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Effective removal of anilines using porous activated carbon based on ureaformaldehyde resin

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Abstract−The effective removal of aniline and its derivatives from wastewater is very important due to the high toxicity. Adsorption with a high-performance adsorbent is an efficient pathway. A novel activated carbon, ACUF-700, was synthesized using homemade ureaformaldehyde resin as the major carbon source carbonized at 700 °C. ACUF-700 is characterized by surface area analyzer, FTIR, elemental analyzer, and SEM. The adsorption properties of ACUF-700 towards anilines are also investigated by using batch methods. The test results showed that the ACUF-700 possesses higher specific surface area and narrower pore size distribution. In virtue of its developed pore structure and nitrogen-containing chemical groups, the adsorption capacities towards aniline, *p*-toluidine and *p*-chloroaniline could reach 95.6, 108.1 and 128.9 mg/g, respectively. The adsorption process could be well described by the intra-particle mass transfer diffusion model and Sips model. Besides, ACUF700 was regenerated easily using diluted hydrochloric acid solution as eluent and ACUF700 possesses better reusability.

Keywords: Activated Carbon, Nitrogen-containing, Adsorption, Anilines, Ureaformaldehyde Resin

INTRODUCTION

Aniline and its derivatives, as important raw material, are used widely in explosive, dyestuff, pharmaceutical, rubber curing promoter, and medicine industries. However, the aniline-containing wastewater discharged from these industries has caused a series of serious environmental problems. As a kind of blood toxin, anilines can cause transformation of hemoglobin to methemoglobin and further result in cyanosis. Long-term or repeated exposures could also result in anemia, appetite drops, weight loss, and nervous system, kidney, liver and bone marrow damage. Due to the high toxicity of anilines to humans and other animals, the permissible limit of aniline in wastewater is very rigorous in China (1.0 mg/L), USA (6 mg/L), and Canada (2.2 mg/L) [1]. Therefore, the effective removal of anilines from wastewater is very necessary and has attracted considerable research and practical interest.

Various methods, such as degradation [2-5], oxidation [6-9], membrane separation [10], and adsorption [1,11-20], have been established and developed to remove anilines from wastewater. Among these methods, adsorption is effective and widely used due to its higher adsorption capability and relatively simple operability.

Porous activated carbon is an efficient adsorbent because of its high surface area, well-developed internal pore structure and controllable surface functional groups [1,14-16,19-22].

Ureaformaldehyde resins (UF resins) have been widely used as adhesives, finishes, medium density fiberboard (MDF), and molded objects. Taking into account of its high content of nitrogen which can form coordination and hydrogen bond interaction with other ions or molecules, UF resins can be used as a starting material for the fabrication of nitrogen-containing activated carbon.

In this work, porous activated carbon was prepared using ureaformaldehyde resin as raw material. The pore structure was determined, and its adsorption properties towards anilines were investigated.

EXPERIMENTS

1. Materials and Instruments

Urea (AR), formaldehyde (AR), $NaHCO_3$ (AR), and anilines (AR) were both purchased from Beijing Chemical Reagents Factory, China. The instruments used in this study were as follows: THZ-92C constant temperature shaker (Boxun Medical Treatment Equipment Factory of Shanghai, China), Unic-2602 UV spectrophotometer (Unic, American), JW-BK132F surface area analyzer (Beijing JWGB SCI &TECH, China), S-4800 field emission microscope (Hitachi, Japan), Vario EL elemental analyzer (Elementar, Germany), and FTIR4800S infrared spectrometer (Shimadzu, Japan).

2. Preparation of ACUF-700

First, 18 g of $NaHCO_3$, 35 ml of formaldehyde and 15 g of urea was mixed in a beaker. The mixture was heated to 95 °C and remained for 5 h. The resultant solid resins were placed in a vacuum oven for 24 h at 80 °C to ensure complete dryness. Subsequently, the powdered resin was carbonized in charcoal furnace at 700 °C for 2 h with heating rate of 2 °C/min and N_2 flow of 50 mL/min. Finally, the resultant samples were washed with distilled water until neutral and dried at 80 °C for 24 h. The washed active carbon was dried at 80 °C in a vacuum oven for 24 h.

