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Adsorption of Organic Amines from Wastewater by Carboxyl Group-Modified Polyacrylonitrile Fibers

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ABSTRACT: In this study, hexamethylenediamine (HMD) and hexamethyleneimine (HMI) were removed from a real wastewater by carboxyl group-modified polyacrylonitrile (RPFC-I) fibers. Adsorption of organic amines by fibrous absorbents is a new technique. Adsorption by fibers has advantages of fast kinetic, high adsorption capacity, and efficiency. Moreover, the fibers could be repeatedly used after regeneration. Batch adsorption tests were conducted to investigate adsorption comparison of the three fibers, adsorption kinetic, adsorption isotherms, regeneration, and readsorption stability. The experiments showed that RPFC-I fibers had excellent adsorption capacity for HMI and HMD. The adsorption equilibrium was achieved very fast within about 5 min, and the removal rate of total nitrogen (TN) was above 99%. The adsorption kinetic could be well fitted by the pseudo-second-order equation. And the adsorption isotherm could be well fitted by the Langmuir model. The estimated maximum adsorption capacity was 105.2 mg g^{-1}, nearly similar with cation exchange capacity (CEC) of RPFC-I fibers. Results from adsorption stability tests demonstrated that the RPFC-I fibers could be fully regenerated by HCl and the regenerated fibers could be repeatedly used even after 12 adsorption–desorption cycles. Analyses from Fourier transform infrared and the adsorption tests suggested that chemical reaction between carboxyl groups and organic amines was the main mechanism for removal of HMI and HMD from the wastewater. The RPFC-I fibers prepared in the current study have a wide application in wastewater treatment and useful substance recovery. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 4124–4129, 2013

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INTRODUCTION

With the development of modern industry, water crisis resulted from fresh water shortage and pollution has become one serious problem around the world. A remarkable contribution to water pollution is the discharge of organic wastewaters from industries like chemical syntheses, dyeing, medicine, and pesticide.[1] These wastewaters are characterized by high concentration and high toxicity of pollutants.[2] Thus they cannot be efficiently treated by traditional biodegradation techniques.[3,4]

Hexamethylenediamine (HMD) is widely used for the production of polymers such as nylon 6-6. Typical method for HMD production is hydrogenation of adiponitrile. During this process, some amounts of organic wastewater were discharged which contained extremely high contents of HMD and other by-products such as hexamethyleneimine (HMI).[5,6] These pollutants are highly toxic and can be hardly biodegraded by microorganisms. Considering that they are important chemical raw materials in large demands, it's necessary to develop an efficient technology to treat the wastewater and to recover the valuable amines simultaneously.

Up to present, technologies for treatment and recycle of wastewaters containing HMD and HMI are rarely reported around the world. For example, Liu and Chen[7] reported a multi-stage extraction method for recovery of HMD and HMI from organic wastewaters by methylbenzene. The total recovery rate was very low, i.e., around 50%. Yin and Zhang[8] reported a rectification technique which was more efficient for wastewaters containing extremely high contents of organic amines. However, the effluents could not meet the wastewater discharge standard of People's Republic of China. Adsorption is an extensively investigated technique for simultaneous wastewater treatment and organic amine recovery (e.g., aniline and *p*-nitroaniline). Widely studied adsorbents include activated carbon,[9,10] synthetic resins,[11] silica gel,[12] etc. Among them, synthetic resins modified by

Table I. Analysis of Composition and Content for Raw Wastewater

	Composition	Content	TN (mg L^{-1})	pH
Organic wastewater	H_2O	99.5%	702.8	12.4
	HMI	0.3%		
	HMD	0.2%		

carboxyl or sulfonic groups are proved to be the best adsorbents considering their large adsorption capacities for organic amines. However, as to treatment and recovery of HMD and HMI, there is still no effective adsorbent reported yet.

