

Adsorption of Sulfamethoxazole on Nanoporous Carbon Derived from Metal-Organic Frameworks

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Abstract

Nanoporous Carbon (NPC) with high surface area of 1379 M²/G and high proportion of micropore and mesopore volume of 2.90 Cm³/G was prepared by carbonization of metal-organic frameworks ZIF-8. The adsorption of NPC towards the representative sulfonamide antibiotics sulfamethoxazole (SMX) from aqueous solutions was explored, in comparison with powder active carbon (AC). The adsorption kinetics and isotherms showed that the maximum adsorption capacity (Q_m) of NPC toward SMX was 757 Mg/G, around 2 times than that of AC adsorption. The high adsorption affinity of NPC was related to the high surface area and special Mic/Mesopore structure. The pore-filling mechanism as well as electrostatic interaction had important influence on the high adsorption of NPC. The results implied that nanoporous carbon derived from mofs could remove the contaminants from aqueous solutions effectively, and would be a promising adsorbent for the removal of contaminants in the future.

Keywords

Metal-Organic Frameworks, Sulfamethoxazole, Adsorption, Mic/Mesopore

1. Introduction

In recent years, many researchers found that some Pharmaceutical and Personal Care Products (PPCPs) and Endocrine Disrupting Chemicals (EDCs) exist in natural water and drinking water. This kind of contaminants can affect the growth and reproduction of aquatic organisms, having negative effects on human health through the biological accumulation [1]. Tracing to the source, researchers found that the sewage treatment process could not effectively deal with

these pollutants [2]. These contaminants in the sewage treatment plant water mainly come from domestic sewage. Antibiotics and other drugs used by humans cannot be completely absorbed by body, and excreted through urine. At the same time, a variety of detergents and personal care products flow into the urban domestic sewage. Therefore, it is very important to have a highly efficient and targeted wastewater treatment method.

Traditional wastewater treatment methods include Gas floatation process, adsorption, membrane technology and advanced oxidation. As a wide-application and good-effect processing method, adsorption is high efficiency, low energy consumption and without by-product. Carbon materials are widely used in the field of adsorption due to their large specific surface area and pore structure, represented by activated carbon, silica gel and zeolite. According to different morphology, the types of activated carbon are divided into powder, granular and fibrous. The pore size distribution of activated carbon, used for the adsorption of pollutants in water, is very wide. Metal organic frameworks (MOFs), polymers with three-dimension pore structure, have been developed rapidly in last ten years. MOFs have the highest specific surface areas reported to date for porous materials (up to 6200 m²/g) [3]. Nanoporous carbon (NPC) materials with high surface area and good chemistry stability, carbonated from MOFs, have been the research hotspot owing to their extensive applications in various fields, including contaminants adsorption, gas uptake and super capacitors. In this study, the ZIFs is a type of metal organic framework material whose organic framework based on nitrogen heterocycles. The stability of the structure is stronger than those whose organic frameworks based on carboxyl. In this work, a typical sulfonamide antibiotic, sulfamethoxazole (SMX), was selected as target pollutants to examine the adsorption behavior of nanoporous carbon derived from ZIF-8 [4].

2. Experimental Section

2.1. Materials and Methods

ZIF-8 was synthesized referring to the reported method, zinc salts (Zn(NO₃)₂ or Zn(CH₃COO)₂) and 2-methylimidazole (Hmim) were dissolved in methanol to generate clear solutions, respectively [5], to make monodispersed ZIF-8 crystals with different particle sizes. Then, both of them were mixed together and aged at room temperature for 24 hours. After that, white powders (ZIF-8 crystals) were precipitated. At room temperature (around 20°C), when Zn(NO₃)₂ was used as zinc source, nano-sized ZIF-8 particles were obtained with an average size of around 50 nm (hereafter abbreviated as small-sized ZIF-8). When using Zn(CH₃COO)₂ as zinc source, the particle size increased to around 500 nm (hereafter abbreviated as middle-sized ZIF-8). At the temperature of 40°C, using Zn(CH₃COO)₂ as zinc source, the particle size increased to around 1µm (hereafter abbreviated as large-sized ZIF-8).

In order to get the nanoporous carbon, a quartz boat containing ZIF-8 powder was placed into the vacuum tube furnace. Next, in order to ensure the optimum

temperature of carbonization, the vacuum tube furnace was heated from room temperature to 950°C, 1000°C and 1100°C under the protection of argon, with a heating rate of 10°C/min. Then the temperature was maintained for 7 h. After natural cooling, the nanoporous carbon (NPC) was obtained.