3. Characterizations

The N_2 adsorption-desorption isotherms were obtained at 77 K using the surface area analyzer. The samples were degassed under vacuum at 300 °C for 3 h prior to the measurement. The surface areas

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(S_{BET}) were estimated by BET (Brunauer-Emmett-Teller) method. The total pore volumes (V_{total}) were evaluated from the liquid volume of N_2 at a relative pressure (p/p_0) of 0.99. The average pore diameters were obtained from S_{BET} and V_{total} assuming an open-ended cylindrical pore model without pore networks. Micropore volume ($V_{micropore}$) was determined by HK (Horvaih-Kawazoe) method, and mesopore volume ($V_{mesopore}$) was calculated by subtracting off $V_{micropore}$ from V_{total}. The pore size distribution was determined by BJH (Barret-Joyner-Halenda) model.

The morphology was observed by field emission microscope. Fourier transform infrared spectrum was measured by FTIR spectrometer using the usual KBr pellet technique. The element content was measured by elemental analyzer.

4. Adsorption Experiments

Batch adsorption experiments were performed using about 0.01 g of ACUF-700 and 50 mL of anilines solution. After adsorption reached equilibrium, the adsorbent separated from the samples by centrifugation and the concentration of anilines was analyzed with UV spectrophotometer. The influences of contact time, initial anilines concentration, and dosage of adsorbent were investigated. The adsorption capacity (Q_e, mg/g) and removal fraction (RF) was calculated according to the following equation:

$$Q_e=[(C_0-C_e)/m]\times V \quad (1)$$

$$RF=(C_0-C_e)/C_0 \quad (2)$$

where, C_0 and C_e is the initial and equilibrium concentration of anilines in the solution (mg/L), V is the volume of the solution (L), and m is the dosage of adsorbent (g).

5. Adsorption Kinetic Models

To present the kinetic equation representing the adsorption of anilines onto ACUF-700, the Lagergren-first-order model, pseudo-second order model, and intra-particle mass transfer diffusion model were used to test the experimental data [1]:

$$\ln (Q_e-Q_t)=\ln Q_e-k_1 t \quad (3)$$

$$t/Q_t=1/(k_2Q_e^2)+t/Q_e \quad (4)$$

$$Q_t=k_{id}t^{1/2}+c \quad (5)$$

where Q_t (mg/g) is the adsorption capacity at time t (min), Q_e (mg/g) is the equilibrium adsorption capacity, k_1 (1/min), k_2 (g/mg/min) and k_{id} (mg/g/min$^{-1/2}$) are the adsorption rate constant.

6. Repeated Use Experiment

The reusability is an important factor for a good adsorbent. Desorption of the adsorbed aniline from the ACUF-700 was also studied by batch experimental. Hydrochloric acid solution with concentration of 2 mol·L^{-1} was used as eluent. To test the reusability of ACUF-700, the adsorption-desorption procedure was repeated ten times.

RESULTS AND DISCUSSION

1. Characterization of ACUF-700 Structure

The N_2 adsorption-desorption isotherms of ACUF-700 are shown in Fig. 1.

It can be seen that ACUF-700 gives steep type I. The adsorption of N_2 increases rapidly at low relative pressure (p/p_0<0.10) and then approaches a plateau with increasing the relative pressure. The adsorption-desorption curves were almost overlapped, which indicates that a large amount of micropores with a highly narrow pore size distribution were developed.

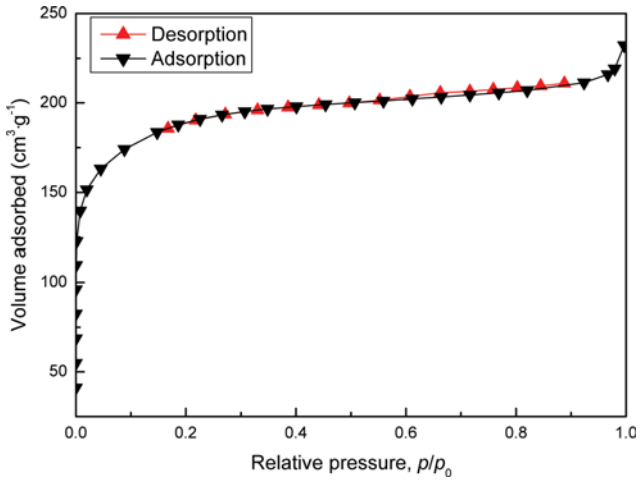

Fig. 1. N_2 adsorption-desorption isotherms.

