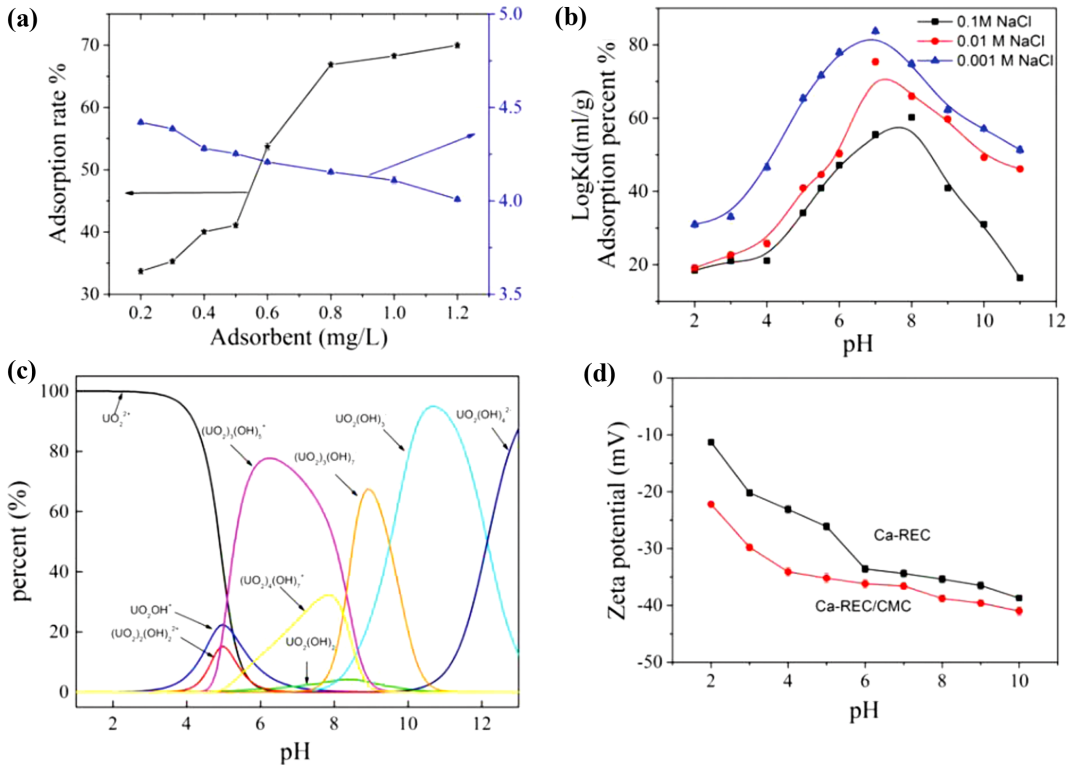



**Fig. 4. (a) Effect of solid content on U(VI) adsorption on Ca-REC/CMC. pH=5.0±0.1, T=293 K, $C_0$=20 mg/L, I=0.1 mol/L NaCl. (b) Effect of ionic strength on U(VI) adsorption to Ca-REC/CMC. m/V=0.5 g/L, $C[U(VI)]_{initial}$=20 mg/L, I=0.1, 0.01 and 0.001 mol/L NaCl, and T=293 K. (c) Relative proportion of 20 mg/L U(VI) species in solution. (d) Surface charge of Ca-REC and Ca-REC/CMC.**