The AC was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Before using, the AC was pretreated by HCl, and then washed with milli-Q water for several times.

2.2. Characterization

The morphology and pore structure of NPC were observed by field emission scanning electron microscope (FE-SEM, Hitachi S-4800). The specific surface area was obtained by the method of multi-point Brunauer-Emmett-Teller (BET), calculated by the adsorption-desorption isotherms of N₂ at 77 K. The total volume of mesopore and macropore was the difference between total pore volume and micropore volume which was calculated by the method of V-t plot. The pore width distribution was calculated by the DFT method. The method of X-ray photoelectron spectroscopy (XPS), implemented on a surface analysis system (Thermal ESCALAB 250) using Al K α radiation, was used to measure the element content of NPC. Fourier transform infrared spectroscopy (FT-IR) was recorded by using a Vertex70, Bruker Vector FTIR spectrometer. The Raman spectrum was obtained via a Renishaw micro-Raman system 2000 spectrometer (Renishaw, UK), which was operated with He-Ne laser excitation.

Zeta potential at different pH was measured by zetasizer nano-ZS equipment (Malvern instrument company, USA). Before the measurement, NPC, SWNT and PAC were dispersed in 1 mM KCl solution, followed by sonicating for 30 min. The solution pH was adjusted by HCl (1 M) and NaOH (0.1 M) before measurement.

2.3. Adsorption Experiment

The batch adsorption experiments on different-sized NPCs of SMX were carried out in 50 mL quartz vessels with 30 mL adsorption solution. Background solution containing 0.5 mM CaCl₂ and 200 mg/L NaN₃ was mixed with about 2 mg NPCs. The batch adsorption experiments were conducted at 200 rpm on an orbital shaker at fixed temperature of 20°C \pm 1°C. The concentration of solution was in the range of 5 mg/L to 100 mg/L. The volume ratio of methanol in solution of each vial was controlled to be less than 0.1% to minimize cosolvent effect. The vials were sealed and placed in the shaker for 48 hours (kinetics experiments indicated that apparent equilibrium was reached before 48 hours) [6].

The pH value of solution was 4.82 for SMX, which didn't change during the adsorption process. After adsorption experiments, the adsorbents and the aqueous solution were separated by centrifugation. The concentrations of SMX was determined by a high-performance liquid chromatograph (HPLC, Waters 2695, Waters, USA) equipped with a C18 column (15 cm \times 4.6 mm \times 5 μ m) and a UV detector at a column temperature of 30°C. SMX was detected at 271 nm,

with a mobile phase of 45:55 (v:v) acetonitrile: 0.1% acetic acid aqueous solution, at flow rate of 1 mL/min.

In order to investigate the effect of pH, the adsorption experiments were carried out at the concentrations of 10 mg/L for SMX. HCl (1 M) and NaOH (0.1 M) were applied to adjust the pH value of the solution in the range of 2.0-11.0 [7].

3. Results and Discussion

3.1. Characterization of NPCs

NPC was prepared through carbonization by different-sized ZIF-8, which were named as S-NPC (the traditional structure), M-NPC and L-NPC. **Figure 1** showed the geometric shape of the ZIF-8, which usually were demonstrated as rhombic dodecahedra, and also showed the rhombic dodecahedra of three sized ZIF-8, small-sized ZIF-8(S-ZIF8), middle-sized ZIF-8(M-ZIF8) and large-sized ZIF-8 (L-ZIF8). In order to ensure the carbonization being at the optimal temperature, the small-sized ZIF-8 has been carbonated at three temperatures. At above 908°C, we can gain the NPCs almost without zinc. So the carbonization temperature is at 950°C, 1000°C and 1100°C. The specific surface area of S-NPC at 950°C, 1000°C and 1100°C is 1017.5 m²/g, 1378.7 m²/g and 809.8 m²/g, respectively. This result showed that 1000°C is the most suitable temperature, at which we can obtain the largest specific surface area. Then explore the adsorption kinetics of SMX on NPCs. The result is in accord with the specific surface area. **Table 1** showed the selected physical parameters of NPCs.