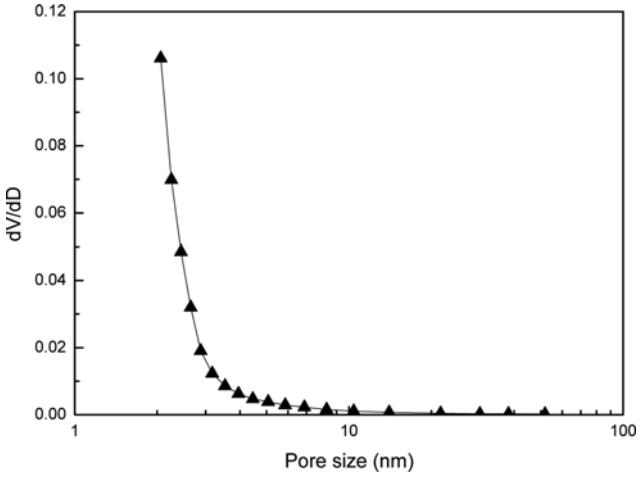

Fig. 2. Pore size distributions of porous carbons.

Table 1. The pore structure parameters

Samples	S_{BET} (m^2/g)	V_{total} (cm^3/g)	$V_{micropore}$ (cm^3/g)	$V_{mesopore}$ (cm^3/g)	Pore size (nm)
ACUF-700	702.3	0.359	0.335	0.024	2.044

The pore size distribution of ACUF-700 is shown in Fig. 2. The pore properties ACUF-700 are listed in Table 1.

The pore size distribution is relatively narrow, and the average pores size is 2.044 nm. The $V_{micropore}$ accounted for 93.3% of V_{total}. These indicate again that there is a large amount of micropores in ACUF-700. The developed pore structure was observed easily from SEM (Fig. 3), and these pores are suitable for binding with anilines molecules.