Fiber materials[13–16] are new types of adsorbents having advantages of high efficiency, rapid adsorption velocity, large adsorption capacity, and multiple application forms, etc. In the current study, the RPFC-I fibers were prepared to treat the organic wastewater. Similar material was once synthesized to use for different purposes. For example, Zhang et al.[16] reported the carboxyl group-modified polyacrylonitrile (PAN) fibers which were synthesized for the removal of heavy metals. By comparison, there were some differences between reaction conditions and synthesis process during production of modified PAN fibers. In this study, the RPFC-I fibers were prepared and applied for removal of organic amines from a real wastewater at first. Batch adsorption tests were conducted to investigate the adsorption kinetics, adsorption isotherms, regeneration, and readsorption stability. Fourier transform infrared (FTIR) analyses were conducted to demonstrate the change of functional groups on RPFC-I fibers during the modification and adsorption processes.

EXPERIMENTAL

Materials

The PAN fibers (purchased by Anqing petrochemical corporation, China) as original materials were functionalized to synthesize RPFC-I fibers.[17] The properties of PAN fibers were 65 mm in length, 3-denier in size, and more than 93% of the nitrile base content. The RPFC-I fibers were prepared in our laboratory as follows. First, 70 g of hydrazine hydrate and 3 g of PAN fibers were reacted at 112 °C for 3 h in a round bottom flask. Then 70 mL of 3% NaOH solutions were added and the reaction was continued at the same temperature for 1.5 h. After natural cooling to room temperature, the resultant fibers were changed to their H-forms (RPFC-I) by reacting with 70 mL of 5% HCl for 6 h. Analyses from FTIR and acid–base titration demonstrated that great amounts of carboxyl groups were successfully grafted onto the fibers, attaining a cation exchange capacity (CEC) of 6.85 mmol g^{-1}.

For comparison, sulfonic group-modified PAN fibers (RPFS-I, CEC = 2.73 mmol g^{-1}, self-made) and commercial carboxyl group-modified PAN fibers (Fiban-X1, CEC = 3.27 mmol g^{-1}, donated by IPOC, Belarus) were also tested for their adsorption characteristics of the organic amines.

Organic wastewater used in the current study was provided by China Pingmei Shenma Group (Table I). Analyses from gas chromatography (GC2014C, Shimadzu, Japan) showed that the wastewater was comprised of 0.3 mass % of HMI and 0.2 mass % of HMD. Thus, the pH was extremely high (pH = 12.4). The original concentration of total nitrogen (TN), which was proportional to concentration of organic amines, was 702.8 mg L^{-1} as determined from Multi N/C 2100 analyzer (Analytik Jena, Germany). The wastewater was used as received throughout the adsorption experiments.

Batch Adsorption Experiments

For adsorption comparison of the three fibers (i.e., RPFC-I, RPFS-I, Fiban-X1), 0.5 g of fibers with 50 mL of organic wastewater were added in the flask and shaken at 25 °C. The original concentration of TN was 702.8 mg L^{-1} in organic wastewater. After 5 min reaching adsorption equilibrium, the supernatant was sampled and filtered, and the filtrate was analyzed for TN. Adsorption capacity (Q_e, mg g^{-1} or Q_e', mmol g^{-1}) and removal rate (R, %) of the fibers for organic amines (represented by TN throughout the following text) at equilibriums were calculated by conducting a mass balance of TN before and after adsorption.

In kinetic studies, 0.5 g of RPFC-I was mixed with 100 mL of organic wastewater at 25 °C. After predetermined time intervals, 1 mL of solution was withdrawn for TN analyses. Adsorption capacity (Q_t, mg g^{-1}) and removal rate (R, %) of TN versus time t (min) was plotted. Both pseudo-first-order and pseudo-second-order kinetic equations were used to fit the adsorption data as follows: Equation I

$$\text{Pseudo-first-order}: Q_t = A \times e^{(-K_1 t)} + Q_e \quad (1)$$

$$\text{Pseudo-second-order}: \frac{t}{Q_t} = \frac{1}{K_2 \times Q_e^2} + \frac{t}{Q_e} \quad (2)$$

Equation I: Kinetic equation of pseudo-first-order (1) and pseudo-second-order (2).where Q_t and Q_e (mg g^{-1}) are adsorption capacity at time t (min) and equilibrium, k_1 (min^{-1}) and k_2(g mg^{-1} min^{-1}) are rate constants of the pseudo-first-order kinetic model and the pseudo-second-order kinetic model, respectively.

