RSC Advances

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Synthesis of the activated carbon based urea formaldehyde resin and its adsorption and recognition performance towards Fe(Ⅲ)

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Abstract: Rare earths are very important strategic resources. However, impurities, such as Fe(III), have great adverse impact on the properties of rare earth material. Therefore, efficient and easy removal of non-rare earth impurities from rare earth is extremely important. A novel activated carbon, $AC_{UF}700$, was synthesized by homemade urea formaldehyde resin carbonized at 700 °C. The $AC_{UF}700$ was characterized by surface area analyzer, FT-IR, element analysis, and SEM methods. The adsorption and recognition properties of $AC_{UF}700$ towards Fe(Ⅲ) ion were studied. The BET special surface area of $AC_{UF}700$ was 702.3 $cm^3 \cdot g^{-1}$, and the average pore diameter was 2.044 nm. The $AC_{UF}700$ possesses strong adsorption affinity and excellent recognition selectivity for Fe(III). The adsorption capacity could reach to 12.8 $mg \cdot g^{-1}$, and relative selectivity coefficients relative to La(III) was 28.0. Besides, the $AC_{UF}700$ was regenerated easily using diluted hydrochloric acid solution as eluent and $AC_{UF}700$ possesses better reusability.

Keywords: activated carbon; adsorption; selectivity; Fe(III); urea formaldehyde resin

1. Introduction

The rare earths elements (REEs) are composed of scandium, yttrium, and the lanthanides metallic elements. As one of the most important strategic and critical mineral resources, REEs have a significant role on luminescence, electronics, magnetism, catalysis, metallurgy, and the ceramic industry [1,2]. As a non-rare earth impurity, Fe(III) have great adverse impact on the properties of rare earth material [3]. Removals of non-rare earth impurity get more and more attention. Therefore, efficient and easy removal of non-rare earth impurities from high purity rare earth is extremely

important. Researchers have been done some related studies in the last century [4.5]. Solvent extraction method and extraction-elution resin (solvent impregnated resin) method are mainly used. However, some shortcomings, such as low separating efficiency, are concomitant. So, researching a new effective separation material is important for economic and social benefit.

Porous carbons have been widely used as adsorbents [6,7], catalyst supports [8], and electrode materials [9] due to their developed pore structure, high specific surface and easy to surface modification. The pore structure and surface chemical property of porous carbon determine its application properties [10-12]. Direct preparation using nitrogen-containing compounds as precursor is an effective route to introduce nitrogen into carbon matrix [13, 14].

Urea formaldehyde resins (UF resins) have been widely used in adhesives, finishes, medium density fiberboard (MDF), and molded objects. Taking into accounts of its high content of nitrogen, UF resins can be used as a raw material for the fabrication of nitrogen-containing activated carbon [15-18].

In this study, activated carbon was synthesized using UF resins as raw material. The pore structure, surface chemical groups were characterized, and its adsorption and recognition properties for Fe(III) were investigated.

2. Experimental

2.1 Preparation and characterizations of $AC_{UF}700$

For preparing UF resin, 18 g of $NaHCO_3$, 35 ml of formaldehyde aqueous solution (37%) and 15 g of urea was mixed in a beaker. The mixture was heated to 95

°C for 5 h. The resultant solid resins were placed in vacuum oven for 24 h at 80 °C to ensure complete dryness. The powdered resin was carbonized in charcoal furnace at 700 °C for 2 h with heating rate of 2 °C·min^{-1} and N_2 flow of 50 ml·min^{-1}. Finally, the samples were washed with distilled water until neutral and dried at 80 °C for 24 h.

Nitrogen adsorption-desorption isotherm was measured with a surface area analyzer (Beijing JWGB BF-JW132F) by nitrogen absorption at 77 K using the Brunauer-Emmett-Teller (BET) method. Before measurements, the sample was degassed at 180 °C in a vacuum for more than 3h. The surface area was calculated by the BET method from the adsorption branch in the relative pressure range (P/P_0) of 0.005 to 0.1. The SEM images were obtained on a S-4800 Field Emission-Scanning Electron Microscope (Hitachi, Japan) operated at 1 kV. Fourier transform infrared (FTIR) spectra of the samples were measured on a Nicolet FT-IR 4800s (Shimadzu, Japan) spectrometer using the conventional KBr pellet method. The element content was measured with Vario EL elemental analyzer (Elementar, Germany).

