

Synthesis of Ordered Mesoporous Phenol/Formaldehyde Resin and Its Application in Adsorption of Aniline

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Ordered mesoporous phenol/formaldehyde resin with high surface area (827 m²/g) and large pore volumes (0.74 cm³/g) has been synthesized by the evaporation-induced triconstituent co-assembly method. The adsorption isotherms were determined from batch tests and studied by Langmuir and Freundlich models. The equilibrium data were best represented by Freundlich isotherm model, showing adsorption capacity at equilibrium which is approximately twice as high as that of activated carbon. The resulted ordered mesoporous phenol/formaldehyde resin is a suitable adsorbent for removal of aniline from aqueous solution.

Keywords: Ordered mesoporous phenol/formaldehyde resin, Aniline, Equilibrium, Adsorption isotherm.

INTRODUCTION

Aniline is one of the most common pollutants found in effluents from the pharmaceutical, pesticide, dyestuff, petrochemicals and agrochemical industries. Aniline-containing wastewater has created a series of serious environmental problems due to its high toxicity and environmental accumulation. Traditionally, aniline-containing wastewater is treated with photodecomposition¹, electrolysis², adsorption^{3,4}, oxidation⁵, biodegradation⁶ and other processes. Among those, adsorption on the activated carbon (AC) is used the most extensively^{7,8}. But its use is limited in application by its wide pore size distributions and poor adsorption selectivity⁹.

In recent years, polymeric adsorbents have increasingly been viewed as an alternative to activated carbon for efficient removal of specific organics from contaminated water due to their good properties and mechanical strength. Among them ordered mesoporous phenol/formaldehyde resins are reported to be an ideal adsorbent for a wide variety of organic compounds¹⁰. Ordered mesoporous phenol/formaldehyde resins with low surface area (652 m²/g) and small pore volumes (0.63 cm³/g) (denoted FDU-14, -15, -16) are synthesized as described by Zhao *et al.*^{11,12}. Therefore, it is of significance to effectively synthesize ordered mesoporous phenol/formaldehyde resin with high specific surface area and large volume.

In this study, ordered mesoporous phenol/formaldehyde resin which exhibits high surface area (872 m²/g) and large pore volumes (0.74 cm³/g) has been synthesized by the evaporation-induced triconstituent co-assembly method. The characterization of the prepared resin was carried out. The application as a sorbent was demonstrated by using aniline as model compound at different initial concentrations. The equilibrium was fitted to different models then evaluated to study the adsorption process of aniline on the prepared resin further.

EXPERIMENTAL

Poly(propylene oxide)-block-poly(ethylene oxide)-block-poly(propylene oxide) triblock copolymer Pluronic F127 (PEO₁₀₆PPO₇₀PEO₁₀₆) was purchased from Sigma-Aldrich Corp (St. Louis, USA). Tetraethyl orthosilicate (TEOS), phenol, formaldehyde solution (37%), NaOH, HCl, HF solution (40%) and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The activated carbon (AC) was purchased from Nanjing Linda Active Carbon Co., Ltd. (Nanjing, China). All the above chemicals were used as received without any further purification. Doubly distilled water was used in all experiments.

Preparation of phenol/formaldehyde (PF) resins: The resol precursor, a low molecular-weight, soluble phenolic resin, was prepared from phenol and formaldehyde in a base-catalyzed process. In a typical procedure, 0.61 g of phenol

was melted at 40–42 °C in a flask and mixed with 0.13 g of 20 wt. % NaOH aqueous solution under stirring. After 10 min, 1.05 g of formalin (37 wt % formaldehyde) was added dropwise below 50 °C. Upon further stirring for 1 h at 70–75 °C, the mixture was cooled to room temperature and the pH value was adjusted to about 7 by HCl solution. After water was removed by vacuum evaporation below 50 °C, the final product was dissolved in ethanol (20 wt % ethanolic solution).