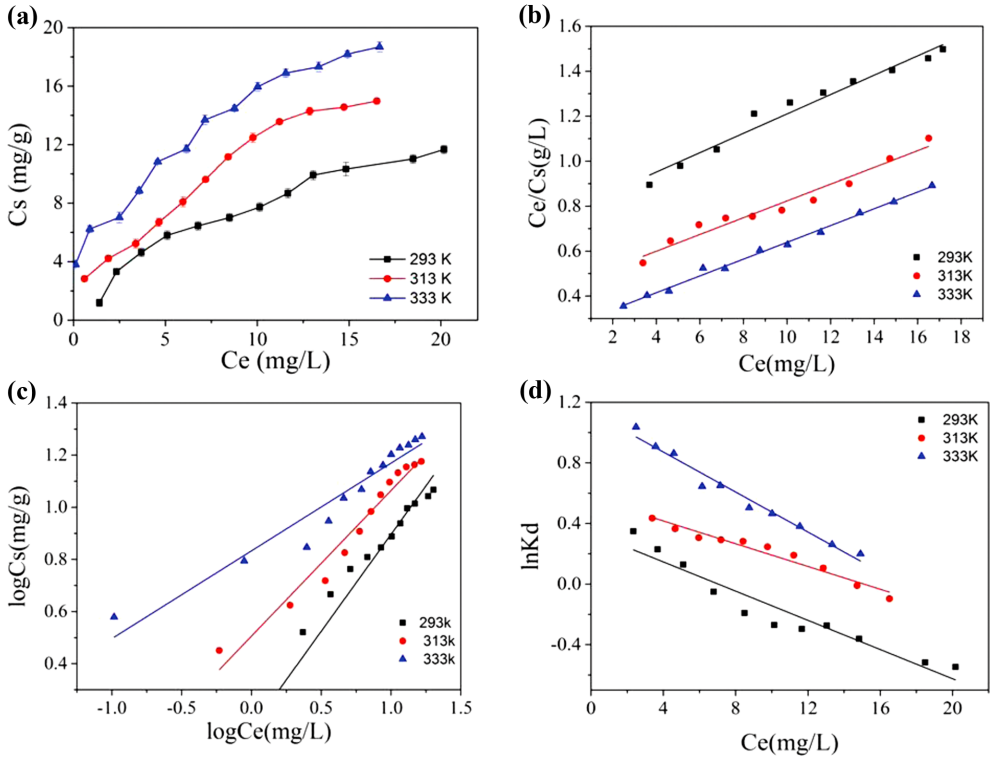



**Fig. 5. (a) Adsorption isotherms of U(VI) onto Ca-REC/CMC at different temperatures; (b) the Langmuir isotherm model; (c) the Freundlich isotherm model; (d) linear plots of $\ln K_d$ versus $C_e$. pH=5.0±0.1, m/V=0.5 g/L, I=0.1 mol/L NaCl.**

the adsorption was closely related to pH. To further demonstrate pH dependence of adsorption U(VI), uranyl ions in different forms in solution were calculated by the hydrolysis constants using the software of Visual MINTEQ (Fig. 4(c)). It can be seen that pH<4, $UO_2^{2+}$ was primary ion in the solution. And between pH 4-8, $(UO_2(OH)^+$, $(UO_2)_3(OH)_5^+$, $(UO_2)_4(OH)_7^+$, $UO_2(OH)_2)$ came out. AT pH>8, the positive ions were changed into negatively charged species in solution [28,29]. Moreover, the zeta-potentials of Ca-REC and Ca-REC/CMC were measured from pH 2 to 10 (Fig. 4(d)). The negative values of zeta potential of the Ca-REC modified by CMC were apparently larger than those of pure Ca-REC at the same pH value, especially pH<6. And the values were −26.1 and −35.2 mV, respectively at pH=5. The greater number of negative surface charges of Ca-REC/CMC could be attributed to the stronger electrostatic attraction, which might be conducive to higher adsorption ability. Moreover, at low pH, the adsorbent was positively charged and the functional groups on the adsorbent surface were protonated; the excessive $H^+$ reacted with the groups (e.g., carboxyl) of Ca-REC/CMC and occupied the adsorption active sites on the surface of Ca-REC/CMC. At high pH, chemical precipitation happened. U(VI) was accumulated on the surface of adsorbent, which caused the material properties to change [30]. Therefore, pH value had an important influence on the adsorption of U(VI).

The effects of IS on the adsorption of U(VI) onto Ca-REC/CMC in 0.001, 0.01, and 0.1 mol/L NaCl are shown in Fig. 4(b). It indicates that the adsorption ability of Ca-REC/CMC gradually decreased with increasing concentration of IS. Commonly, IS has a vital influence on the outer-sphere surface complexation, while the inner-sphere surface complexation exhibited little influence [31]. Therefore, the adsorption mechanism of Ca-REC/CMC was mainly outer-sphere surface complexation.