The FTIR spectra of UF and ACUF700 are shown in Fig. 4. Table

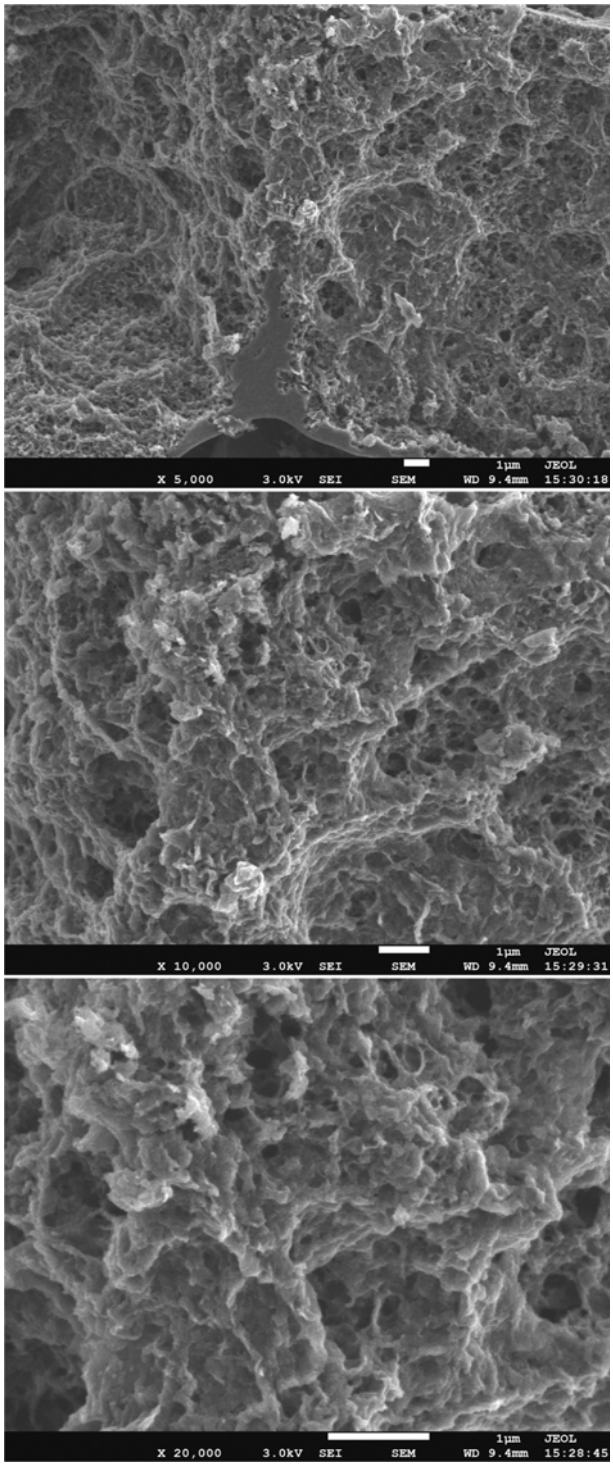

Fig. 3. SEM images of porous carbons.

2 is the elemental analysis results.

As for UF resin synthesized here, the band between 3,200 and 3,500 cm^{-1} is attributed to NH stretching vibrations, and the band between 1,500 and 1,600 cm^{-1} is attributed to C=C stretching vibrations. Three bands at 1,080, 1,039 and 875 cm^{-1} were assigned to asymmetric stretching vibration of the ether, C-O stretch of C-OH, and cyclic ether linkages. ACUF700 exhibits broader and overlapping bands due to the strong IR absorption of carbon and complex rearranged structure. But the band of amine functional group was still observed in ACUF700 spectra.

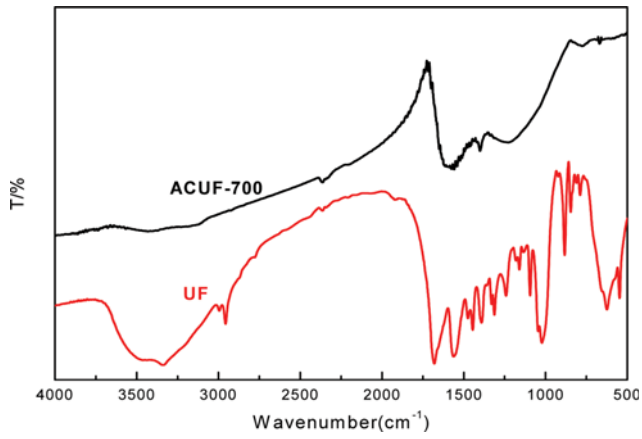

Fig. 4. FTIR spectra of UF and ACUF-700.

Table 2. Elemental analysis results

C (%)	N (%)	H (%)	O (%)
43.99	34.63	2.06	19.32

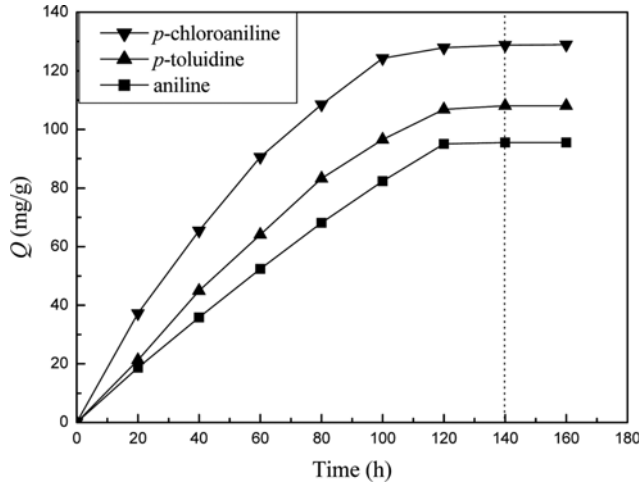

Fig. 5. Adsorption kinetic curves of ACUF-700 for anilines. Temperature: 20 °C; pH 7; Initial concentration: 100 mg/L.