Preparation of ordered mesoporous phenol/formaldehyde resin: The ordered mesoporous phenol/formaldehyde resin was prepared by triconstituent co-assembly of resols, oligomer silicates from TEOS and F127 template. In the preparation, 2.3 g of block copolymer F127 was dissolved in 4 g of ethanol with 1 g of 0.2 M HCl and stirred for 1 h at 40 °C to afford a clear solution. Then 2.08 g of TEOS and 10 g of 20 wt % resols' ethanolic solution were added in sequence. After being stirred for 2 h, the mixture was transferred into dishes. It took 5–8 h at room temperature to evaporate ethanol and 24 h at 100 °C in an oven to thermopolymerize. The as-made products, flaxen and transparent films or membranes, were scraped from the dishes and ground into fine powders. Calcination was carried out in a tubular furnace at 600 °C for 2 h under N₂ flow to get ordered mesoporous phenol/formaldehyde resin-silica, followed by immersing in 10 wt % HF solutions to remove silica for obtaining ordered mesoporous phenol/formaldehyde resin.

Characterization: The X-ray diffraction (XRD) measurements were taken on a TTR-III (Rigadu, Japan) using CuK_α radiation (40 KV, 200 mA). Transmission electron microscopy (TEM) measurements were taken on a JEOL 2010 microscope (Japan) operated at 200 KV; the samples were suspended in ethanol and dropped onto holey carbon film supported on a Cu grid. Nitrogen adsorption-desorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 analyzer and the samples were degassed in a vacuum at 200 °C for 6 h prior to tests. The Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) model were utilized to calculate the specific surface areas, the pore volumes and the pore size distributions, respectively. The total pore volumes were estimated from the adsorbed amount at a relative pressure P/P₀ of 0.994. Weight changes of products were monitored using SDT Q600 analyzer (TA, USA) from room temperature to 850 °C under air with a heating rate of 10 °C/min. Fourier transform infrared (FT-IR) experiments were performed with EQUINOX55 (Bruker, Germany) using KBr pellets of the solid samples.

Batch equilibrium studies: The isotherms of aniline adsorption from aqueous solutions were measured using the static method. The details of adsorption experiment procedure were as follows. 4 mg adsorbent was added into each 25 mL flasks containing 5 mL aniline solution of different initial concentrations ranging from 8 to 408 mg/L at 25 °C for 24 h to ensure the adsorption process reached equilibrium. The concentrations of aniline before and after adsorption were determined by HPLC (Agilent 1100). The amount of adsorption at equilibrium, q_e (mg/g), was calculated by eqn. 1. For comparison, activated carbon was also tested as adsorbent in the same conditions.

$$q_e = (C_0 - C_e)V/W \quad (1)$$

where C₀ and C_e (mg/L) are the concentrations of aniline initially and at equilibrium, respectively. V is the volume of the solution (L) and W is the mass of adsorbent (g).

The equilibrium data were then fitted using two kinds of typical isotherm models for single component adsorption, namely Langmuir and Freundlich models. The model equations are as follows.

$$\frac{C_e}{q_e} = \frac{1}{(Q_0 b)} + \left(\frac{1}{Q_0}\right) C_e \quad \text{Langmuir model} \quad (2)$$

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad \text{Freundlich model} \quad (3)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q₀ and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. K_F and n are Freundlich constants with n giving an indication of how favorable the adsorption process. The best isotherm model is selected on the basis of correlation coefficient (R²).

RESULTS AND DISCUSSION

The ordered mesoporous phenol/formaldehyde resin was prepared by triconstituent co-assembly of preformed resols, silica oligomers from acid-catalyzed hydrolysis of TEOS and triblock copolymers F127 in ethanol solution. The presence of silica in the nanocomposite can be efficiently reduce framework shrinkage during calcination as compared to pure polymer which is utilized in the synthesis of FDU-14, -15, -16. Besides mesopores, smaller pores inside the pore walls caused by the removal of silica contribute to its high surface area and large pore volumes.