### 3. Adsorption Isotherms

To explore the adsorption performance of U(VI) onto the synthesized Ca-REC/CMC, the adsorption isotherms at 293, 313 and 333 K were studied (Fig. 5(a)). At the three temperatures, the quality of U(VI) adsorbed on absorbents increased with the content of U(VI) increasing. Higher initial concentration of U(VI) had higher driving forces, which were conducive to transfer metal ions from solution to the surface of materials [32]. In Fig. 5(a), the adsorption ability increased with increasing the temperature, which indicates that higher temperatures were more propitious to adsorbing U(VI). To further analyze the adsorption mechanism of U(VI) onto Ca-REC/CMC, thermodynamic models were applied to simulate the adsorption isotherms. The Langmuir and Freundlich models are described in supplementary information (S6-9) [33,34].

As shown in Fig. 5(b) and 5(c), the adsorption isotherms of Ca-REC/CMC were fitted by Langmuir and Freundlich models; the fitting parameters are shown in Table 1. According to correlation analysis, the Langmuir model was appropriate to describe the whole adsorption process, including monolayer adsorption on the entire surface and chemical-adsorption [35,36]. To evaluate the property of adsorption of Ca-REC/CMC, the adsorption ability of Ca-REC/CMC to U(VI) was compared with that of other reported absorbents [37], as listed in Table 2. At the same conditions of pH and temperature, the Ca-REC/CMC had the highest adsorption capacity

**Table 1. Langmuir model and Freundlich model parameters for the adsorption of U(VI) onto Ca-REC/CMC at 293, 313 and 333 K**

| T (K) | Langmuir model | | | Freundlich model | | |
|---|---|---|---|---|---|---|
| | $C_{s,max}$ (mg/g) | b (L/mg) | $R^2$ | $LogK_F$ ($mg^{1-n}L^n/g$) | n | $R^2$ |
| 293 | 24.3 | 54.1 | 0.992 | 0.744 | 0.152 | 0.913 |
| 313 | 26.8 | 82.8 | 0.991 | 0.559 | 0.505 | 0.961 |
| 333 | 28.3 | 132.9 | 0.993 | 0.337 | 0.833 | 0.934 |

**Table 2. Comparison of maximum U(VI) adsorption ability of Ca-REC/CMC with other adsorbents**

| Absorbent | pH | T (K) | $C_{s,max}$ (mg/g) | Ref. |
|---|---|---|---|---|
| Manganese oxide coated zeolite | 4.0 | 293 | 15.1 | 37 |
| Natural clinoptilolite zeolite | 6.0 | 293 | 2.87 | 38 |
| PANI/bentonite | 5.0 | 293 | 14.1 | 13 |
| Colloidal magnetite | 7.0 | 298 | 1.4 | 39 |
| Ca-REC/CMC | 5.0 | 293 | 24.3 | This study |

**Table 3. Thermodynamic parameters for the adsorption of U(VI) onto Ca-REC/CMC**

| T (K) | $\Delta G^0$ (KJ/mol) | $\Delta H^0$ (KJ/mol) | $\Delta S^0$ (J/mol/K) |
|---|---|---|---|
| 293 | −0.825 | | |
| 313 | −1.47 | 14.7 | 53.3 |
| 333 | −3.76 | | |

owing to the carboxyl group and anionic polyelectrolyte of CMC.

**4. Adsorption Thermodynamics**

The thermodynamic parameters of $\Delta H^0$, $\Delta G^0$, $\Delta S^0$ of the adsorption of U(VI) onto Ca-REC/CMC could be obtained from the different temperature adsorption results. The reaction equations are listed in the supplementary information (S10-13).

$\Delta G^0$, $\Delta S^0$, and $\Delta H^0$ are shown in Table 3. $\Delta H^0$=16.95 kJ $mol^{-1}$ depicted clearly that the adsorption process was endothermic, which is conducive to adsorbing U(VI) from solution at high temperatures. In solution, some uranyl ions were produced by means of dehydration sheaths and the process needed to consume energy. Dehydration sheaths were propitious to adsorbing U(VI) onto the Ca-REC/CMC. This energy exceeded the heat release of cations and adhered to the solid surface [38]. The Gibbs free energy ($\Delta G^0$) was negative, which indicated that the reaction was a spontaneous process. As shown in Table 3, with increasing reaction temperature, the $\Delta G^0$ became more negative, which demonstrated that adsorption was more efficient at higher temperature. According to all the adsorption data and models, the process of adsorption U(VI) onto Ca-REC/CMC surface was a spontaneous and endothermic [39].