The high N content of ACUF-700 can be also seen from Table 2. As the hydrogen bond acceptor, these N atoms could form hydrogen bond with amine groups of anilines.

2. Adsorption Properties of ACUF-700 Towards Anilines

The kinetic adsorption curves of ACUF-700 towards anilines are shown in Fig. 5.

The saturated adsorption capacity of ACUF-700 towards aniline, *p*-toluidine and *p*-chloroaniline is 95.6, 108.1 and 128.9 mg/g, respectively. These are higher than that of previously reported porous carbons [1,14-20], and the comparisons are shown in Table 3. This illustrates that ACUF-700 possesses very strong adsorption ability and high affinity for anilines, and can be used to remove anilines.

Table 3. Comparisons of adsorption capacity (mg/g) of ACUF-700 by other AC adsorbents

AC adsorbents	Aniline	*p*-Chloroaniline	*p*-Toluidine	Ref.
ACUF-700	95.6	128.9	108.1	This study
BAC-raw	85.5	--	--	[1]
BAC-O8	97.8	--	--	[1]
GAC supplied by Zeo-Tech Adsorbents	15.8	--	--	[14]
AC provided by Aguas de Levante	20	--	--	[15]
SMWCNTs (10-20)	23.2	--	--	[16]
SMWCNTs (40-60)	20.8	--	--	[16]
RTAC	0.55	0.35	0.38	[18]
$RTAC_{OX}$	0.58	0.50	0.68	[18]
MWCNTs/ferrite nanocomposite	2.05	--	--	[19]
Coal based carbon purchased from Kermel Reagent Co., Ltd.	83.4	--	--	[20]

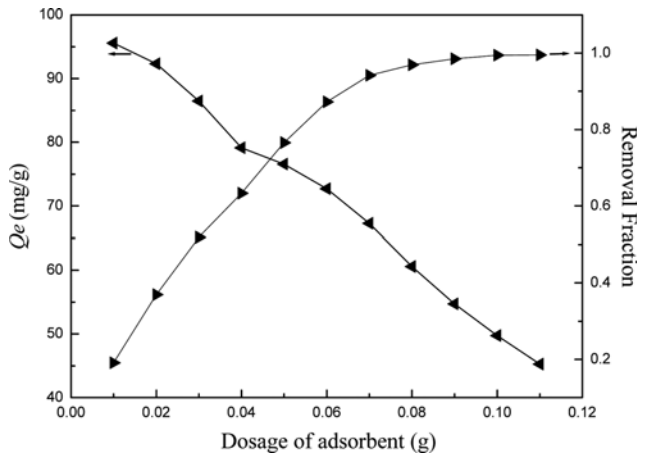

Fig. 6. The influence of adsorbent dosage on removal fraction. Temperature: 20 °C; Time: 180 min; pH 7; Initial concentration: 100 mg/L.

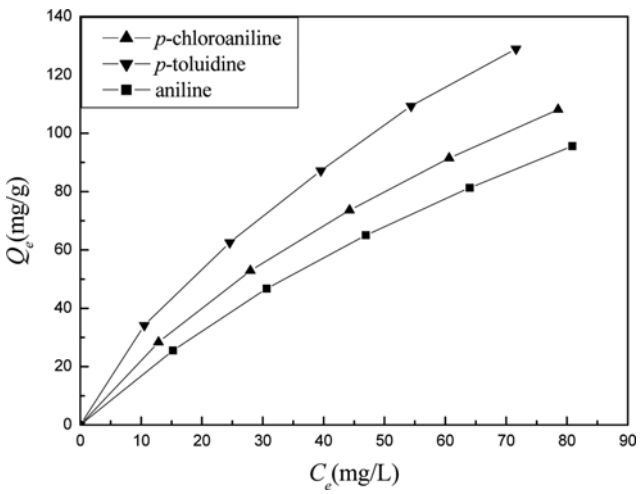

Fig. 7. Adsorption isotherms of ACUF-700 towards aniline. Temperature: 20 °C; Time: 180 min; pH 7.