Characterization: The small-angle XRD pattern (Fig. 1) for the prepared resin exhibits one diffraction peaks at a 2θ range of 0.5 to 2° that can be indexed as (10) reflection associated with ordered structure. The intense (10) peak reflects a d-spacing of 10.5 nm, which corresponds to a large unit-cell parameter (10.7 nm). A more detailed texture property is revealed by TEM images which consist of large domains of highly ordered stripe, as shown in Fig. 2. The TEM images further confirm an ordered structure existed in the prepared resin.

N₂ sorption isotherm and pore size distribution curves of ordered mesoporous resin are shown in Fig. 3a and 3b, respectively.

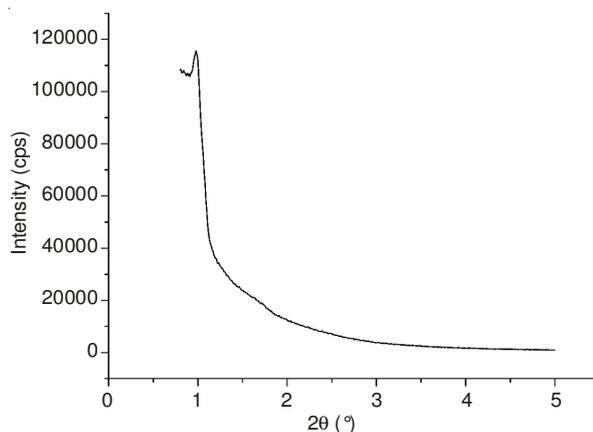


Fig. 1. XRD spectra of the ordered mesoporous phenol/formaldehyde resin

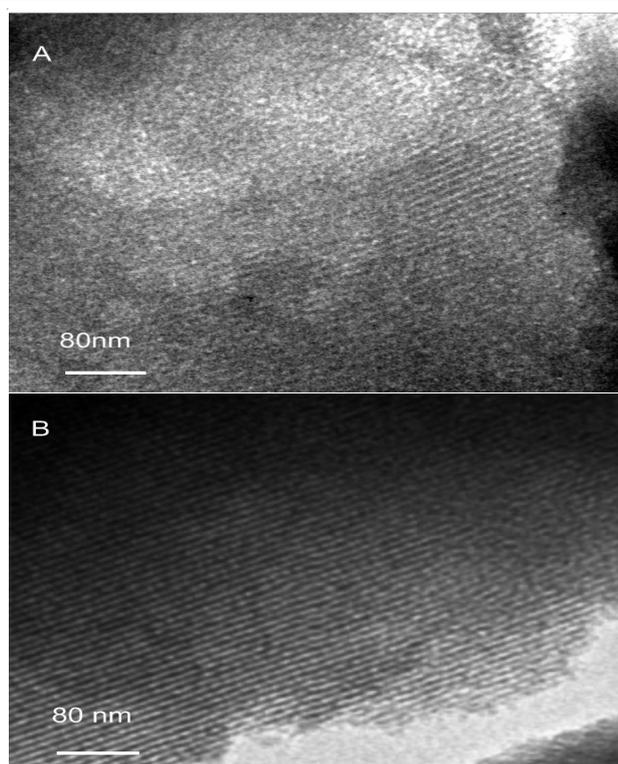


Fig. 2. TEM images of the ordered mesoporous phenol/formaldehyde resin. Both A and B are the images viewed from 110 direction

