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Zeolitic Imidazolate Framework-8 for Fast Adsorption and Removal of Benzotriazoles from Aqueous Solution

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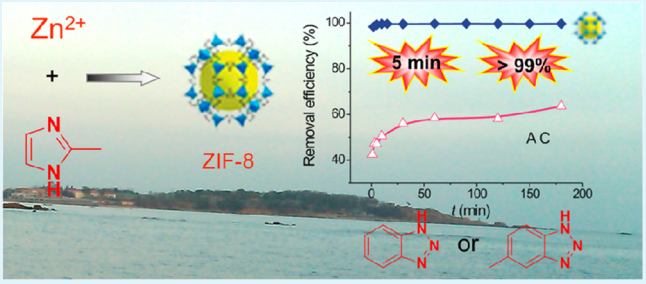
Supporting Information

ABSTRACT: 1*H*-benzotriazole (BTri) and 5-tolyltriazole (5-TTri) are emerging pollutants; the development of novel materials for their efficient adsorption and removal is thus of great significance in environmental sciences. Here, we report the application of zeolitic imidazolate framework-8 (ZIF-8) as a novel adsorbent for fast removal of BTri and 5-TTri in aqueous solution in view of adsorption isotherms, kinetics and thermodynamics, desorption, and adsorbent regeneration. The adsorption of BTri and 5-TTri on ZIF-8 was very fast, and most of BTri and 5-TTri were adsorbed in the first 2 min. The adsorption for BTri and 5-TTri follows a pseudo-second-order kinetics and fits the Langmuir adsorption model with the adsorption capacity of 298.5 and 396.8 mg g^{-1} for BTri and 5-TTri at 30 °C, respectively. The adsorption was a spontaneous and endothermic process controlled by positive entropy change. No remarkable effects of pH, ionic strength, and dissolved organic matter on the adsorption of BTri and 5-TTri on ZIF-8 were observed. The used ZIF-8 could be regenerated effectively and recycled at least three times without significant loss of adsorption capacity. In addition, ZIF-8 provided much larger adsorption capacity and faster adsorption kinetics than activated carbon and ZIF-7. The hydrophobic and $\pi-\pi$ interaction between the aromatic rings of the BTri and 5-TTri and the aromatic imizole rings of the ZIF-8, and the coordination of the nitrogen atoms in BTri and 5-TTri molecules to the Zn^{2+} ions in the ZIF-8 framework was responsible for the efficient adsorption. The fast adsorption kinetics, large adsorption capacity, excellent reusability as well as the pH, ionic strength, and dissolved organic matter insensitive adsorption create potential for ZIF-8 to be effective at removing benzotriazoles from aqueous solution.



KEYWORDS: *metal–organic frameworks, ZIF-8, adsorption, benzotriazoles, water treatment*

INTRODUCTION

Benzotriazoles are well-known corrosion inhibitors for copper or silver materials, which have been widely utilized in cooling and hydraulic fluids, antifreezing products, aircraft deicer, anti-icer fluid, and dishwasher detergents.[1−3] The annual production of benzotriazoles is at least 9000 tons worldwide.[4] The excessive use of benzotriazoles makes them become a class of widespread environmental contaminants. Recently, benzotriazoles such as 1*H*-benzotriazole (BTri) and tolyltriazoles (TTri, including 4- and 5-isomer) have been considered as emerging contaminants due to their toxicity and wide distribution in aquatic environment.[5−8] BTri and TTri are characterized by high water solubility (28 and 7 g L^{-1}), low vapor pressure, low octanol–water distribution coefficients (log K_{ow} 1.23 and 1.89, respectively), and weakly basic compounds.[7] They are resistant to biodegradation and are only partly removed in wastewater treatment.[9] In recent years, quite a few papers on the occurrence of benzotriazoles in rivers and lakes have been published.[10] The concentrations of BTri and TTri have been found to be even as high as 126 and 198 mg L^{-1} (17 mg L^{-1} for 4-TTri and 181 mg L^{-1} for 5-TTri), respectively, in the subsurface water close to an airport.[11]

To date, there have been a few methods reported to remove benzotriazoles from aqueous solution, such as photoeletrocatalytic degradation,[12] membrane bioreactor,[13] oxidation,[4,14,15] and adsorption.[16,17] Ozonation is an effective method for degrading BTri in water, but its limitations arise from the complex oxidation process, high costs, and uncertainty about the type and toxicity of byproducts.[14] The adsorption on porous adsorbents is an economical and efficient way for the removal of benzortiazoles from water. The use of soil as adsorbent for the adsorption of BTri and 5-TTri gave low adsorption capacity (<0.5 mg g^{-1}).[16] Though the adsorption of BTri on Zn–Al–O binary metal oxide was fast at low concentrations, the adsorption capacity was also quite limited (<10 mg g^{-1}).[17] Therefore, exploring novel adsorbents for efficient adsorption and removal of benzotriazoles is still of great significance and challenge.