For adsorption isotherm, a series of diluted organic wastewater was prepared by transferring 5, 10, 40, 80, 100 mL of the raw wastewater to reaction flasks and adding enough water to make a total volume of 100 mL. Then the diluted wastewater was mixed with 0.1 g of RPFC-I fibers at 25 °C. After reaching adsorption equilibrium, the equilibrated TN (C_e, mg L^{-1}) was analyzed and Q_e was calculated as above. Both Langmuir and Freundlich equations were used to fit the adsorption data as follows: Equation II.

$$\text{Langmuir}: \frac{C_e}{Q_e} = \frac{1}{b \times Q_m} + \frac{C_e}{Q_m} \quad (3)$$

$$\text{Freundlich}: \log Q_e = \log k + \frac{1}{n} \times \log C_e \quad (4)$$

Equation II: Adsorption isotherm equation of Langmuir (3) and Freundlich (4).where C_e (mg L^{-1}) is equilibrated TN, Q_e (mg g^{-1}) is adsorption capacity at equilibrium, Q_m (mg g^{-1}) is estimated maximum adsorption capacity, b is Langmuir constant, and k and n are Freundlich constants.

Table II. Adsorption of Organic Amines by the Three Fibers; Wastewater Initial pH = 12.4 (Unadjusted), Adsorbent Dosage = 1 g L^{-1}

Fibers	Functional group	CEC (mmol g^{-1})	Q_e (mg g^{-1})	Q_e' (mmol g^{-1})	R (%)
RPFC-I	—COOH	6.85	68.2	4.87	97.0
RPFS-I	—SO_3H	2.73	44.8	3.20	63.7
Fiban-X1	—<COOH COOH	3.27	49.2	3.51	69.9

To study stability of RPFC-I fibers for TN adsorption, multiple adsorption–desorption cycles were repeated. For each cycle, 2 g of fibers and 200 mL of wastewater were used. After adsorption equilibrium, the solution was separated for TN analysis, while the fibers were regenerated by 10 mL of 1 mol L^{-1} HCl and reused for purification of the wastewater.

Characterization

Chemical structure of RPFC-I fibers both before and after TN adsorption was investigated by FTIR spectroscopy (Thermo Electron, America).

RESULTS AND DISCUSSION

Adsorption Comparison of the Three Fibers

Results from the adsorption comparison test (Table II) demonstrated that all the three fibers could be used to remove organic amines from the wastewater. RPFC-I fibers decreased TN of the wastewater from 702.8 mg L^{-1} to 20.96 mg L^{-1}, achieving a removal rate of 97.0% and an adsorption capacity of 68.2 mg g^{-1} (i.e., 4.87 mmol g^{-1}). By comparison, the other two fibers were less efficient. They could only remove 63.7% and 69.9% of TN, respectively, and their adsorption capacities were 44.8 mg g^{-1} (i.e., 3.20 mmol g^{-1} for RPFS-I) and 49.2 mg g^{-1} (i.e., 3.51 mmol g^{-1} for Fiban-XI), respectively. This indicated that both carboxyl and sulfonic groups could adsorb organic amines efficiently. However, the uptake capacities varied directly with the CEC of the fibers (Table II). The higher uptake capacity of RPFC-I for TN was suggested due to its higher CEC value, i.e., 6.85 mmol g^{-1}.

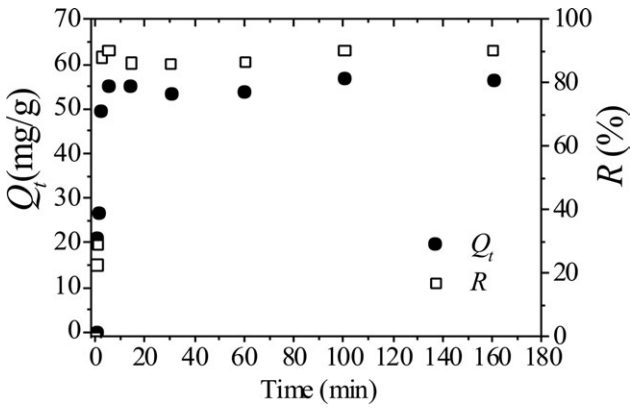

Figure 1. Adsorption kinetics of TN on RPFC-I fibers; wastewater pH = 12.4 (unadjusted), adsorbent dosage = 5 g L^{-1}.