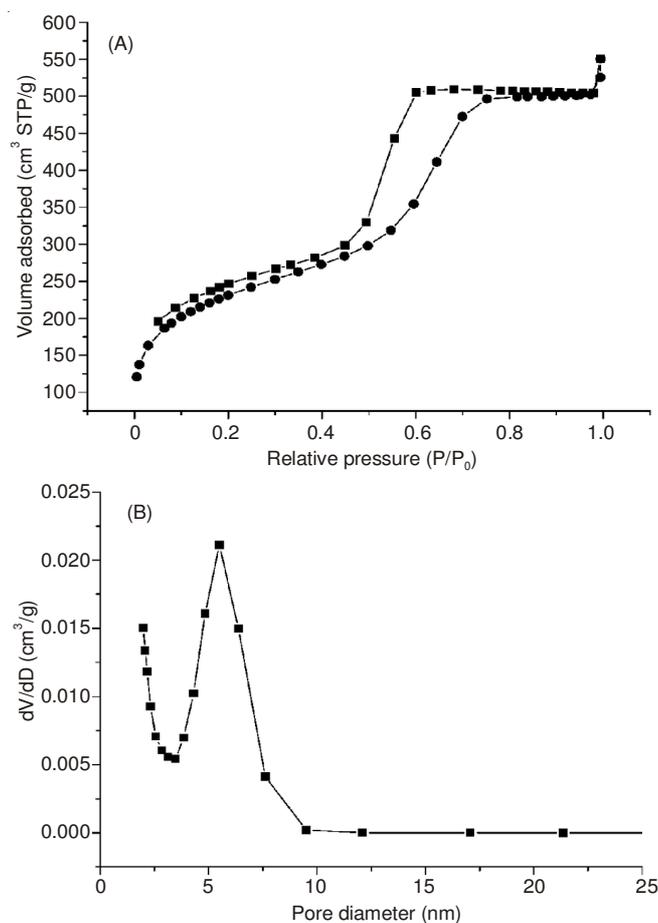


Fig. 3. (A) the N_2 sorption isotherm of the ordered mesoporous phenol/formaldehyde resin at 77 K; (B) the pore-size distribution curve of the ordered mesoporous phenol/formaldehyde resin

The corresponding pore characters including BET surface areas ($827 \text{ m}^2/\text{g}$), pore volumes ($0.74 \text{ m}^3/\text{g}$) and pore diameters (5.5 nm) are obtained. The prepared resin exhibits type-IV curves with distinct capillary condensation steps and an obvious H_1 -type hysteresis loop, suggesting narrow mesopore size distributions and well-ordered cylinder mesopore channels¹³. It is coincident with its highly ordered mesostructures, confirmed by XRD and TEM results. A distinctly adsorption at the relative pressure (P/P_0) of 0.1-0.3 is observed, suggesting smaller pores which caused by etching of silica frameworks below 3.5 nm ¹⁴.

Thermogravimetric measurements shown in Fig. 4 show that the prepared resin can be combust completely in air at temperature range from 25 to $850 \text{ }^\circ\text{C}$. It indicates that silica has been successfully removed from phenol/formaldehyde resin-silica composites by dissolution in HF ¹⁴. FT-IR spectra of resin shown in Fig. 5, shows a broad band at 3400 cm^{-1} and a weak band at 1610 cm^{-1} attributed to the characteristic stretching vibration of phenolic resin. And the absorbance at 942 cm^{-1} ascribed to Si-OH vibration is not found. Results of TGA and FT-IR demonstrate that there is no silica but abundant phenolic resin in the product.

Effect of initial concentration on adsorption equilibrium: The application as a sorbent was demonstrated by using aniline as model compound at different initial concentrations. The test result (Figure not shown) indicated that the adsorption