**5. Stability and Regeneration Studies**

To reduce the cost of wastewater treatment, recycling experiments were conducted. After adsorption saturation, the used Ca-REC/CMC was washed by HCl (pH 1) with stirring for 6 h to elute U(VI) out, followed by rinsing Ca-REC/CMC with Milli-Q water. The rinsed neutral Ca-REC/CMC was then dried at 60 °C. As shown in Fig. 6, compared with the raw Ca-REC/CMC, the adsorption capacity of reused Ca-REC/CMC to U(VI) decreased slightly with increasing the reused times. The adsorption efficiency was less than 5% decreased after six times of recycling, which displayed the good reusability and stability of Ca-REC/CMC.

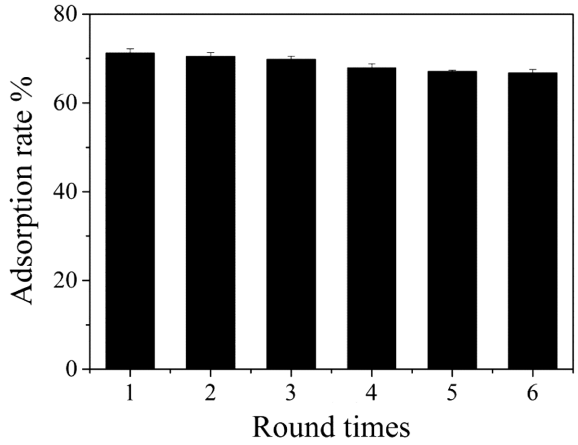



**Fig. 6. Recycling of Ca-REC/CMC in the removal of U(VI) from aqueous solutions. T=293±1 K, $C[U(VI)]_{initial}$=20.0 mg/L, m/V=0.5 g/L, pH=5.0±0.1, I=0.01 mol/L NaCl.**

**6. Adsorption Mechanisms**

To investigate the adsorption mechanism of Ca-REC/CMC and U(VI), XPS technology was applied into before and after adsorption experiments. As shown in Fig. 7, the XPS spectra survey shows C 1s, O 1s, N 1s, and U 4f before and after U(VI) adsorption. According to the survey spectra (Fig. 7(a)), there were two new peaks of U 4f (382.31 eV, U $4f_{7/2}$ and 393.19 eV, U $4f_{5/2}$) appearing after adsorption, which made it clear that U(VI) was successfully fixed on the surface of Ca-REC/CMC. As shown in Fig. 7(b), the C-O peak shifted from 285.72 to 286.02 eV, and the C=O peak shifted from 287.51 to 288.58 eV at the same peak position, which was in accordance with the work published by Ding et al. [40]. Fig. 7(c) shows that the peak position of Si-O and Al-O for the Ca-REC/CMC was 532.03 eV, which was shifted to 532.17 eV [41]. The binding energy of C-O followed the same trend from 523.73 to 523.86 eV. The results make it clear that U(VI) interacted with oxygenic groups to produce stable complexes. According to Francis et al. [42], the unpaired spins electrons multiply broke up into forming double peaks. The peaks of at 382.31 and 393.19 eV were