This excellent adsorption ability is attributed to the developed pore structure and abundant N content.

The influence of adsorbent dosage on removal fraction (RF) is shown in Fig. 6.

It can be seen that the RF of anilines improved along with increasing the adsorbent dosage. When the adsorbent dosage is less, the adsorption can fully reach saturation. So, the adsorption capacity is high, but the RF is lower due to the excessive anilines adsorbate. The RF increases with increasing the adsorbent dosage. The RF could reach 0.995 at the adsorbent dosage of 0.11 g. This indicates again that ACUF-700 can be used as effective adsorbent to remove anilines.

The adsorption isotherms of ACUF-700 towards anilines are shown in Fig. 7.

To investigate the equilibrium adsorption behavior of anilines on ACUF-700, it is important to have a satisfactory description of the equation. The adsorption isotherm is fitted by the Langmuir (Eq. (6)), Freundlich (Eq. (7)), Sips (Eq. (8)), Temkin (Eq. (9)), and Dubinin-Radushkevich (D-R) model (Eq. (10)) [23,24].

$$C_e/Q_e=C_e/Q_0+1/(KQ_0) \quad (6)$$

$$\ln Q_e=\ln k+(1/n)\ln C_e \quad (7)$$

$$Q_e=Q_0 b C_e^m/(1+bC_e^m) \quad (8)$$

$$Q_e=B_T \ln C_e+B\ln A_T \quad (9)$$

$$\ln Q_e=\ln Q_0-K_{ad}\varepsilon^2 \quad (10)$$

where C_e (mg/L) is the equilibrium concentration, Q_e (mg/g) is the equilibrium adsorption capacity, Q_0 (mg/g) is the monolayer sorption capacity, K (L/mg) is the Langmuir constant related to the adsorption energy, k is adsorption equilibrium constant which represents the strength of the adsorptive bond, n is the heterogeneity factor which represents the bond distribution, b is the adsorption equilibrium constant and m the dissociation parameter, $B_T=(RT)/b_T$, b_T is related to the heat of adsorption, A_T (L/min) is the equilibrium adsorption constant corresponding to the maximum adsorption energy, K_{ad} (mol^2/kJ^2) is a constant related to the adsorption energy, ε (J/mol) is the Polanyi potential, $\varepsilon=RT\ln(1+1/C_e)$. The Sips isotherm is a combination of the Langmuir and Freundlich isotherms. In the Sips isotherm, if the value of b approaches 0, the Sips isotherm will become a Freundlich isotherm. While the value of m equals 1 or is closer to 1, the Sips isotherm equation reduces

Table 4. Parameters for plotting adsorption isotherms

Model	Langmuir		Freundlich		Sips		Temkin		D-R	
Parameter	K	Q_0	n	k	b	m	B_T	b_T	Q_0	K_{ad}
Aniline	0.005	263.2	1.26	3.02	0.002	1.85	41.6	58.6	81.5	0.00005
p-Chloroaniline	0.010	243.9	1.35	4.35	0.004	1.70	43.6	56.8	89.7	0.00004
p-Toluidine	0.014	256.4	1.47	6.67	0.007	1.59	48.9	50.6	104.6	0.00002

Table 5. Adsorption linear regression equations of ACUF-700 towards aniline

Adsorption model	Linear regression equation	R^2
Langmuir	$C_e/Q_e=0.0038C_e+0.8395$	0.9954
Freundlich	$\ln Q_e=0.792\ln C_e+1.11$	0.9978
Sips isotherm	$Q_e=95.6*0.0021*C_e^{1.85}/(1+0.0021*C_e^{1.85})$	0.9991
Temkin	$Q_e=41.6\ln C_e-91.28$	0.9797
Dubinin-Radushkevich	$\ln Q_e=-0.00005\varepsilon^2+4.401$	0.8917

