Adsorption Mechanism for Aniline on the Hypercross-Linked Fiber

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ABSTRACT: *A type of novel hypercross-linked fiber adsorbent was obtained by sulfonation and cross-linking reaction of polypropylene fiber grafted styrene-divinylbenzene. The aim of the fiber sulfonation and cross-linking method was to prepare rigid three dimensional networks in the entire fiber and change the ion exchange capacity of fiber. The hypercross-linked fiber adsorbent possesses a principally different structure and could offer new possibility for adsorption, which is characterized by high adsorption capacity for aniline in this paper. A series of static adsorption tests were made. The results showed that the adsorbent has excellent adsorption capacity for aniline and the adsorption equilibrium data can be well fitted by Freundlich model. Adsorption of aniline on adsorbent was chemical adsorption and high temperature was favourable to endothermic chemisorption process. In addition, the kinetic studies were also carried out. The hypercross-linked fiber adsorbent showed faster adsorption rate than the base fiber. The quicker attainment of adsorption equilibrium (within 20 minutes) for aniline on adsorbent is advantageous for practical use. The pseudo-second-order rate model was suitable to describe the process. The pseudo-second-order model gave an excellent fit to all experimental data and adsorption capacities calculated by pseudo-second-order rate model were close to the values actually measured.*

KEY WORDS: *Fibers, Aniline, Adsorption, Thermodynamics, Kinetics.*

INTRODUCTION

Aniline is a kind of common organic contaminant in industrial wastewater. And it is noxious and harmful to human being and environment. The removal of aniline from wastewater has become a social concern. Several ways are used to dispose of wastewater containing aniline at present, such as the oxidation with strong oxidant, extraction, biochemical decomposition and adsorption. Among all of these methods, the adsorption is an effective way to remove aniline from wastewater and numerous adsorbents have been developed for it [1,2].

Three dimensional polystyrene networks (homogeneous, heterogeneous, and hypercross-linked) serve as the basis of various absorbents widely used both in laboratory practice and industrial technology [3,4]. Simplicity of synthesis and availability of initial materials, therefore the operational properties of absorbents has made polystyrene networks to earn much-deserved popularity. These polymeric networks can be divided into three large groups. The first group consists of homogeneous networks, which are obtained by the radical copolymerization of styrene and divinylbenzene monomers. The second group consists of heterogeneous networks, which are prepared by

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the copolymerization of styrene with a large amount of divinylbenzene in the presence of an inert diluent. The third group consists of hypercross-linked networks, the properties and structure of which differ in principle from the homogeneous and heterogeneous networks. Hypercross-linked polymers have been obtained by cross-linking linear polystyrene chains in solution using bifunctional compounds, which react with phenyl rings via the Friedel-Crafts reaction (In the Lewis acid catalyst, aromatics reacts with alkyl halide, and alkyl derivatives will be obtained. The result of the reaction is the introduction of alkyl to the benzene) [5]. The three dimensional resins obtained in this way have been thoroughly researched [6-8]. Compared with resins, ion exchange fibers as new materials have a number of advantages: greater ion exchange rate, shorter reclaiming time, easier to elute and can be made in a form of filaments, staple fiber, nonwoven fabrics, threads, cloths, and plenty of other textile items. This creates new technological possibilities for the current arrangements of ion exchange processes, as well as opening new fields for their applications. Therefore, ion exchange fibers have been widely used in the fields of commercial production and scientific research [9-12]. However, studies of three dimensional networks in fibrous form obtained by introducing additional cross-linking bridges according to Friedel-Crafts reaction have been reported rarely [13-15].

The present work is aimed at investigation of the adsorption behavior of aniline onto the newly developed hypercross-linked fiber adsorbent HXS, which was prepared by sulfonation of HX fiber obtained by the Friedel-Crafts reaction using bifunctional compounds. The adsorption isotherms, the thermodynamic changes of the adsorption process and the kinetics of HXS for aniline were all investigated in detail.

EXPERIMENTAL SECTION

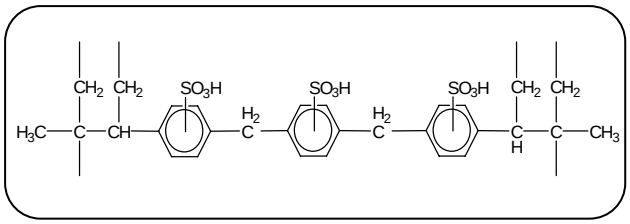
Materials

The polypropylene grafted styrene-divinylbenzene (PP-ST-DVB) fibers were provided by the Henan University of Technology. It was extracted with benzene before use. 1,2-dichloroethane was boiled and distilled over fresh portion of the dryer. Nitrobenzene and aniline were distilled at temperatures under its boiling range. Aluminum trichloride, p-XylyeneDiChloride (XDC), Sulfuric acid, acetone and other chemicals used were all analytical reagents.