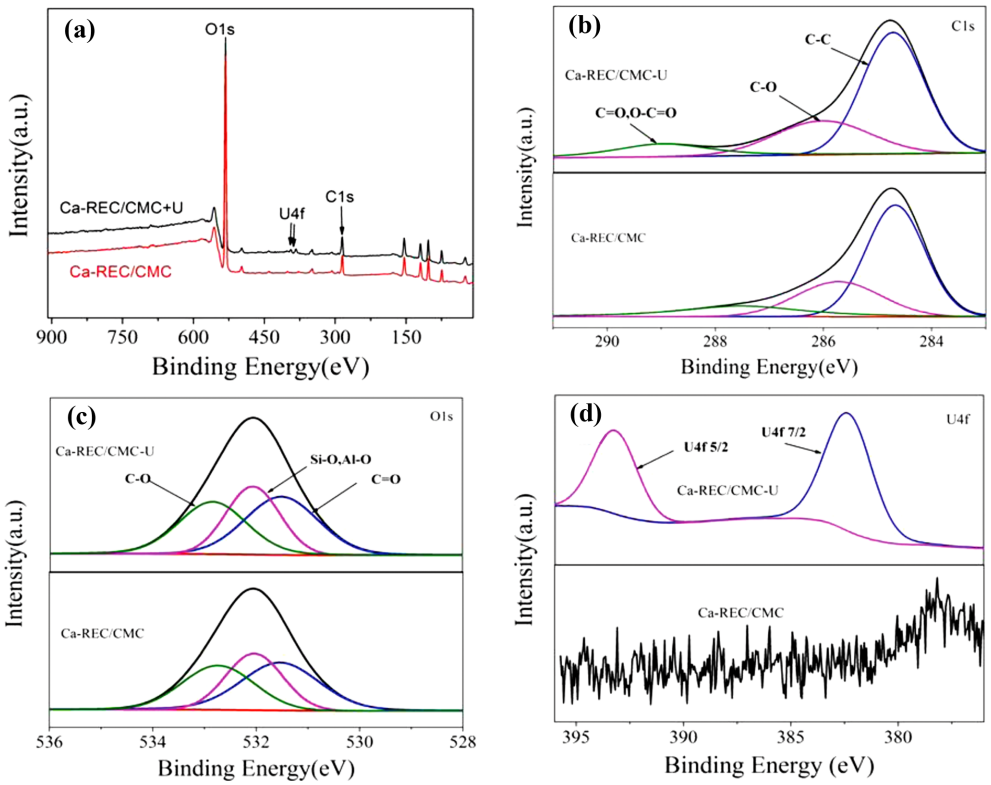



**Fig. 7. XPS spectra of Ca-REC/CMC before and after the adsorption of U(VI): wide scan (a) and high-resolution spectra of C 1s (b), O 1s (c), U4f (d).**

in accordance with U $4f_{7/2}$ and U $4f_{5/2}$, respectively (Fig. 7(d)). As shown in Fig. 7(b) and 7(c), the positions of C 1s and O 1s offset higher values, which illustrates that a new bond was generated by the interaction between U(VI) and Ca-REC/CMC. Based on the bond energy to analyze the generated functional groups, 532.17 eV was attributed to Al-O-$UO^{2+}$ and Si-O-$UO^{2+}$, 532.86 eV was assigned to C-O-$UO^{2+}$ (Fig. 7(c)), and 285.96 eV and 287.85 eV belonged to COO-$UO^{2+}$ (Fig. 7(b)).

## CONCLUSION

Batch experiments were conducted on the adsorption ability of Ca-REC/CMC for removal U(VI) from solution. By materials characterization, CMC was successfully loaded onto Ca-REC. The adsorption of U(VI) onto Ca-REC/CMC was a spontaneous and endothermic process. And all the adsorption processes could be expressed by pseudo-second-order kinetics model and the Langmuir model. Furthermore, the adsorbent process was related to pH value and ionic strength. XPS revealed the adsorption mechanism; entrapment was achieved through the complexation of U(VI) with oxygen-containing functional groups on the Ca-REC/CMC surface. Finally, the potential of Ca-REC/CMC is valuable in practical applications.

## NOTES

The authors declare no competing financial interests.

## ACKONWLEDGEMENTS

Financial supports from the National Natural Science Foundation of China (11675210), the NSAF (U1530131), the Research Fund Program of Guangdong Provincial Key Laboratory of Radionuclides Pollution Control and Resources (GZDX2016K004), the specialized research fund for the doctoral program of Hefei University of Technology (JZ2016HGBZ0769), National key R&D program inter-governmental/Hong Kong, Macao and Taiwan special project (2017YFE0115200) are acknowledged.

## SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

## REFERENCES

1. A. Galhoum, M. Mahfouz, A. Atia, S. Abdel-Rehem, N. Gomaa, T. Vincent and E. Guibal, *Ind. Eng. Chem. Res.*, **54**, 12374 (2015).
2. Y. Zhao, J. Li, L. Zhao, S. Zhang, Y. Huang, X. Wu and X. Wang, *Chem. Eng. J.*, **235**, 275 (2014).
3. Y. Zhao, J. Li, S. Zhang, H. Chen and D. Shao, *Rsc Adv.*, **3**, 18952 (2013).
4. P. Bhalara, D. Punetha and K. Balasubramanian, *J. Environ. Chem. Eng.*, **2**, 1621 (2014).