According to the pore structure comparison diagram of S-ZIF8 and S-NPC, the specific surface area of S-ZIF8 becomes bigger after carbonization. The size of M-ZIF8 and L-ZIF8 showed same tendency. The zeta potential of these three materials is 3.6, 4.8 and 6.3, respectively. The isoelectric point, the important factor of adsorption, increases with the increase of the crystal size. **Figure 2** is

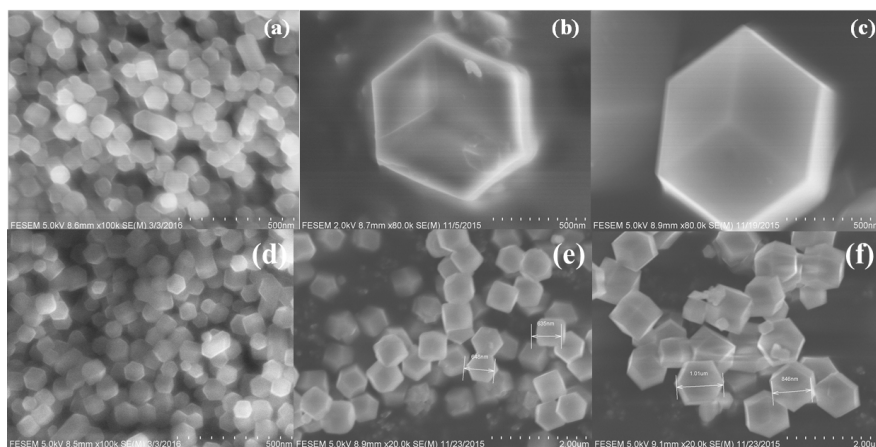


Figure 1. The SEM images of ZIF-8 (a) small-sized ZIF-8(S-ZIF-8); (b) m-sized ZIF-8 (M-ZIF-8); (c) large-sized ZIF-8(L-ZIF-8); (d) small-sized NPC(S-NPC); (e) m-sized NPC(M-NPC); (f) large-sized NPC(M-NPC).

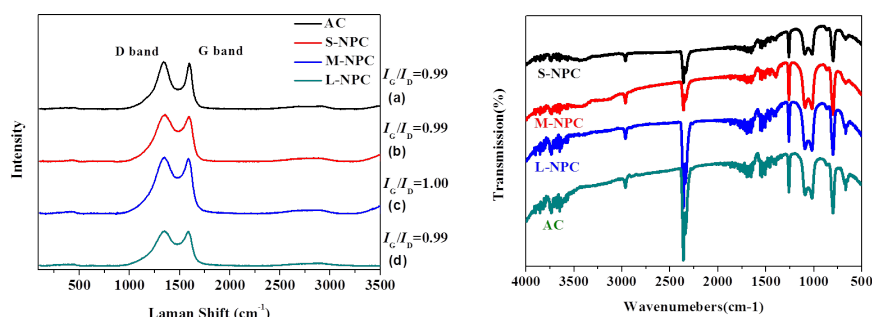


Figure 2. The Raman spectrogram and the FTIR spectra of three NPCs and AC

Table 1. Selected physical parameters of NPCs.

Name	S-NPC	M-NPC	L-NPC	AC
Specific surface area $S/(m^2/g)$	1378.7	998.4	872.9	685.8
Pore volume $V/(mL/g)$	2.90	0.62	0.55	0.60
Pore width $D/(nm)$	0.61	0.61	0.61	0.57

the Raman spectrogram and the FTIR spectra of three NPCs and AC. In these kinds of grams, D-band corresponds to defect, while G band relates to graphite. The relative ratios of G bands to D bands (I_G/I_D) in Raman spectra are important parameters for understanding the crystallization degree of graphitic carbon.

3.2. Adsorption Kinetics

For adsorption of SMX on different-sized NPCs, we can see the secondary kinetic fitting is linear (**Figure 3**). And the fitting results were displayed in **Table 2**. The simulation results demonstrated the existence of chemical adsorption and the adsorption capacity related to the numbers of active sites on adsorbents.

It was obvious that the adsorption equilibrium was reached within 10 h for all of the samples, and the rapid adsorption occurred during the first 3 hours, indicating fast initial transfer of chemicals to the adsorbents surface (**Figure 3**). For all of the adsorbents, adsorption capacity on NPCs was much higher than those on AC.

3.3. Adsorption Isotherms

Adsorption isotherms of SMX on the four adsorbents were displayed in **Figure 4**, all of which were nonlinear. The experimental data was simulated by Langmuir and Freundlich models respectively. The related parameters were listed in **Table 3**. Langmuir model is based on the hypothesis of monolayer adsorption, with adsorbents possessing uniform adsorption sites on the surface, while Freundlich model is an empirical equation that depicts a multilayer adsorption on heterogeneous surface. It could be observed in **Table 3** that, for NPCs and AC, Langmuir model could better fit the adsorption of SMX than Freundlich model, which indicates homogeneous surface of NPCs with identical adsorption sites on it.