Adsorption Kinetics

For quantitative analysis of TN removal capability of the as-synthesized RPFC-I fibers, a batch adsorption test was performed within 180 min in the raw wastewater with an initial pH 12.4. As shown by the observed adsorption of TN versus adsorption time (Figure 1), the adsorption equilibrium[18] was reached very fast and took only about 5 min to achieve a removal rate of 90% and an adsorption capacity of 55.2 mg g^{-1}. The rapid adsorption of RPFC-I fibers for organic amines was suggested to be due to the fact that carboxyl groups were directly on the large external surface of fibers. Thus, amines reach adsorption sites very easily without additional diffusion resistance of pores which is usually the rate-controlling step for granular adsorbents and powder adsorbents.[19,20] The extremely fast adsorption velocity of fiber materials was also reported by previous studies.[21,22]

Both the pseudo-first-order and the pseudo-second-order equations were applied to model the kinetics of TN adsorption onto RPFC-I fibers (Table III). The correlation coefficient (R^2) for the pseudo-first-order equation was about 0.73. While, R^2 for the pseudo-second-order equation was above 0.99. Besides, the calculated Q_e value (i.e., 56.8 mg g^{-1}) agreed very well with the experimental value (55.2 mg g^{-1}). These results indicated that the pseudo-second-order kinetic model was more appropriate for the entire adsorption process, which meant that chemical reaction other than diffusion was more significant in the rate-controlling step.[23–25]

Adsorption Isotherm

The experimental results were fitted with the traditional models of Langmuir and Freundlich in order to understand the adsorption mechanisms of organic amines onto RPFC-I fibers (Figure 2). The adsorption isotherm was obtained at 25 °C, while the values of parameters and correlation coefficients obtained were listed in Table IV. By comparing the correlation coefficients (R^2) for the two models, it can be inferred that the Langmuir model is better than the empirical Freundlich model in describing

Table III. Parameters of Two Kinetic Models for Adsorption of TN Onto RPFC-I Fibers

Pseudo-second-order kinetic			Pseudo-first-order-kinetic		
Q_e (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2	Q_e (mg g^{-1})	K_1 (min^{-1})	R^2
56.8	0.026	0.99	54.0	49.95	0.73

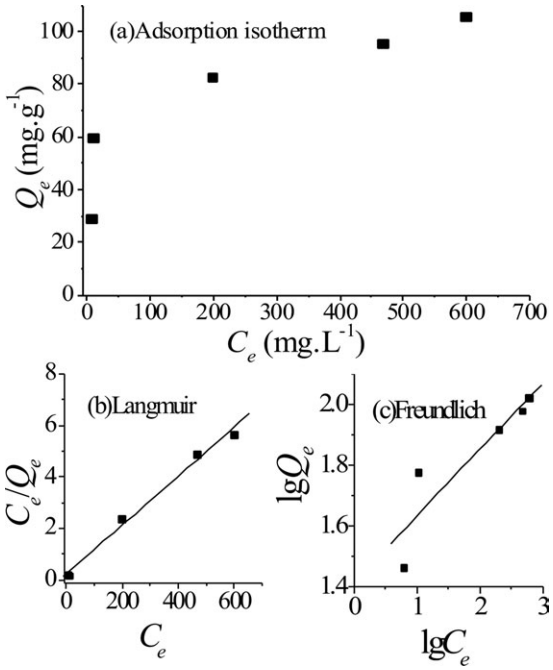

Figure 2. Adsorption isotherm of TN (a) by RPFC-I fibers at 25 °C, adsorbent dosage 1 g L^{-1}; isotherm fitting by Langmuir (b) and Freundlich (c) models.

adsorption of organic amines onto RPFC-I. This indicated a homogeneous adsorption surface of RPFC-I fibers and a consequent monolayer adsorption of the organic amines. The maximum adsorption capacity was 105.2 mg g^{-1} (i.e., 7.51 mmol g^{-1}) at initial TN of 702.8 mg L^{-1} at 25°C. The value was nearly similar with CEC of RPFC-I fibers (i.e., 6.85 mmol g^{-1}), demonstrating that cation exchange or electrostatic attraction might be the main mechanism for adsorption of organic amines on RPFC-I fibers.