Metal–organic frameworks (MOFs) are a novel class of fascinating porous materials formed by metal ions or clusters

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and organic ligands.[18−21] Owing to their numerous structures, tunable pore sizes, and high surface areas, MOFs have received great attention in diverse applications.[22−26] The special structures and specific features also make MOFs a class of excellent adsorbents for adsorptive application from small molecules to biological molecules.[27]

Herein, we report the application of zeolitic imidazolate framework-8 (ZIF-8) as a novel adsorbent for the fast adsorption and removal of BTri and 5-TTri from aqueous solution. ZIF-8 has the formula $Zn(2\text{-methylimidazole})_2$ with a sodalite-related zeolite type structure containing narrow six-membered-ring pore windows (3.4 Å) and much larger pores (11.4 Å).[28−30] The adsorption kinetics, thermodynamics, and regeneration of the adsorbent for the removal of BTri and 5-TTri from river water on ZIF-8 were studied in detail. The fast adsorption kinetics, large adsorption capacity, excellent chemical and solvent stability, and good reusability make ZIF-8 a highly potential adsorbent for the removal of BTri and 5-TTri from environmental water.

EXPERIMENTAL SECTION

Materials and Reagents. Zinc nitrate hexahydrate (99%) and benzimidazole were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). 2-Methylimidazole (97%), BTri (99%), and 5-TTri (98%) were supplied by Alfa Aesar (Tianjin, China). Methanol (HPLC grade) was obtained from Concord Fine Chemical Research Institute (Tianjin, China). Activated carbon and humic acid (HA) were obtained from Guangfu Fine Chemical Research Institute (Tianjin, China). Pure water was supplied by Wahaha Group Co. Ltd. (Tianjin, China). River water samples were collected from Weijin River (Tianjin, China) and were pretreated by filtering through 0.22 μm Millipore cellulose membrane before use.

Instrumentation. The X-ray diffraction spectrometry (XRD) patterns were recorded with a D/max-2500 diffractometer (Rigaku, Japan) using Cu Kα radiation (λ = 1.5418 Å) over the angular range from 3° to 80°. The BET surface area, pore volume, and pore size distribution of adsorbents were measured on an ASAP 2010 micropore physisorption analyzer (Micromeritics, Norcross, GA) using nitrogen adsorption at 77 K in the range $0.02 \leq P/P_0 \leq 0.20$. Thermogravimetric analysis (TGA) was performed on a PTC-10A thermal gravimetric analyzer (Rigaku, Japan) from room temperature to 800 °C at a ramp rate of 10 °C min^{-1}. The scanning electron microscopy (SEM) image was recorded on a Nova Nano SEM 430 field emission gun scanning electron microscope (FEI, Hillsboro, Oregon, USA). Zeta potentials of ZIF-8 in pure water were measured on a zeta potential analyzer (Malvern, UK). The X-ray photoelectron spectroscopy (XPS) measurements were recorded on a Kratos Axis Ultra DLD spectrometer fitted with a monochromated Al Kα X-ray source ($h\nu$ = 1486.6 eV), hybrid (magnetic/electrostatic) optics, and a multichannel plate and delay line detector (Kratos, Manchester, UK). ^{1}H NMR spectra were recorded on Bruker AMX-400 spectrometers. Chemical shifts were reported in ppm downfield from internal $Si(CH_3)_4$ and external 85% H_3PO_4, respectively. The TEM image was recorded on a JEOL 100CX II microscope (Akishima, Japan) operating at a 100 kV accelerating voltage. The absorption spectra were recorded on a UV-3600 UV−vis−NIR spectrophotometer (Shimadzu, Japan) with 1 cm path-length cells.