Methods

(a)Preparation of HXS Adsorbent

The basic PP-ST-DVB fibers and p-xylyenedichloride were swollen in 20mL nitrobenzene for 12h and the mixture was cooled to 273K with an ice bath and then aluminum trichloride was added as the catalyst to the mixture. The mixture was placed in a flask equipped with reflux condenser. The mixture was carefully stirred and it was heated at 373K for more than 15h. The fiber was then washed with acetone, a mixture of acetone and 0.5N HCl, water, and was dried at 333 to 353K under vacuum. Thus the HX fiber was obtained. Then the HXS fiber adsorbent was prepared by the sulfonation reaction of HX fiber with H_2SO_4 at 343K for 90mins. The PSDS fiber adsorbent was obtained by the sulfonation reaction of basic PP-ST-DVB fibers with H_2SO_4 at 343K for 4h. The chemical structure of adsorbent HXS is:



(b) Measurement of Ion Exchange Capacity

The PSDS and HXS adsorbents (0.5g) were placed into 100mL of 1N NaCl solution for 8h, respectively. The mixture was carefully stirred. A few drops of phenolphthalein indicator were added to the mixture. The mixture was titrated with 0.1N NaOH solution. When the solution becomes reddish, the titration was stopped and the consumption of NaOH solution was written down. The ion exchange capacity of the fiber can be calculated according to the Eq. (1) [16]:

$$Q=NV_1/W \quad (1)$$

Where Q is ion exchange capacity (mmol/g). N and V_1 are the concentration of NaOH solution (mol/L) and the consumption volume of NaOH solution (mL), respectively. W is the mass of the fiber (g).

(c) Measurement of BET Surface Area

A Brunauer-Emmet-Teller (BET) experiment for adsorption and desorption of nitrogen was performed by an automatic analyzer (American NOVA 2000e).

Table 1: The physical properties of the two adsorbents.

Property	Cross-linking agent	BET surface area (m^2/g)	Ion exchange capacity (mmol/g)
PSDS	------	0.01	3.28
HXS	XDC	84.53	3.91

From the nitrogen isotherms at -196ºC, specific surface area was measured with an accuracy of 0.1% according to the BET theory. The physical properties of the PSDS and HXS fiber adsorbents were shown in Table 1.

(d) Study of Adsorption Equilibria

The PSDS and HXS adsorbents (0.1g) were placed into 100mL of aniline solution, respectively. The concentrations of aniline solutions used were 55.56, 81.50, 193.35, 406.90, 607.81, 839.95, 987.03mg/L. The adsorption experiments were conducted under constant stirring at controlled temperatures for 24h. The concentrations of aniline in the residual solutions were analyzed by means of the TU-1810 ultravio-let-visible spectrophotometer. The wavelength to analyze concentration of aniline is 230 nm. The adsorption capacities were calculated according to a mass balance of aniline in the solutions and were represented in units of milligram of aniline per gram of adsorbent. The adsorption capacities at equilibrium were computed according to the Eq. (2):

$$q_e=(C_0-C_e)V/m \quad (2)$$

where q_e and C_e are the amount adsorbed (mg/g) and the residual concentration (mg/L) at equilibrium, respectively; C_0 is the initial concentration of aniline (mg/L). V and m are the volume of aniline solution (L) and the mass of adsorbent used (g), respectively.

(e) Study of Adsorption Kinetics

A 0.2g sample of the PSDS and HXS was placed in 200mL of aniline solution. The initial concentration of aniline solution was 193.35mg/L. The adsorption experiments were conducted under constant stirring at 288K for 12h. The concentration of aniline during the adsorption process was analyzed by means of the TU-1810 ultravio-let-visible spectrophotometer.

RESULTS AND DISCUSSION

Adsorption equilibrium of aniline on adsorbents

Adsorption isotherms were measured for aniline on various adsorbents at 288, 303, 318K and the results were shown in Fig. 1. It was found that HXS has larger adsorption capacity than the PSDS fibers at similar temperature, which was resulted from it larger ion exchange capacity. The adsorption capacity of the adsorbent is seen to increase as the concentration of aniline in water increased. With rise of temperature, the adsorption capacity tends to increase. Adsorption isotherms were simulated by Langmuir, Freundlich and Redlich-Peterson models using Eqs. (3), (4), (5) [17]:

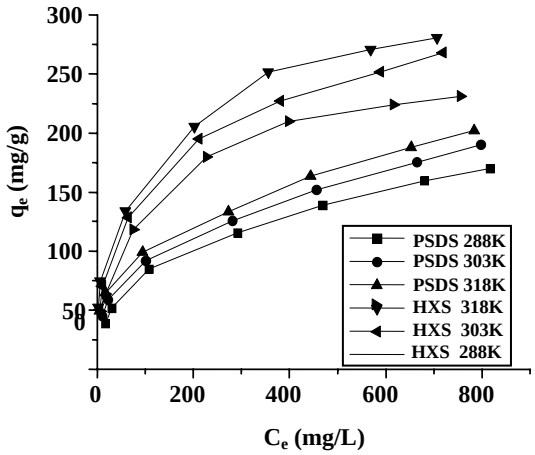


Fig. 1: Adsorption isotherms of aniline on adsorbents (Experimental conditions: absorbent 0.1g; temperature 288,303,318K; initial concentration of aniline solution 55.56, 81.50, 193.35, 406.90, 607.81, 839.95, 987.03mg/L; aniline solution100mL; time 24h.)

$$\frac{C_e}{q_e}=\frac{1}{q_m K_L}+\frac{C_e}{q_m} \quad (3)$$

$$\log q_e=\log K_f+\frac{1}{n}\log C_e \quad (4)$$

$$q_e=\frac{AC_e}{1+(BC_e)^g} \quad (5)$$

where q_m is maximum adsorption capacity (mg/g), K_L is Langmuir constant. K_f and n are parameters indicating the capacity and intensity of adsorption, respectively. A and B are thermodynamic parameters (L/g), $(L/mg)^g$ respectively. Because the fitted parameter by the

Table 2: Freundlich parameters for aniline on HXS fiber.

Temperature (K)	Freundlich equation		
	K_f	*n*	*R*
288	25.13	2.87	0.998
303	31.25	3.01	0.999
318	38.91	3.24	0.997

Table 3: Adsorption thermodynamics parameters for aniline on HXS fiber.

q_e (mg/g)	ΔH (kJ/mol)	ΔG (kJ/mol)			ΔS (J/mol·K)		
		288K	303K	318K	288K	303K	318K
60	28.05				121.25	117.59	115.16
120	21.78				99.48	96.90	95.44
180	18.12	-6.87	-7.58	-8.57	86.77	84.82	83.93
240	15.51				77.71	76.20	75.72
300	13.49				70.69	69.54	69.37

Freundlich model was the most close to 1 among the three models, the Freundlich model was employed. The corresponding parameters of adsorbent were summarized in Table 2. In table 2, the value of n >1 indicates that the adsorption of aniline on adsorbent is easily achieved. The value of K_f increases with increasing temperature, and it is obvious that high temperature is helpful for adsorption and the mechanism of the adsorption is chemical adsorption.

To further understand the adsorption mechanism of aniline on HXS, thermodynamic analysis was performed. The isosteric enthalpies of adsorption were calculated with a derivative Van't Hoff Eq. (6):

$$\Delta H = R\left(\frac{T_1T_2}{T_2 - T_1}\right)\ln\left(\frac{C_{e1}}{C_{e2}}\right) \quad (6)$$

where C_{e1} and C_{e2} are the equilibrium concentrations of solutions (mg/L) at the same q_e, at the absolute temperature T_1 (K) and T_2 (K), respectively; ΔH is the isosteric enthalpy change in adsorption (J/mol) and R is the gas constant (8.314J/K·mol).

If the adsorption can be simulated by Freundlich model, the Gibbs free energy change of adsorption process is obtained with a derivative Eq. (7) [18]:

$$\Delta G = -nRT \quad (7)$$

where ΔG is the Gibbs free energy change in adsorption (J/mol). The adsorption entropies were calculated according to Gibbs-Helmholtz Eq. (8):

$$\Delta S = (\Delta H - \Delta G)/T \quad (8)$$

where ΔS is the entropy change in adsorption (J/mol·K). The calculated isosteric enthalpy changes (ΔH), Gibbs free energy changes (ΔG) and entropy changes (ΔS), of the adsorbent are presented in Table 3. Based on analysis of the results in Table 3, an endothermic adsorption process is suggested by the positive values of all enthalpy changes. The negative values of all Gibbs free energy changes imply that the adsorption of aniline on HXS can happen spontaneously. The adsorption of aniline on HXS is an irreversible chemical reaction, which is suggested by the positive values of all entropy changes.