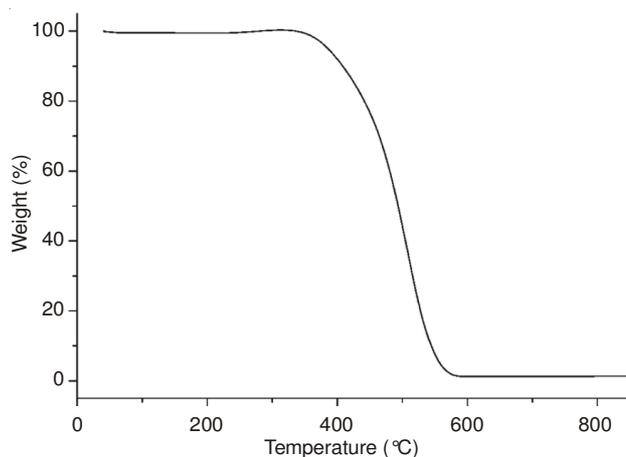


Fig. 4. TG recorded in air of the ordered mesoporous phenol/formaldehyde resin

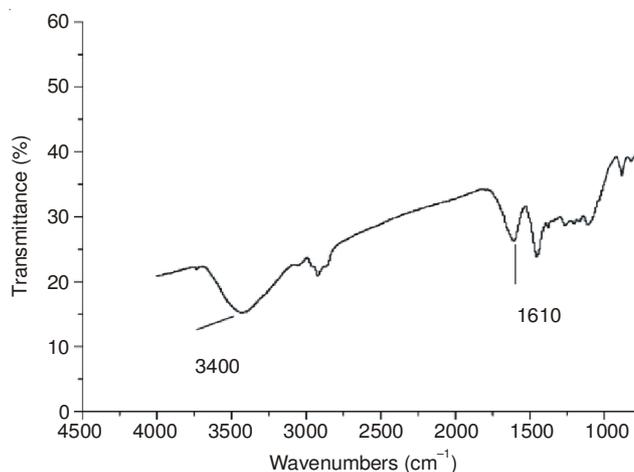


Fig. 5. FT-IR of the ordered mesoporous phenol/formaldehyde resin

adsorption capacities of aniline on the prepared resin and activated carbon at equilibrium (q_e) increased with the increasing initial concentration. When the initial concentration increased, the mass transfer driving force would become larger, resulting in higher adsorption amount of aniline. It can also be found that the adsorption capacity of resin at equilibrium is approximately twice as high as that of activated carbon. This phenomenon is a credit to the different pore-structures of the prepared resin and activated carbon. Resin has the similar primary mesopores with activated carbon and abundant complementary mesopores which is absent in activated carbon¹⁵. The diameter of complementary mesopores of the prepared resin is below 3.5 nm, which is accessible for aniline molecule with 0.7 nm diameter. The interaction between resin and aniline in aqueous solution constitutes another factor for its extraordinary adsorption capacity.

Adsorption isotherms: The adsorption isotherm is important to indicate how solute interact with the sorbent^{6,16}. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes. The equilibrium adsorption isotherm of aniline on the prepared resin and activated carbon was shown in Fig. 6. It exhibits a steep increase showed concentrations, indicating high affinity towards the aniline. Langmuir and Freundlich models were carried out to study the adsorption isotherm. The applicability of the isotherm equation to describe the adsorption process was judged by the correlation coefficients, R^2 values.

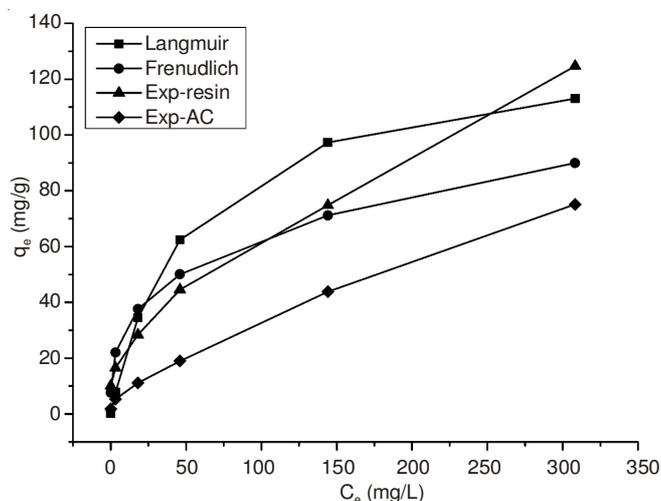


Fig. 6. Equilibrium adsorption isotherm of aniline on the ordered mesoporous phenol/formaldehyde resin and activated carbon at 25 °C. And comparing the results of adsorption isotherms of aniline on the ordered mesoporous phenol/formaldehyde resin for experimental Langmuir model and Freundlich model

Fig. 7a presents the fitted curves using Langmuir isotherm model. A straight line with slope of $1/Q_0$ is obtained when C_e/q_e is plotted against C_e . The Langmuir constants b , Q_0 and the correlation coefficients R^2 were calculated and shown in Table-1. For Langmuir isotherm, R_L is used to show the essential character and it can be calculated using $R_L = 1/(1 + bC_0)$, where C_0 is the highest initial concentration of aniline (mg/L) and b (L/mg) is the constant^{17,18}. The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear

($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The value of R_L in this work was found to be 0.82 indicating that the sorption of aniline is favorable. Fig. 7b shows the plot of $\log q_e$ versus $\log C_e$ for the Freundlich isotherm. The plot yields a straight line with slope of $1/n$, which indicated that adsorption of aniline on the resin is favorable. Accordingly, Freundlich constants K_F , n and the correlation coefficients R^2 were calculated and listed in Table-1.