The HPLC system consists of a Waters 510 HPLC pump and a 486 tunable absorbance detector. The separation of benzotriazoles was performed on a BaseLine ODS column (25 cm long × 4.6 mm i.d., BaseLine Co. Ltd., Tianjin, China) using an isocratic elution of water/methanol (3:7, v/v) at a flow rate of 1.0 mL min^{-1} with an UV detection at 259 nm.

Preparation of ZIF-8 Nanocrystals and BTri and 5-TTri Solutions. ZIF-8 nanocrystals were synthesized according to the work of Cravillon et al.[31] Briefly, a solution of $Zn(NO_3)_2{\cdot}6H_2O$ (1.173 g) in 80 mL methanol was added into a solution of 2-methylimidazole (2.595 g) in 80 mL methanol under stirring with a magnetic bar. After keeping at room temperature for 1 h, ZIF-8 was formed, and then separated by centrifugation at 10 000 rpm for 10 min and washed with methanol three times. The obtained white solid was dispersed in methanol and characterized by TEM and SEM. The solid was dried at 90 °C for 12 h and ground with an agate mortar for 15 min. The obtained white powder was characterized by XRD, TGA, TEM, Zeta potential, and N_2 adsorption.

The aqueous solutions of BTri or 5-TTri with different concentrations (50−1000 mg L^{-1}) were prepared by dissolving certain amount of BTri or 5-TTri in pure water. In order to study the adsorption clearly, the concentration of BTri or 5-TTri solution was chosen as 400 mg L^{-1} for the regeneration experiments, and the effects of pH, ionic strength, and HA because almost all the analytes could be removed at the concentration below 200 mg L^{-1}.

Effects of pH, Ionic Strength, and HA. To study the effect of pH, BTri or 5-TTri was dissolved in the aqueous solution of 0.01 M NaCl as the control of ionic strength, and the pH was adjusted with NaOH and HCl. To evaluate the effects of ionic strength and HA, the BTri or 5-TTri solutions were prepared by dissolving BTri or 5-TTri in pure water including different concentrations of salt and HA.

Kinetics for the Adsorption of BTri and 5-TTri on ZIF-8. To study the adsorption kinetics, 5 mL of a fixed initial concentration of BTri or 5-TTri solution was added into a 10 mL centrifugal tube containing 10.0 mg ZIF-8 at 30 °C. After adsorption for a predetermined time (from 2 to 240 min), the mixture was filtered with 0.22 μm Millipore cellulose membrane, and the filtrate was sampled for HPLC analysis.

Adsorption Isotherm and Thermodynamics for the Adsorption of BTri and 5-TTri on ZIF-8. To study the adsorption isotherm and thermodynamics, 5 mL BTri or 5-TTri aqueous solution was poured into 10 mL centrifugal tube containing 10.0 mg of ZIF-8 and kept in the water bath at a predetermined temperature (20−60 °C) for 12 h. The mixture was then centrifuged at 10 000 rpm for 10 min, and the concentration of BTri or 5-TTri in the supernatant was determined by HPLC.

Desorption Experiments. To prepare BTri or 5-TTri preadsorbed ZIF-8 for the desorption experiments, 50.0 mg of ZIF-8 were mixed with 25 mL of 400 mg L^{-1} BTri or 5-TTri solution for 12 h. The mixture was then separated by centrifugation at 10 000 rpm for 10 min, and the obtained solid was used as the preadsorbed ZIF-8.

Methanol alone, 1 M NaOH/methanol (5:95, v/v), and 1 M NaOH/methanol (10:90, v/v) were used as the desorption solvent to desorb the BTri or 5-TTri from preadsorbed ZIF-8. A 2 mL portion of desorption solution was added into a 10-mL centrifugal tube containing 10.0 mg of preadsorbed ZIF-8. After ultrasonication for 5 min, the mixture was centrifuged at 10 000 rpm for 10 min, and the concentration of BTri or 5-TTri in the supernatant was determined by HPLC. The desorption efficiency was calculated as the percentage of the mass of analyte in the supernatant of the total mass of analyte adsorbed on ZIF-8. The same procedure was followed to evaluate the effect of the solvent volume on the desorption of BTri or 5-TTri from preadsorbed ZIF-8. Finally, the desorbed ZIF-8 was washed with pure water twice, and dried for reuse.