2.2 Batch adsorption of activated carbon toward Fe(III)

2.2.1 Kinetic adsorption curve and adsorption isotherm

About 0.05 g of $AC_{UF}700$ was introduced into a conical flask directly. 25 ml of Fe(III) aqueous solution with concentration(C_0) of 100 mg·L^{-1} and pH of 2 was then added into the conical flask. This conical flask was placed in a shaker at a presettled temperature. At different times, the concentrations (C_t) of Fe(III) solution were determined by inductive coupled plasma emission spectrometer. The adsorption capacity (Q) was calculated according to Eq. (1).

$$Q = \frac{V(C_0 - C_t)}{m} \quad (1)$$

where V is the volume of the solution (L); m is the weight of absorbent carbon material (g).

Several same conical flasks were prepared and about 0.05 g of $AC_{UF}700$ was introduced into each flask directly. 25 ml of Fe(III) aqueous solutions with different concentrations (C_0) and same pH of 2 were then added into each conical flask. The conical flasks were placed in a shaker at a presettled temperature. After the adsorption reached equilibrium, the equilibrium concentrations (C_e) of Fe(III) solutions in different flasks were determined by inductive coupled plasma emission spectrometer. The equilibrium adsorption capacities (Q_e) were calculated according to Eq. (1).

2.2.2 Selectivity experiments

The binary mixed solution of Fe(III)/La(III) was prepared, the concentrations of Fe(III) and La(III) were 10 $mg \cdot L^{-1}$ and 100 $mg \cdot L^{-1}$, respectively. The batch adsorption experiment was performed. After adsorption reached equilibrium, the concentrations of Fe(III) and La(III) in the remaining solutions were determined. Distribution coefficients (K_d) of Fe(III) and La(III) were calculated by Eq. (2).

$$K_d = \frac{Q_e}{C_e} \quad (2)$$

Selectivity coefficient (k) of $AC_{UF}700$ for Fe(III) with respect to the competitor species La(III) can be obtained by Eq.(3).

$$k = \frac{K_d(Fe^{3+})}{K_d(La^{3+})} \quad (3)$$

2.3 Dynamics adsorption experiment

2.0 g of $AC_{UF}700$ was filled in a glass column with 10 ml of the bed volume. The mixture solution of Fe(III) and La(III) with the initial concentrations of 10 $mg \cdot L^{-1}$ and 100 $mg \cdot L^{-1}$, respectively. And the mixture solution pH of 2 was allowed to flow gradually through the column at a rate of 5 $BV \cdot h^{-1}$. 1 BV of effluent was collected and the concentration was determined. Then the dynamics adsorption curve was plotted.

2.4 Repeated use experiment

The reusability is an important factor for a good absorption material. Desorption of the adsorbed Fe(III) from the $AC_{UF}700$ also studied by batch experimental. 5 mL of hydrochloric acid solution with concentration of 2 $mol \cdot L^{-1}$ was used as eluent for 0.2 g of adsorbent, and the desorption time was 30 min. In order to test the reusability of $AC_{UF}700$, Fe(III) adsorption-desorption procedure was repeated nine times.

3. Result and Discussion

3.1 Characterization of $AC_{UF}700$

The Fourier transformed infrared (FTIR) spectra of UF and $AC_{UF}700$ were shown in Fig.1.

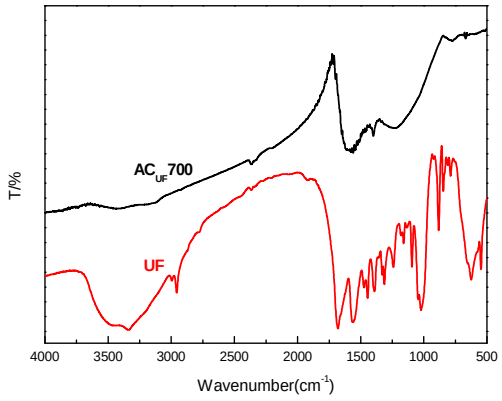

Fig.1 FTIR spectra of UF and $AC_{UF}700$

The FT-IR spectra of UF and $AC_{UF}700$ were shown in Fig.1. As for UF resin synthesized here, the band's assignment is in well agreement with the literature report [19]. The band between 3200 and 3500 cm^{-1} attributed to NH stretching vibrations, and the band between 1500 and 1600 cm^{-1} attributed to C=C stretching vibrations. Three bands at 1080, 1039 and 875 cm^{-1} were assigned to asymmetric stretching vibration of the ether, C-O stretch of C-OH, and cyclic ether linkages. $AC_{UF}700$ exhibits broader and overlapping bands due to the strong IR absorption of carbon and complex rearranged structure. It can be seen from spectra of $AC_{UF}700$ that $AC_{UF}700$ still retain the amine functional group after carbonization.