5. B. Li, C. Bai, S. Zhang, X. Zhao, Y. Li, L. Wang, K. Ding, X. Shu, S. Li and L. Ma, *J. Mater. Chem. A*, **3**, 23788 (2015).
6. Y. Xie, C. Chen, X. Ren, X. Wang, H. Wang and X. Wang, *Prog. Mate. Sci.*, **103**, 180 (2019).
7. W. Hang, L. Ma, K. Cao, J. Geng, J. Liu, Q. Song, X. Yang and S. Li, *J. Hazard. Mater.*, **229-230**, 321 (2012).
8. Y. Xie, C. Chen, X. Ren, X. Tan, G. Song, D. Chen, A. Alsaedi and T. Hayat, *J. Colloid Interface Sci.*, **550**, 117 (2019).
9. Q. Dai, W. Zhang, F. Dong, Y. Zhao and X. Wu, *Chem. Eng. J.*, **249**, 226 (2014).
10. Z. Lv, H. Wang, C. Chen, S. Yang, L. Chen, A. Alsaedi and T. Hayate, *J. Colloid Interface Sci.*, **537**, A1 (2019).
11. J. Li, X. Wang, G. Zhao, C. Chen, A. Alsaedi, T. Hayatf and X.Wang, *Chem. Soc. Rev.*, **7**, 2232 (2018).
12. J. Wang, Z. Chen, D. Shao, Y. Li, Z. Xu, C. Cheng, A. Asiri, H. Marwani and S. Hu, *J. Mol. Liq.*, **242**, 678 (2017).
13. X. Liu, C. Cheng, C. Xiao, D. Shao, Z. Xu, J. Wang, S. Hu, X. Li and W. Wang, *Appl. Surf. Sci.*, **411**, 331 (2017).
14. F. Xu, C. Xu, H. Chen, D. Wu, Z. Gao, X. Ma, Q. Zhang and K. Jiang, *J. Alloy Compd.*, **780**, 634 (2019).
15. X. Wu and Y. Jing, *Trans. China Pulp Paper*, **31**, 1 (2016).
16. Z. Feng, D. Liu and X. Ma, *Chemosphere*, **144**, 621 (2016).
17. L. Zeng, M. Xie, Q. Zhang, Y. Kang, X. Guo, H. Xiao, Y. Peng and J. Luo, *Carbon. Poly.*, **123**, 89 (2015).
18. H. Peng, M. Guo, Y. Wang, A. Wang, H. Huang and Z. Lei, *J. Power Sources*, **211**, 40 (2012).
19. Q. Qun, Y. Shu and F. Xin, *Adv. Mater.*, **23**, 5574 (2011).
20. Z. Huang, P. Wu, B. Gong, Z. Xing, Z. Liao, P. Chang and X. Hu, *Appl. Clay Sci.*, **142**, 128 (2017).
21. M. Zohuriaan-Mehr, A. Pourjavadi and M. Salehi-Rad, *React. Funct. Polym.*, **61**, 23 (2004).
22. M. Atanasova, A. Vyalikh, U. Scheler and W. Focke, *Appl. Clay Sci.*, **126**, 7 (2016).