Adsorption Stability Tests

Adsorption–desorption cycles were repeated 12 times for the as-synthesized RPFC-I fibers to study the fiber stability in TN adsorption (Figure 3). RPFC-I fibers could decrease TN of the organic wastewater from 702.8 mg L^{-1} to below 25 mg L^{-1}, which was the wastewater discharge limit in People's Republic of China.[26] Even after 12 cycles, RPFC-I fibers still presented high adsorption capacity of TN. These results demonstrated that 1 mol L^{-1} HCl could be applied to fully regenerate RPFC-I fibers and the regenerated fibers had perfect stability in repeated treatment of the wastewater. Additionally, a concentrated solution of organic amines was also obtained. The contents of

Table IV. Isotherm Parameters for TN Adsorption Onto RPFC-I Fibers

Langmuir			Freundlich		
Q_m	b	R^2	n	k	R^2
105.2	0.04	0.99	0.22	26.3	0.83

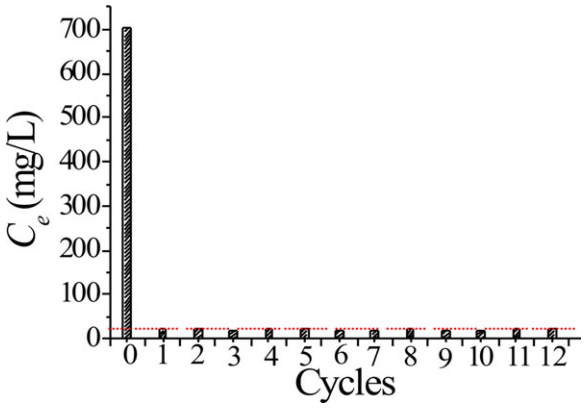

Figure 3. Adsorption–desorption cycles for RPFC-I fibers; adsorbent dosage 10 g L^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

HMD and HMI were about 20 times higher than that in the raw wastewater, which was favorable for the future recovery of these organic amines.

FTIR Analyses and Adsorption Mechanism

Change of surface functional groups on the fiber surface was identified by comparison of FTIR spectra of the raw PAN fibers (a), the as-synthesized RPFC-I fibers (b), and the RPFC-I fibers after TN adsorption (c).[27] As demonstrated in Figure 4, the raw PAN fibers presented several characteristic peaks which could be

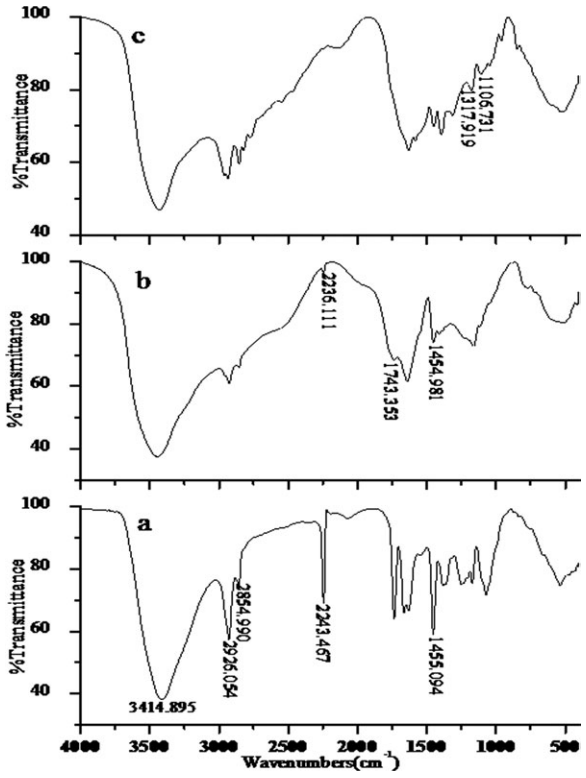

Figure 4. FTIR spectra of raw PAN fibers (a), as-synthesized RPFC-I fibers (b), and RPFC-I fibers after TN adsorption (c).