The morphologies of the $AC_{UF}700$ with different magnification characterized by scanning electron microscopy were shown in Fig.2.

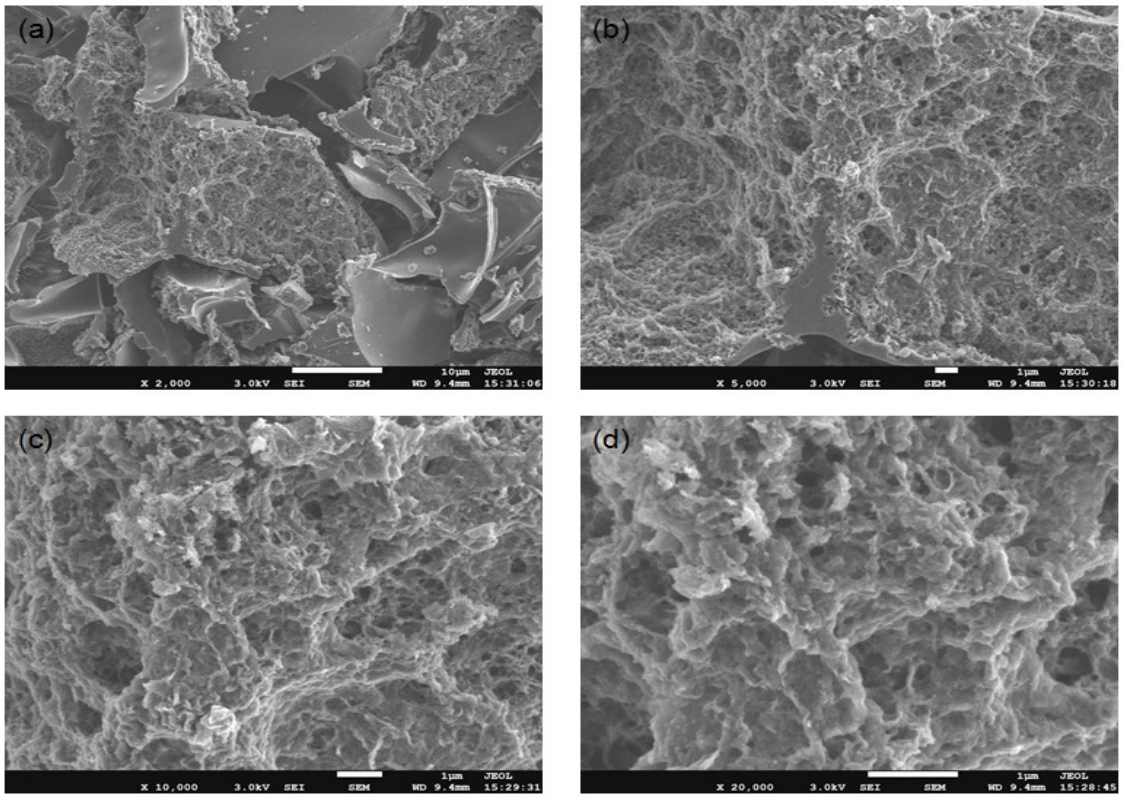

Fig.2 SEM images of $AC_{UF}700$ with different magnification

The developed pore structure was observed easily. The relative data were listed in Table 1.

The surface properties of samples were measured by N_2 adsorption-desorption isotherms (Fig.3). The chemical composition and pore structure parameters of $AC_{UF}700$ were listed in Table 1.

The $AC_{UF}700$ exhibited type I isotherms, and the pore size distribution is narrow.

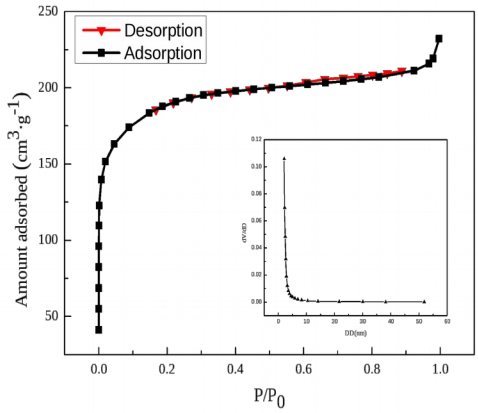

Fig.3 N_2 adsorption-desorption isotherms

Table 1 Chemical composition and structure parameters of AC_{UF}

Sample	Elemental analysis (wt%)			Structure parameter				Yield (%)
	C	N	H	S_{BET} ($m^2 \cdot g^{-1}$)	d (nm)	V_{Micro} ($cm^3 \cdot g^{-1}$)	V_{total} ($cm^3 \cdot g^{-1}$)	
$AC_{UF}400$	55.46	24.54	4.26	3	20.49	0.001	0.015	7.73
$AC_{UF}700$	53.42	15.11	2.68	702	2.04	0.267	0.359	4.22
$AC_{UF}800$	67.80	9.98	2.41	1920	2.77	0.229	1.328	1.21