23. P. I. Carmen, P. Filip, D. Humelnicu, I. Humelnicu, T. Scott and R. Crane, *J. Nucl. Mater.*, **443**, 250 (2013).
24. Y. Sun, Q. Wang, C. Chen, X. Tan and X. Wang, *Environ. Sci. Technol.*, **46**, 6020 (2012).
25. W. Song, X. Wang, Q. Wang, D. Shao and X. Wang, *Phys. Chem. Chem. Phys.*, **17**, 398 (2015).
26. X. Liu, J. Li, X. Wang, C. Chen and X. Wang, *J. Nucl. Mater.*, **466**, 56 (2015).
27. M. Xu, T. Wang, P. Gao, L. Zhao, L. Zhou and D. Hua, *J. Mater. Chem. A*, **7**, 11214 (2019).
28. D. Shao, X. Wang, J. Li, Y. Huang, X. Ren, G. Hou and X. Wang, *Environ. Sci. Water Res. Technol.*, **1**, 169 (2015).
29. X. Wang, D. Shao, X. Wang and J. Hu, *Rsc Adv.*, **6**, 52076 (2016).
30. M. Rafatullah, O. Sulaiman, R. Hashim and A. Ahmad, *J. Hazard. Mater.*, **170**, 969 (2009).
31. L. Cao, X. Wang and W. Gang, *Chem. Eng. J.*, **260**, 469 (2015).
32. L. Jie, C. Chen, K. Zhu and X. Wang, *J. Taiwan Inst. Chem. Eng.*, **59**, 389 (2016).
33. X. Tan, M. Fang, J. Li and X. Wang, *J. Hazard. Mater.*, **168**, 458 (2009).
34. V. L. Halla, R. Hurt, M. Juan and R. J. Rene, *Environ. Sci. Technol.*, **48**, 1166 (2014).
35. B. Wang, Y. Zhou, L. Li and Y. Wang, *Sci. Total Environ.*, **626**, 219 (2018).
36. M. Zeng, Y. Huang, S. Zhang, S. Qin, J. Li and J. Xu, *Rsc Adv.*, **4**, 5021 (2014).
37. R. Han, W. Zou, Y. Wang and L. Zhu, *J. Environ. Radioactiv.*, **93**, 127 (2007).
38. G. Zhao, T. Wen, X. Yang, S. Yang, J. Liao, J. Hu, D. Shao and X. Wang, *Dalton Trans.*, **41**, 6182 (2012).
39. G. Zhang, X. Ren, G. Xing, X. Tan, J. Li, C. Chen and X. Wang, *Dalton Trans.*, **40**, 10945 (2011).
40. C. Ding, W. Cheng, Y. Sun and X. Wang, *Dalton Trans.*, **43**, 3888 (2014).
41. R. Zhao, C. Chen, L. Jie and X. Wang, *Appl. Surf. Sci.*, **349**, 129 (2015).
42. A. Francis, C. Dodge, F. Lu, G. Halada and C. Clayton, *Environ. Sci. Technol.*, **28**, 636 (1994).