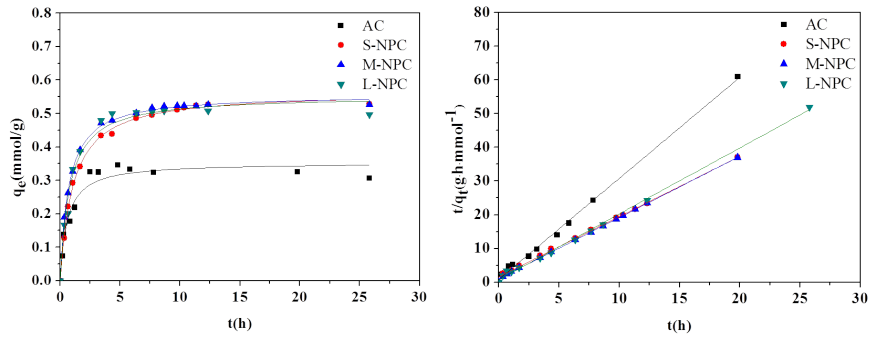


Figure 3. The curve of the amount of contaminants absorbed on NPCs at different time and the kinetics curve of three-sized NPCs.

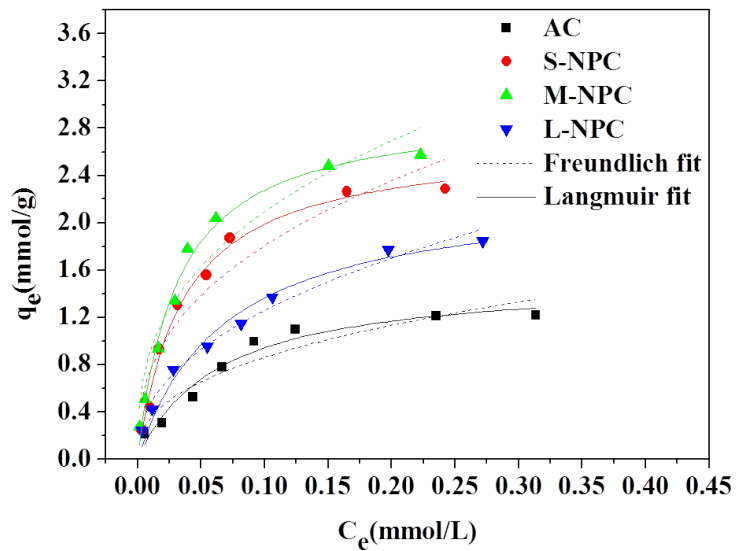


Figure 4. Adsorption isotherms of three-sized NPCs (S-NPC, M-NPC and L-NPC) and AC.

Table 2. Pseudo-second-order parameter of SMX’s adsorption on NPCs.

Adsorbent	C (mg/L)	Pseudo-second-order parameter			R ²
		q _e (mmol·g ⁻¹)	V ₀ (mmol·h ⁻¹ ·g ⁻¹)	K ₂ (g·mmol·h ⁻¹)	
AC	20	0.33	1.15	10.58	0.997
S-NPC	20	0.56	0.63	1.79	0.997
M-NPC	20	0.55	1.00	1.82	0.999
L-NPC	20	0.54	0.71	2.35	0.998

For AC, the maximum adsorption capacities (q_m) of SMX were lower than those of NPCs, demonstrating the excellent adsorption capacity of NPCs. As shown in **Table 3**, the q_m of SMX over NPCs were 686, 757 and 582 mg/g respectively, and the q_m of M-NPC was 2 times larger than that of AC. The higher adsorption capacity of NPCs may be attributed to the much higher specific surface area. The excellent adsorption capacity of NPCs implied that nanoporous

Table 3. Adsorption equilibrium constants of Freundlich model and Langmuir model for contaminants adsorption on NPCs and AC.

Adsorbent	Langmuir constants			Freundlich constants		
	q_m (mmol/g)	b (l/mmol)	R^2	K_F (mmol ⁽¹⁻ⁿ⁾ L ⁿ /g)	n	R^2
S-NPC	2.70	27.98	0.988	4.36	0.38	0.909
M-NPC	2.98	32.39	0.986	4.83	0.36	0.931
L-NPC	2.29	14.69	0.973	3.43	0.44	0.986
AC	1.54	15.85	0.960	2.14	0.40	0.868

carbon derived from MOFs would be a promising adsorbents used for wastewater treatment in the future.

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