3.2 Adsorption properties of $AC_{UF}700$ towards metal ions

3.2.1 Kinetic adsorption curve

The kinetic adsorption curve was shown in Fig.4.

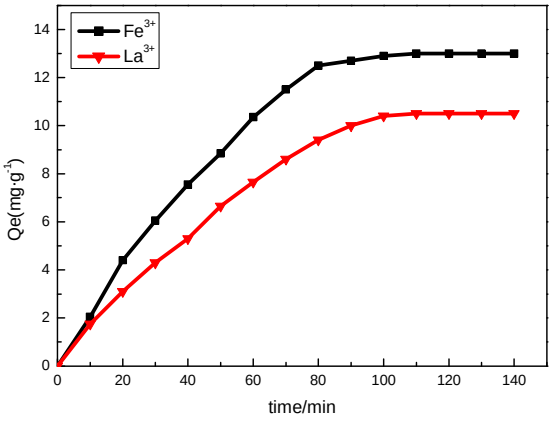

Fig.4 Kinetic adsorption curves of $AC_{UF}700$ for Fe(III) and La(III)

Temperature: 25 °C; pH = 2

The adsorption rate of $AC_{UF}700$ toward the Fe(III) and La(III) ions were vary fast, the adsorption reached to equilibrium within 80 min and 100 min, respectively. It can be seen that the saturated adsorption capacity of $AC_{UF}700$ for Fe(III) and La(III) is 12.8 $mg \cdot g^{-1}$ and 10.3 $mg \cdot g^{-1}$, respectively. It was implied that $AC_{UF}700$ possesses very strong adsorption ability for Fe(III) and La(III) ion.

3.2.2 Adsorption isotherms

Langmuir equation is as follows:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{kQ_m} \quad (4)$$

where C_e ($mg \cdot L^{-1}$) is equilibrium concentration, Q_e ($mg \cdot g^{-1}$) is the equilibrium adsorption capacity, Q_m ($mg \cdot g^{-1}$) is the saturated adsorption capacity, k is the combine constant.

The data of Fe(III) and La(III) in Fig.5 are regressed linearly according to Eq.(4) and Table 2 is obtained. The date in Table 2 fits satisfactorily to the Langmuir

equation obviously, and this indicates fully that the Fe(III) and La(III) are adsorbed on the $AC_{UF}700$ with monomolecular layer.

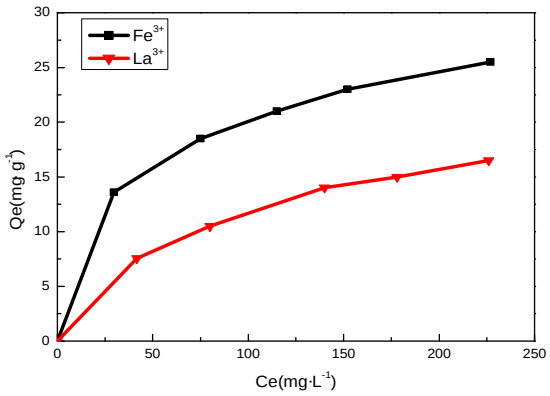

Fig.5 Adsorption isotherms of $AC_{UF}700$ for Fe(III) and La(III)

Temperature: 25 °C; pH = 2; Adsorption time: 12 h

Table 2 Fitting parameters of Langmuir isotherm

Ion	Q_m	k	R^2	Linear equation
Fe^{3+}	29.66	0.02395	0.9974	Y=1.4077+0.03371*X
La^{3+}	22.71	0.01136	0.9985	Y=3.8745+0.04403*X

3.2.3 Adsorption selectivity

Competitive adsorptions of $AC_{UF}700$ for Fe(III) from Fe(III)/La(III) mixtures were researched in batch systems. Table 3 summarized the data of the distribution coefficients K_d and selectivity coefficients k.