Reusability of ZIF-8. To investigate the reusability of ZIF-8 for the adsorption of BTri or 5-TTri, 5 mL of BTri or 5-TTri solution in water/methanol (9:1, v/v) was poured into a 10-mL centrifugal tube containing 10.0 mg of regenerated ZIF-8. The centrifugal tube was then kept in a water bath at 30 °C. The mixture was collected at a predetermined time interval (from 2 to 120) and filtered with 0.22 μm Millipore cellulose membrane. The concentration of BTri or 5-TTri in the supernatant was determined by HPLC.

Comparison of ZIF-8 with Other Adsorbents for the Adsorption of BTri and 5-TTri. To study the adsorption kinetics of BTri on different adsorbents, 5 mL of BTri or 5-TTri solution (100 mg L^{-1}) was added into a 10-mL centrifugal tube containing 10.0 mg of adsorbents. The centrifugal tube was then kept in a water bath at 30 °C. After adsorption for a predetermined time (from 2 to 180 min), the mixture was filtered with 0.22 μm Millipore cellulose membrane and the filtrate was sampled for HPLC analysis.

RESULTS AND DISCUSSION

Characterization of ZIF-8. The prepared ZIF-8 was characterized by XRD, TGA, SEM, TEM, N_2 adsorption, and Zeta potential experiments (Supporting Information Figure S1, S3–S5). The experimental XRD pattern of the synthesized ZIF-8 is in good agreement with the simulated one, showing the successful preparation of ZIF-8 with pure phase (Supporting Information Figure S1A). Moreover, the XRD patterns of ZIF-8 after adsorption, at different pHs, and after desorption are also in good agreement with the simulated one, showing the good stability of ZIF-8. The TGA data reveals that ZIF-8 is stable up to 400 °C (Supporting Information Figure S1B). The average crystallite diameter of as-prepared ZIF-8 is 32 nm (Supporting Information Figure S3), while the average size of the prepared ZIF-8 powder is 135 nm × 330 nm (Supporting Information Figure S4). The N_2 adsorption result shows the BET surface area of ZIF-8 is 1628 $m^2\ g^{-1}$. Pore size distribution of the prepared ZIF-8 estimated by the DFT method gives a pore diameter of 1.2 nm and a pore volume of 0.495 $cm^3\ g^{-1}$ (Supporting Information Figure S5).[28] The zeta potential results show that the ZIF-8 is positive charged in the pH range from 2 to 10 (Supporting Information Figure S1D).

Kinetics for the Adsorption of BTri and 5-TTri on ZIF-8. The time-dependent adsorption of BTri and 5-TTri on ZIF-8 was investigated at four initial concentrations (50, 100, 200, and 400 mg L^{-1}) (Figure 1A and B). The adsorption equilibrium of BTri and 5-Ttri was reached within 5 min at the concentration of 50 mg L^{-1}, revealing the rapid adsorption of BTri and 5-Ttri on ZIF-8. Although more time was needed to reach adsorption equilibrium at higher concentrations, all the adsorption equilibriums were reached within 30 min at the initial concentration less than 200 mg L^{-1}. The adsorption capacities for BTri and 5-TTri increased with the initial BTri and 5-TTri concentration, showing the favorable adsorption of BTri and 5-TTri at high concentrations. It is worth mentioning that most of BTri or 5-TTri was adsorbed in the first 2 min, and nearly all the BTri or 5-TTri was adsorbed from aqueous solution at the initial concentration below 200 mg L^{-1} when the equilibrium was reached.

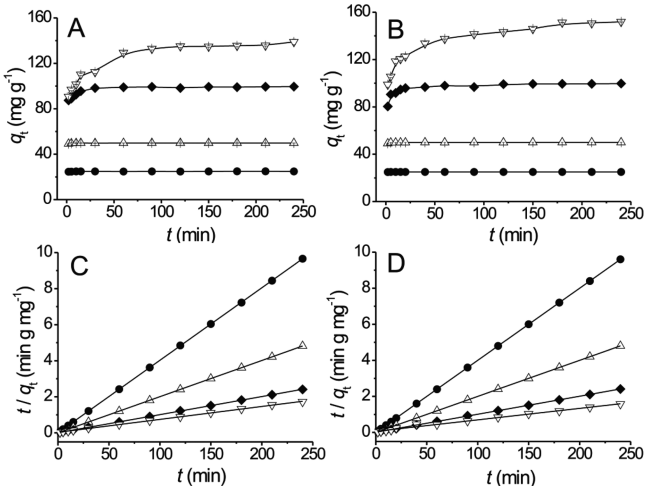

Figure 1. Time-dependent adsorption of BTri (A) and 5-TTri (B) and the plots of pseudo-second-order kinetics for the adsorption of BTri (C) and 5-TTri (D) at different initial concentrations: (●) 50, (Δ) 100, (♦) 200, and (▽) 400 mg L^{-1} on ZIF-8 at 30 °C and pH 7.0.