Table 6. Adsorption kinetic linear regression data

Adsorption model		Linear regression equation	Rate constant	R^2
Lagergren-first-order	Aniline	$\ln(Q_e-Q_t)=4.9076-0.0215t$	0.0215	0.9542
	p-Chloroaniline	$\ln(Q_e-Q_t)=5.1008-0.0248t$	0.0248	0.9651
	p-Toluidine	$\ln(Q_e-Q_t)=5.5073-0.0356t$	0.0356	0.9167
Pseudo-second order	Aniline	$t/Q_t=0.9231+0.004t$	1.7×10^{-5}	0.8241
	p-Chloroaniline	$t/Q_t=0.7376+0.004t$	2.2×10^{-5}	0.8211
	p-Toluidine	$t/Q_t=0.3883+0.005t$	6.4×10^{-5}	0.9583
Intra-particle diffusion	Aniline	$Q_t=11.92t^{1/2}-37.5$	11.92	0.9942
	p-Chloroaniline	$Q_t=13.49\,t^{1/2}-39.5$	13.49	0.9982
	p-Toluidine	$Q_t=15.90\,t^{1/2}-34.0$	15.90	0.9992

to the Langmuir equation.

The parameters of every adsorption equations are listed in Table 4. The linear regression equations and the correlation coefficient are listed in Table 5.

From the values of R^2 summarized in Table 5, it can be concluded that the Langmuir and Freundlich equations fit best to the experimental data (R^2>0.99). The value of b (0.002, 0.004, 0.007) in Sips isotherm approaches 0, which indicates that the Freundlich model is more appropriate to describe the adsorption behavior than the Langmuir model. Thus, the applicability of monolayer coverage of anilines on the activated carbon surface is confirmed.

3. Adsorption Kinetics

The adsorption kinetic data of ACUF-700 towards anilines is fitted with Lagergren-first-order equation, pseudo-second order equation and intra-particle mass transfer diffusion equation. The linear regression equations, rate constant and the correlation coefficient are summarized in Table 6.

Compared with the Lagergren-first-order model and pseudo-second-order kinetic model, the correlation coefficient (R^2) of the intra-particle mass transfer diffusion model is closer to 1.0. This shows that the intra-particle mass transfer diffusion model is more suitable to describe the adsorption process of anilines on ACUF-700.

4. Desorption and Reusability

When hydrochloric acid was used as an eluent, the interaction between aniline and ACUF700 was disrupted and subsequently aniline was released into desorption medium. To show the reusability of the ACUF700, the adsorption-desorption cycle was repeated 10 times by using the same carbon material. Adsorption-desorption cycle is shown in Fig. 8. The result clearly shows that the ACUF700 could be used repeatedly without losing significantly binding amount.

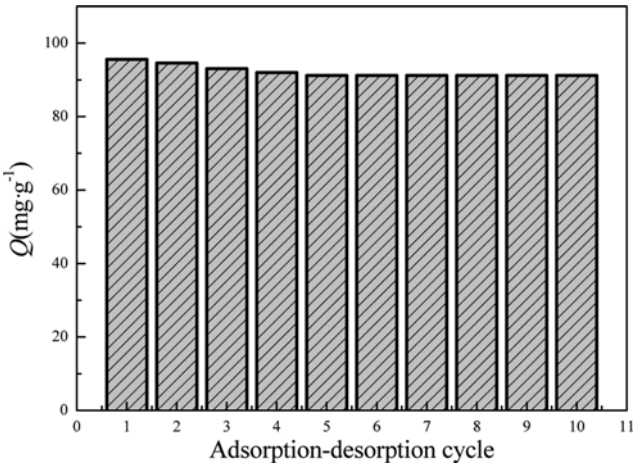

Fig. 8. Adsorption-desorption cycle of ACUF700.

CONCLUSION

Activated carbon ACUF-700 was synthesized successfully by using ureaformaldehyde resin as precursor. ACUF-700 has developed pore structure, high specific surface. The specific surface area could reach 702.3 m^2/g. ACUF-700 displayed fast and high adsorption capacities for anilines. The adsorption capacities towards aniline, *p*-toluidine and *p*-chloroaniline could reach 95.6, 108.1 and 128.9 mg/g, respectively. The adsorption process can be well described by the intra-particle mass transfer diffusion model and Sips model. Besides, ACUF700 was regenerated easily using diluted hydrochloric acid solution as eluent and ACUF700 possesses better reusability.

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