Adsorption kinetics of aniline on adsorbents

Kinetics of adsorption is directly related to the efficiency of adsorption. Adsorption kinetics of hypercross-linked fiber adsorbent HXS was compared with the PSDS fiber (Fig. 2). Fig. 2 indicated that the hypercross-linked fiber adsorbent showed faster adsorption kinetics than the PSDS fiber. In 20 minutes, aniline was adsorbed on adsorbent and adsorption equilibrium could be attained, which was resulted from it larger surface area. At the same time, the HXS showed larger adsorption capacity than the PSDS fiber. Maximum uptake of adsorbent was about 1.5 times larger than that of PSDS fiber at 288K, mainly due to larger ion exchange capacity. Experimental data indicated that

Table 4: Adsorption kinetics parameters of aniline on HXS fiber.

T (K)	q_e(calc) (mg/g)	q_e(meas) (mg/g)	Error (%)	$k\times10^3$ (L/(mg·min))	R
283	112.87	109.46	3.12	2.79	0.997
293	127.23	121.61	4.62	3.46	0.999
303	132.35	128.39	3.08	4.81	0.999

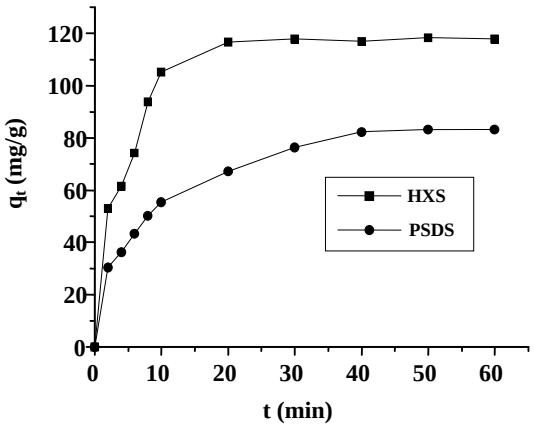


Fig. 2: Adsorption kinetics curves of aniline on adsorbents at 288K (Experimental conditions: absorbent 0.2g; initial concentration of aniline solution 193.35mg/L; aniline solution200mL; temperature 288K).

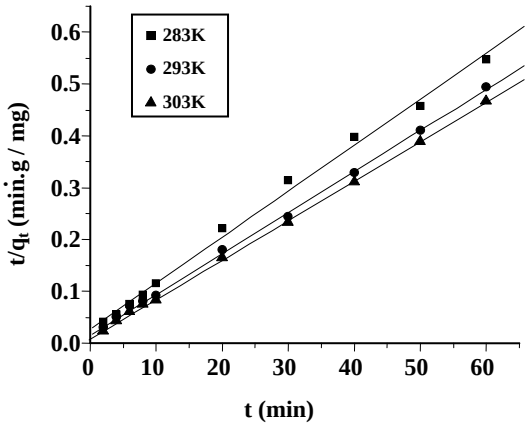


Fig. 3: Adsorption kinetics fitted curves of aniline on HXS fiber (Experimental conditions: absorbent 0.2g; initial concentration of aniline solution 193.35mg/L; aniline solution200mL; temperature 283,293,303K).

adsorption was very fast at beginning and slowed as equilibrium approached. The adsorption rate was described by pseudo-first-order and pseudo-second-order models respectively as:

$$\ln\left(1-\frac{q_t}{q_e}\right)=-k_1 t \tag{9}$$

$$\frac{dq_t}{dt}=k_2\left(q_e-q_t\right)^2 \tag{10}$$

where k_1 and k_2 are pseudo-first-order and pseudo-second-order rate constants (min^{-1}), (L/mg·min), respectively. q_e is adsorption capacity at equilibrium (mg/g) and q_t is adsorption capacity at time t (mg/g). Separating variables in Eq. (10) and integrating gives:

$$\frac{t}{q_t}=\frac{1}{k_2 q_e^2}+\frac{1}{q_e}t \tag{11}$$

Compared to the pseudo-first-order model, the pseudo-second-order model could give an excellent fit to all experimental data (Fig. 3). Equilibrium adsorption capacities calculated according to pseudo-second-order rate model were close to actual measurements (Table 4).

CONCLUSIONS

Hypercross-linked fiber HXS as novel adsorbent was effective in adsorption of aniline and showed higher adsorption capacity because of its higher specific surface area and ion exchange capacity. Hypercross-linked fiber HXS was prepared by sulfonation of HX fiber obtained by means of cross-linking PP-ST-DVB fiber according to the Friedel-Crafts reaction. Freundlich model gave a satisfactory description of measured adsorption isotherms. A thermodynamic study indicated that mechanism of adsorption for aniline on adsorbent was chemical adsorption and high temperature was favourable to endothermic chemisorption process. Kinetic study indicated that the adsorbent showed higher adsorption rate and a pseudo-second-order rate model provided an excellent fitting of experimental data. The quicker attainment of adsorption equilibrium (within 20mins) for aniline on adsorbent was advantageous for practical use, and the adsorbent has therefore exhibited good potential in removing aniline for industrial purpose.

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