To gain insight into the adsorption kinetics, the quantitative kinetic order and adsorption rate constant for the adsorption of BTri and 5-TTri on ZIF-8 were studied (Figure 1C and D). Compared to the pseudo-first-order kinetic model (Supporting Information eq S1), the time-dependence of the adsorption of BTri and 5-TTri on ZIF-8 was much better fitted with the pseudo-second-order kinetic model (eqs 1 and 2)[32−35] (Figure 1C and D, and Table 1 cf. Supporting Information Figure S6 and Table S2).

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}t \quad (2)$$

where q_t and q_e are the adsorption capacity (mg g^{-1}) at a certain time t (min) and equilibrium, respectively, and k_2 is the rate constant for the pseudo-second-order adsorption (g mg^{-1} min^{-1}). The plots of t/q_t against t show good linearity ($R^2 > 0.990$) with a slope of $1/q_e$ and an intercept of $1/(k_2 q_e^{\,2})$. The calculated values of q_e and k_2 are summarized in Table 1. As the initial concentration increased, the value of k_2 decreased, indicating that chemisorption was significant in the rate-limiting step, involving valency forces through sharing or exchange of electrons between BTri or 5-TTri and ZIF-8.[35,36]

Effect of pH on the Adsorption of BTri and 5-TTri. The effect of pH on the adsorption of BTri and 5-TTri was studied in the pH range from 2 to 11 (Figure 2A). The adsorption capacities of BTri and 5-TTri on ZIF-8 slightly decreased as pH increased. The charge of ZIF-8 and the ionization degree of BTri (pK_{a1} = 1.6, pK_{a2} = 8.6) and 5-TTri (pK_{a1}= 2.2, pK_{a2} = 8.8) are affected by pH.[17] The zeta potential results show the ZIF-8 is positively charged in the pH range of 2−10 (Supporting Information Figure S1D). The charge of BTri and 5-TTri could be positive at pH < pK_{a1}, zwitterion in the pH range of pK_{a1} to pK_{a2}, or negative at pH > pK_{a2}. The above results show the electrostatic interaction is not the main mechanisms involving in the efficient adsorption of the BTri and 5-TTri on ZIF-8. The hydrophobic and $\pi-\pi$ interaction between the aromatic rings of the BTri and 5-TTri and the aromatic imizole rings of the ZIF-8 should be considered in the

Table 1. Kinetic Parameters for the Adsorption of BTri and 5-TTri on ZIF-8 at Different Initial Concentrations at 30 °C

			pseudo-second-order kinetic model		
	C_0 (mg L^{-1})	$q_{e(exp)}$ (mg g^{-1})	$q_{e(cal)}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
BTri	50	24.82 ± 0.11	24.86 ± 0.02	4.420×10^{-1}	0.9999
	100	49.83 ± 0.15	49.83 ± 0.01	3.357×10^{-1}	1
	200	99.50 ± 0.06	99.60 ± 0.14	1.759×10^{-2}	0.9999
	400	138.9 ± 2.52	139.3 ± 0.95	1.864×10^{-3}	0.9995
5-TTri	50	24.99 ± 0.01	24.99 ± 0.01	11.23	1
	100	49.97 ± 0.01	49.98 ± 0.01	1.137	1
	200	99.72 ± 0.02	100.0 ± 0.22	9.833×10^{-3}	0.9999
	400	152.0 ± 1.12	156.7 ± 4.35	6.782×10^{-4}	0.9909