# Supporting Information

# Removal of U(VI) from aqueous solution using carboxymethyl cellulose-modified Ca-rectorite hybrid composites

**Xinghao Liu*,**,***, Shuheng Hu**,†, Di Xu****,†, and Dadong Shao***,†**

*Center for Environment and Water Resource, College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P. R. China
**School of Resources & Environmental Engineering, Hefei University of Technology, Hefei 230009, Anhui, P. R. China
***Jiangsu Key Laboratory of Chemical Pollution Control and Resources Reuse, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China
****State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China
(*Received 27 October 2019 • accepted 12 January 2020*)

The adsorption percentage (R, %) and adsorption quantity ($Q_e$, mg/g) of U(VI) of Ca-REC/CMC can be calculated by the equations (Eqs. (1) and (2)):

$$R = \frac{C_0 - C_e}{C_0} * 100\% \quad (1)$$

$$Q_e = \frac{(C_0 - C_e) * V}{m} \quad (2)$$

Where $C_0$ (mg/L) and $C_e$ (mg/L) represents the initial and equilibrium concentration of element in solution, respectively. V (L) and m (g) are the volume of the suspension and the mass of Ca-REC/CMC, respectively. All results of experiment were the average of three times. And the average error ranges were less than 5%.

The kinetic reaction equations are expressed (3-4):

$$\ln(q_e - q_t) = \ln q_t - k_f * t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_s * q_e^2} + \frac{t}{q_e} \quad (4)$$

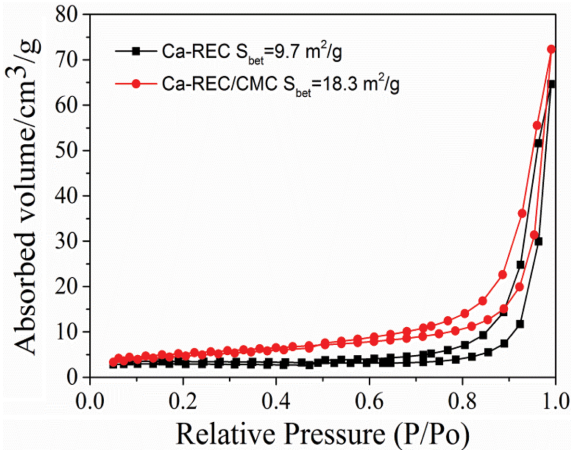



**Fig. S1. $N_2$ adsorption-desorption isotherms of Ca-REC and Ca-REC/CMC.**

$q_e$ (mg/g) and $q_t$ (mg/g) are the adsorbed amounts of U(VI) at equilibrium and reaction time t, respectively. $k_f$ and $k_s$ present rate constants of the pseudo-first kinetic order model and pseudo-second order kinetic model, respectively.

The $K_d$ is calculated by the following equation:

$$K_d = \frac{C_0 - C_e}{C_0} * \frac{V}{m} \quad (5)$$

The Langmuir model supposes that the adsorption only arises at a fixed quantity of localized sites on the surface with all adsorption sites identically and energetically equivalent, which can be represented by the following equation [1]:

$$C_S = \frac{bC_{S,\max}C_e}{1 + bC_e} \quad (6)$$

then transformed in a linear equation:

$$\frac{C_e}{C_s} = \frac{1}{bC_{s\max}} + \frac{C_e}{C_{s\max}} \quad (7)$$

where $C_e$ (mg/L) is the equilibrium concentration of U(VI) in the liquid phase, $C_s$ (mg/g) is the amount of U(VI) adsorbed on the solid phase at equilibrium, $C_{s,\max}$ (mg/g) is the maximum amount of U(VI) adsorbed at complete monolayer coverage, b (L/g) is a constant related to the enthalpy of adsorption.

The Freundlich expresses an exponential equation with the assumption of a heterogeneous adsorbent surface, which is used to describe the adsorption on heterogeneous surfaces. The model can be expressed by the following equation [2]:

$$C_s = K_F C_e^n \quad (8)$$

then transformed in a linear equation:

$$\log C_S = \log K_F + n \log C_e \quad (9)$$

where $K_F$ ($(mol^{1-n}L^n g^{-1})$) is the Freundlich constants representing the adsorption capability when the metal ion equilibrium concentration equals to 1 and n is the adsorption intensity of dependence

of adsorption at equilibrium concentration.

The thermodynamic parameters of $\Delta H^0$, $\Delta G^0$, $\Delta S^0$ of the adsorption of U(VI) onto Ca-REC/CMC can be get from the different temperature adsorption results [3]. The standard free energy change ($\Delta G^0$) can be calculated from the following relationship:

$$\Delta G^0 = -RT\ln K^0 \tag{10}$$

where R (8.314 J $mol^{-1}$ $K^{-1}$) is the gas constant and $K^0$ is thermodynamic equilibrium constant, which can be calculated by plotting $\ln K_d$ versus $C_e$ (Fig. 5(d)) and extrapolating $C_e$ to zero. The values of $\Delta H^0$ and $\Delta S^0$ can be calculated from the following relationship:

$$\ln K^0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{11}$$

$$\Delta S^0 = -\left(\frac{\partial \Delta G^0}{\partial T}\right)_P \tag{12}$$

The slope and intercept of the plot of $\ln K^0$ versus 1/T are $-\Delta H^0/R$ and $\Delta S^0/R$, respectively. The average standard enthalpy change ($\Delta H^0$) is then calculated from the equilibrium:

$$\Delta H^0 = \Delta G^0 + T\Delta S^0 \tag{13}$$

## REFERENCES


1. X. Tan, M. Fang, J. Li and X. Wang, *J. Hazard. Mater.*, **168**, 458 (2009).
2. V. L. Halla, R. Hurt, M. Juan and R. J. Rene, *Environ. Sci. Technol.*, **48**, 1166 (2014).
3. X. Liu, C. Cheng, C. Xiao, D. Shao, Z. Xu, J. Wang, S. Hu, X. Li and W. Wang, *Appl. Surf. Sci.*, **411**, 331 (2017).