Table 3 Distribution coefficient and selectivity coefficient data of $AC_{UF}700$

Adsorbent	K_d(L·g^{-1})		k
	Fe(III)	La(III)	
$AC_{UF}700$	2.80	0.10	28.0

It can be seen that $AC_{UF}700$ has high selectivity for Fe(III). This suggests that the adsorption recognition of $AC_{UF}700$ for Fe(III) is very strong.

3.3. Column adsorption characteristics of $AC_{UF}700$ toward Fe(III)

3.3.1 Dynamic adsorption curve

Fig.6 shows the dynamic adsorption curve of $AC_{UF}700$ for mixture solution of Fe(III) and La(III) with the initial concentrations of 10 $mg \cdot L^{-1}$ and 100 $mg \cdot L^{-1}$, respectively.

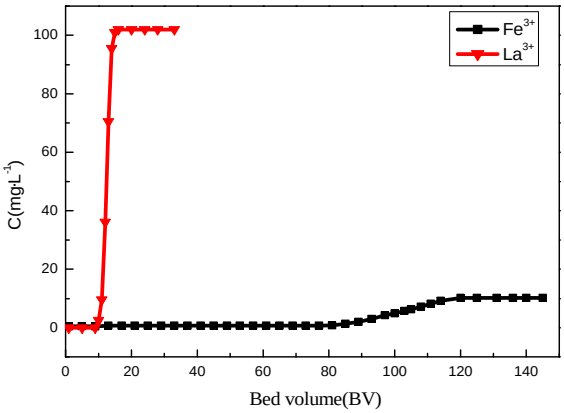

Fig.6 Dynamic adsorption curve of $AC_{UF}700$ towards mixture of Fe(III) and La(III)

Temperature: 25 °C; pH = 2

The leaking bed volume for Fe(III) is 120 BV and La(III) is 18 BV. In addition, the leaking concentration of Fe(III) is less than 5 $mg \cdot L^{-1}$ before 100 BV. This indicated that Fe(III) can be recognized better by $AC_{UF}700$ and $AC_{UF}700$ can selectively remove Fe(III) from La(III) solution.

3.4 Desorption and reusability

When hydrochloric acid was used as an eluent, the interaction between Fe(III) and $AC_{UF}700$ is disrupted and subsequently Fe(III) are released into desorption medium. In order to show the reusability of the $AC_{UF}700$, adsorption-desorption cycle was repeated 9 times by using the same carbon material. Adsorption-desorption cycle of Fe(III) $AC_{UF}700$ was shown in Fig.7. The result clearly shows that the $AC_{UF}700$

could be used repeatedly without loosing significantly binding amount.

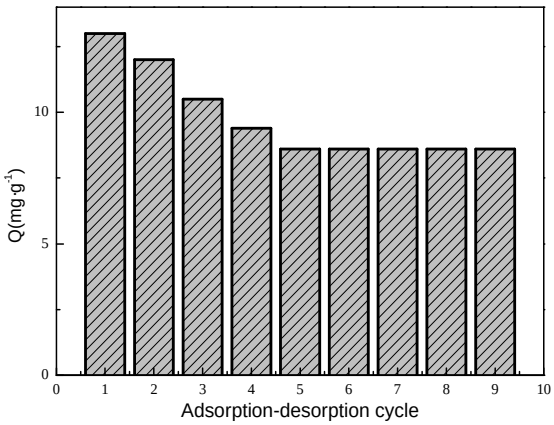

Fig.7 Adsorption-desorption cycle of $AC_{UF}700$

4. Conclusion

In this paper, high-performance activated carbon $AC_{UF}700$ was synthesized successfully by homemade urea formaldehyde resin carbonized at 700 ºC. The BET special surface area could be reached 702.3 $m^2 \cdot g^{-1}$。The average pore size was 2.044 nm. $AC_{UF}700$ possesses strong adsorption affinity, specific recognition ability, and excellent selectivity for Fe(III). The adsorption capacity could reach to 12.8 $mg \cdot g^{-1}$, and relative selectivity coefficients relative to La(III) is 28.0. Besides, $AC_{UF}700$ was regenerated easily using diluted hydrochloric acid solution as eluent and $AC_{UF}700$ possesses better reusability.

Acknowledgments

The authors gratefully acknowledge the financial support of this work by the International Science & Technology Cooperation Program of China (No. 2011DFA51980), Shanxi Science & Technology Cooperation Program of China (No.

2015081043), and Science Foundation of Shanxi Province (No. 20130321022-02, 2013021012-3, 20140313002-4).

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