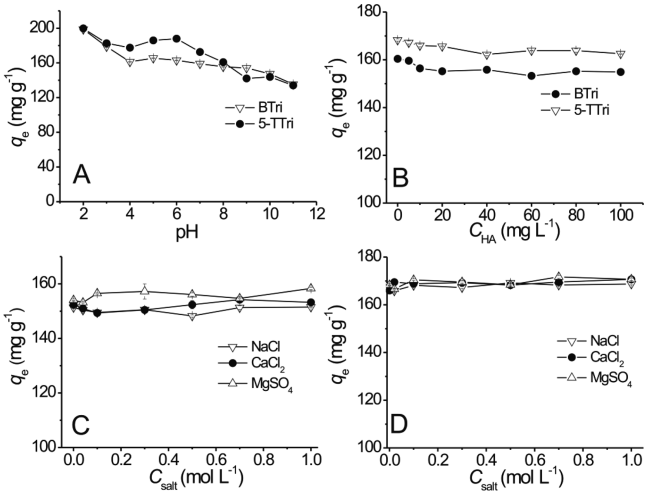

Figure 2. Effects of pH (A), HA (B), and ionic strength (C) BTri, (D) 5-TTri, on the adsorption of BTri and 5-TTri on ZIF-8.

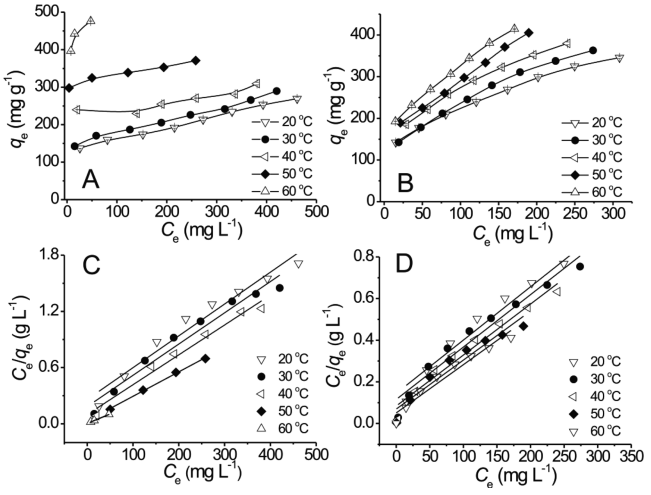

Figure 3. Adsorption isotherms for the adsorption of BTri (A) and 5-TTri (B) on ZIF-8 in the temperature range of 20–60 °C and their corresponding Langmuir plots for BTri (C) and 5-TTri (D).

adsorption of the BTri and 5-TTri on ZIF-8. UV–vis spectra were used to show the $\pi-\pi$ interaction between BTri and 5-TTri and ZIF-8 (Supporting Information Figure S7). Addition of the ZIF-8 or 2-methylimizole led to a decrease in the main absorption at 259 nm for both BTri and 5-TTri, but an increase in the absorption at higher wavelength (273 nm for BTri and 276 nm for 5-TTri). The bathochromic shift of the main absorption peaks indicates $\pi-\pi$ interaction between BTri and 5-TTri and ZIF-8.[37]

Effect of HA on the Adsorption of BTri and 5-TTri. There are a lot of natural organic materials in nature water, and HA is recorded as the representative of dissolved organic matter in nature water. To explore the potential application of ZIF-8 for the adsorption and removal of BTri and 5-TTri in nature water, the effect of HA concentration on the adsorption capacity of BTri and 5-TTri on ZIF-8 was investigated (Figure 2B). Although the adsorption capacity decreased in the presence of HA, the adsorption capacity did not decrease significantly as the concentration of HA increased. Therefore, ZIF-8 has the potential application for the adsorption of BTri or 5-TTri in nature water.

Effect of Ionic Strength on the Adsorption of BTri or 5-TTri. As there are various salts and metal ions in environmental water, it is necessary to examine the effect of ionic strength on the adsorption of BTri and 5-TTri on ZIF-8. Different concentrations of NaCl, $CaCl_2$, and $MgSO_4$ were used to evaluate the influence of ionic strength on the adsorption of BTri and 5-TTri on ZIF-8 (Figure 2C and D). The results show no significant change of the adsorption capacity in the presence of NaCl, $CaCl_2$, and $MgSO_4$.