TABLE-1
LANGMUIR AND FREUNDLICH ISOTHERM MODEL
PARAMETERS AND CORRELATION COEFFICIENTS
FOR ADSORPTION OF ANILINE ON THE ORDERED
MESOPOROUS PHENOL/FORMALDEHYDE RESIN

Langmuir isotherm		Freundlich isotherm	
$b(\text{L mg}^{-1})$	0.02	$1/n$	0.31
$Q_0(\text{mg g}^{-1})$	131.8	$K_F[\text{mg g}^{-1}(\text{L g}^{-1})^{1/n}]$	15.4
R^2	0.86	R^2	0.89
R_L	0.82		

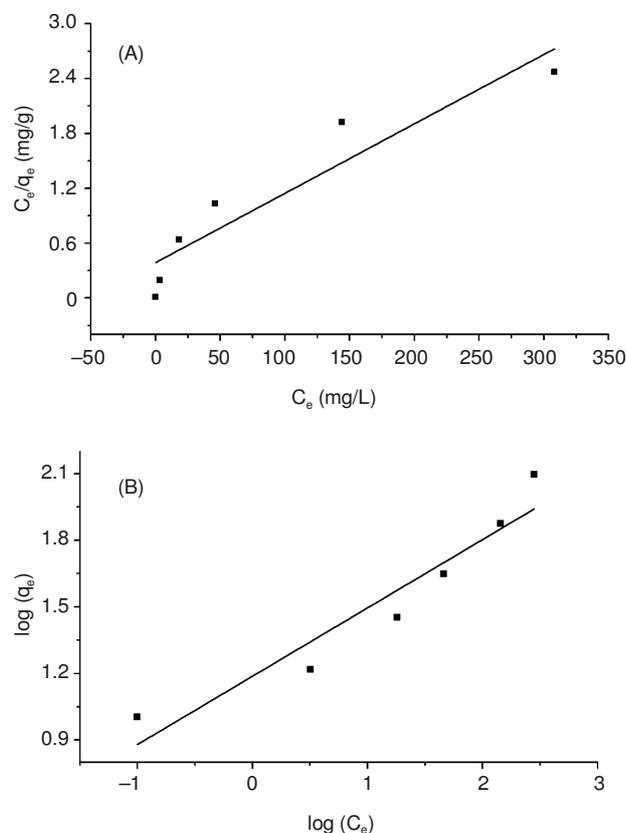


Fig. 7. Adsorption isotherm models of aniline on the ordered mesoporous phenol/formaldehyde resin at 25 °C. A is the Langmuir model; B is the Freundlich model

The experimental isotherm data and the two adsorption isotherm models used in this study are plotted in Fig. 7. It is obvious from Table-1 and Fig. 7 that the Freundlich model yielded the better fit with R^2 value higher than 0.89, as compared to the Langmuir model.

Conclusion

In summary, the self-assembly of phenol/formaldehyde resin, TEOS and F127 with proper thermal treatment affords ordered mesoporous phenol/formaldehyde resin with high specific surface areas ($827 \text{ m}^2/\text{g}$) and large pore volumes (0.74

cm³/g). The adsorption capacity of prepared resin is approximately two times as high as those of activated carbon at equilibrium when aniline was used as the modal compound. And the equilibrium data were best described by Freundlich isotherm model. The ordered mesoporous phenol/formaldehyde resin is shown to be a promising substituent adsorbent of activated carbon for removal of aniline from industrial effluents or tobacco smoke.

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