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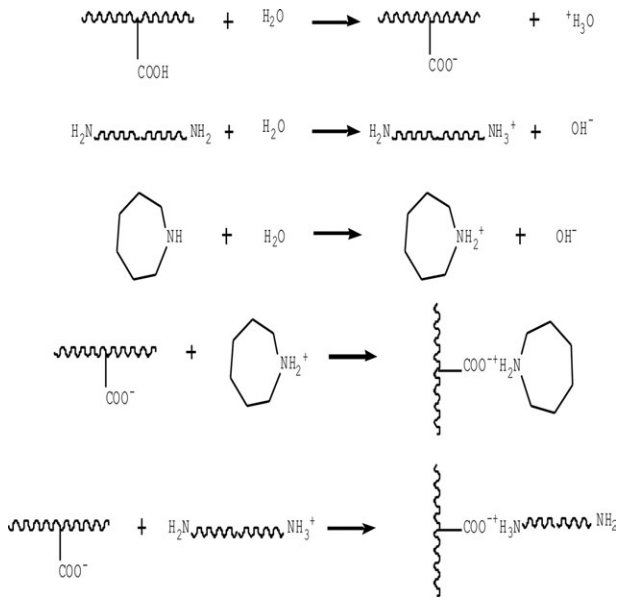

Figure 5. Suggested adsorption mechanism for HMD and HMI on RPFC-I fibers.

assigned as follows: broad band near 3414 cm^{-1} (stretching vibration of OH and NH groups), 2926, 2854, 1455 cm^{-1} (C—H stretching and blending), 2243 cm^{-1} (C≡N stretching in nitrile group). After carboxyl-group grafting, a new strong band appeared at 1743 cm^{-1}, which could be assigned to C=O stretching vibration of carboxyl groups on RPFC-I fibers. After TN adsorption, however, this band at 1743 cm^{-1} disappeared. Contrarily, two new bands appeared at 1317 cm^{-1} (C—N stretching in amidocyanogen groups) and 1106 cm^{-1} (N—H stretching in amidocyanogen groups). These results indicated that carboxyl groups were successfully grafted onto RPFC-I fibers. During TN adsorption, these carboxyl groups were the main adsorption sites for reaction with organic amines.

On the basis of the above results, an adsorption mechanism was proposed for removal of organic amines from the studied wastewater by RPFC-I fibers. As illustrated in Figure 5, the amidocyanogen groups on HMI and HMD compounds undergo hydrolyzation in aqueous solutions, resulting in the production of hydroxyl ions and protonated amines. When in contact with the carboxyl group-grafted fibers (RPFC-I), these protonated organic amines carrying positive charges will diffuse into surface film of the fibers and then chemically react with the carboxyl groups. Since the carboxyl groups are directly on the large external surface of the fibers, amines reach adsorption sites very easily without additional diffusion resistance of pores. Thus the adsorption velocity is extremely fast for fiber materials as compared with other granular and powder adsorbents.

CONCLUSIONS

The RPFC-I fibers revealed better adsorption properties than the others because of its higher CEC value (i.e., 6.85 mmol g^{-1}). The adsorption equilibrium was achieved very fast within 5 min, and the removal rate of TN was above 99%. The adsorption kinetic could be better fitted by the pseudo-second-order equation. The adsorption isotherm was well fitted by the Langmuir isotherm model. And the estimated maximum adsorption capacity was 105.2 mg g^{-1}. Cation exchange or electrostatic attraction was suggested to be the main mechanism for monolayer adsorption of organic amines on RPFC-I fibers. After regeneration by 1 mol L^{-1} HCl, the RPFC-I fibers could be repeatedly used for removal of organic amines even after 12 adsorption–desorption cycles. FTIR analyses further testified that chemical reaction between carboxyl groups and organic amines was the main mechanism for purification of the wastewater.

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