Adsorption Isotherms and Thermodynamics for the Adsorption of BTri and 5-TTri on ZIF-8. The adsorption isotherms were studied at five different temperatures (20–60 °C) in the concentration range of 50–1000 mg L^{-1} (Figure 3). The adsorption capacities of BTri and 5-TTri increased with the initial concentration of BTri and 5-TTri, showing favorable adsorption of BTri and 5-TTri on ZIF-8 at high concentrations. To evaluate the maximum adsorption capacities of BTri and 5-TTri on ZIF-8, the adsorption isotherms were fitted with the Langmuir equation (eq 3).[38,39]

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \tag{3}$$

where C_e (mg L^{-1}) is the equilibrium concentration of BTri or 5-TTri, q_e (mg g^{-1}) is the equilibrium adsorption capacity of BTri or 5-TTri, Q_0 is the maximum adsorption capacity (mg g^{-1}), and b is the Langmuir constant (L mol^{-1}). The plots of C_e/q_e against C_e gave a good linear plot at all of the tested initial concentrations, indicating the adsorption of BTri and 5-TTri on ZIF-8 follows a Langmuir model (Figure 3C and D). Table 2 summarizes the obtained Langmuir parameters. The maximum adsorption capacities increased from 294 to 495 and 390 to 431 mg g^{-1} for BTri and 5-TTri, respectively, as temperature increased from 20 to 60 °C, suggesting the adsorption of BTri and 5-TTri on ZIF-8 is favorable at high temperatures with an endothermic process. The adsorption could be viewed as two steps: the desorption of water molecules from BTri and 5-TTri and the adsorption of BTri and 5-TTri by ZIF-8. The first step gives an endothermic process and the second step gives an exothermic process. The endothermic desorption of water molecules should dominate the whole procedure.[34,39] The equilibrium adsorption capacity increased as temperature increased, indicating chemisorption was responsible for the adsorption.[40] The maximum adsorption capacity for BTri on ZIF-8 is 30 to 50 times larger than that on Zn–Al–O binary metal oxide,[17] revealing the high potential of ZIF-8 for the adsorption and removal of BTri in aqueous solution.

To further study the adsorption mechanism, the adsorption equilibrium constant (K_0), free energy change (ΔG, kJ mol^{-1}), enthalpy change (ΔH, kJ mol^{-1}), and entropy change (ΔS, J mol^{-1} K^{-1}) for the adsorption of BTri and 5-TTri on ZIF-8 were calculated based on eqs 4–6.[35,41]

$$K_0 = \frac{q_e}{C_e} \tag{4}$$

$$\Delta G = -RT \ln K_0 \tag{5}$$

$$\ln K_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{6}$$

where q_e (mg g^{-1}) is the amount of BTri and 5-TTri adsorbed on ZIF-8, C_e (mg L^{-1}) is the equilibrium concentration of BTri or 5-TTri, T is the temperature, R is the gas constant. The values of K_0 were obtained by ln (q_e/C_e) vs q_e and extrapolating q_e to zero.[41] The values of ΔH and ΔS were obtained by ln K_0 against $1/T$ (Supporting Information Figure S8). Table 2 shows the calculated ΔG, ΔH, and ΔS. The negative values of ΔG suggest the spontaneous adsorption of BTri and 5-TTri on

Table 2. Langmuir and Thermodynamic Parameters for the Adsorption of BTri and 5-TTri on ZIF-8

	Langmuir parameters				thermodynamic parameters			
	T (°C)	Q_0 (mg g^{-1})	b (L mol^{-1})	R^2	ln K_0	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
BTri	20	294.1	1.561	0.9542	1.871	−4.560	221.3	762.2
	30	298.5	2.184	0.9565	2.516	−6.340		
	40	304.8	5.167	0.9667	6.583	−17.14		
	50	371.7	19.83	0.9967	9.561	−25.69		
	60	495.0	64.00	0.9999	12.03	−33.32		
5-TTri	20	390.6	2.357	0.9674	2.699	−6.578	16.92	79.00
	30	396.8	2.909	0.9487	2.728	−6.876		
	40	408.2	3.895	0.9592	2.856	−7.435		
	50	425.5	4.528	0.9223	3.114	−8.368		
	60	431.0	6.100	0.9461	3.564	−9.870		

ZIF-8. The positive values of ΔH confirm the endothermic process for the adsorption of BTri and 5-TTri, agreeing with the increase of adsorption capacity with temperature. The positive values of ΔS imply the increased randomness with adsorption of BTri and 5-TTri on ZIF-8 probably because the number of desorbed water molecules is larger than that of the adsorbed BTri and 5-TTri molecules. Therefore, the efficient adsorption of BTri and 5-TTri on ZIF-8 is controlled by the positive entropy change.

Comparison with Other Adsorbents for the Adsorption of BTri and 5-TTri. To show the advantage of ZIF-8 for the adsorption of BTri and 5-TTri, the time-dependent adsorption of BTri and 5-TTri on activated carbon and ZIF-7 were evaluated for comparison. The results shown in Figure 4

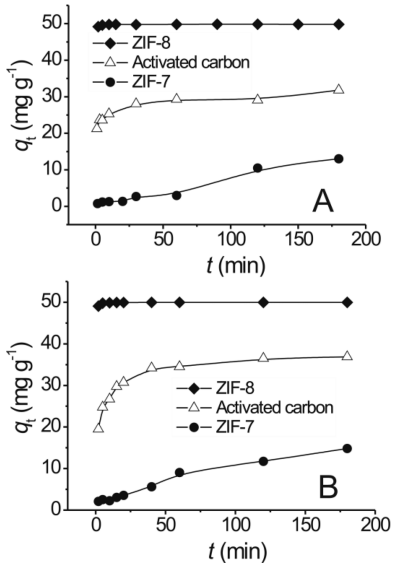

Figure 4. Time-dependent adsorption of BTri (A) and 5-TTri (B) on different adsorbents at 30 °C.

show that ZIF-8 provided much larger adsorption capacity and faster adsorption kinetics than activated carbon and ZIF-7.

Except for the hydrophobic and $\pi-\pi$ interaction between BTri and 5-TTri and ZIF-8, the interaction of the N atom of BTri with ZIF-8 is also responsible for the efficient adsorption of BTri and 5-TTri on ZIF-8. To address this issue, XPS experiments were carried out on ZIF-8 before and after adsorption (Supporting Information Figure S9). The XPS spectra shows that the adsorption of BTri and 5-TTri on ZIF-8 led to the shift of the Zn 2p peak for ZIF-8 to higher energy (from 1021.2 to 1021.5 and 1044.2 to 1044.5 eV for BTri and 5-TTri, respectively), suggesting the weak binding or coordination of Zn in ZIF-8 to BTri and 5-TTri.

^{1}H NMR measurements were further performed to confirm the interaction of BTri and 5-TTri with ZIF-8 (Supporting Information Figure S10). The ^{1}H NMR results show the chemical shift for N−H at 12.5 ppm of BTri disappeared after adsorption on ZIF-8, indicating the interaction of the N atom of BTri with ZIF-8. Although ZIF-7 has the similar structure to ZIF-8, the lower surface area (Supporting Information Table S1) and the larger ligand of ZIF-7 may become the bafflement to prevent the interaction between analyte and adsorbent.

Desorption of BTri and 5-TTri from ZIF-8. Easy desorption of analytes from adsorbents and facile regeneration of adsorbents are very important for the reuse of both analytes and adsorbents from the green chemistry and practical application point of view. For this purpose, methanol alone, and the mixture of methanol and NaOH aqueous solution, were tested to desorb BTri and 5-TTri from ZIF-8 (Supporting Information Figure S11). The results show that 1 M NaOH/methanol (10:90, v/v) gave the most efficient desorption of BTri and 5-TTri from preadsorbed ZIF-8.

Regeneration of ZIF-8. The reusability for ZIF-8 was evaluated by comparing the kinetics for the adsorption of BTri and 5-TTri on regenerated and fresh ZIF-8 (Supporting Information Figure S12). No significant loss of the adsorption capacity was observed on the regenerated ZIF-8 for the two times reuse, showing the excellent reusability of ZIF-8 for the adsorption of BTri and 5-TTri.

Adsorption Kinetics of BTri and 5-TTri in River Water on ZIF-8. The adsorption kinetics of BTri and 5-TTri in river water on ZIF-8 was evaluated to demonstrate the feasibility of ZIF-8 for practical adsorption of BTri and 5-TTri in natural water (Supporting Information Figure S13 and Table S3). The results show no significant difference in the adsorption kinetics and adsorption capacity for ZIF-8 to adsorb BTri and 5-TTri in pure water and river water (Figure 1 and Table 1 cf. Figure S13 and Table S3), indicating ZIF-8 is potential for practical removal of BTri and 5-TTri in river water.

CONCLUSIONS

In summary, we have demonstrated the feasibility of ZIF-8 for fast adsorption and removal of BTri and 5-TTri in aqueous solution. The fast adsorption kinetics, good solvent stability, high adsorption capacity, excellent reusability as well as pH, ionic strength, and dissolved organic matter insensitive adsorption kinetics and capacity make ZIF-8 promising as

novel adsorbent for the removal of bentriazoles from aqueous solution.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization of ZIF-7 and additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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