

Research Article

Uptake of Sulfadiazine Sulfonamide from Water by Clinoptilolite

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The interactions between sulfadiazine (SDZ), a sulfonamide antibiotic, and clinoptilolite, a hydrophilic zeolite, were investigated under batch experimental conditions. The uptake of SDZ on the zeolite followed a linear sorption isotherm under neutral pH conditions. Higher SDZ uptake on the zeolite was observed when solution pH was below the pK_{a1} or above the pK_{a2} values of SDZ, while minimal SDZ uptake was observed when the solution pH was between the pK_{a1} and pK_{a2} values of SDZ. These observations suggested that hydrophobic interaction between SDZ and the zeolite was minimal due to the hydrophilic nature of the substrate. Electrostatic interactions and ion bridging were attributed to the elevated SDZ uptake under low and high pH conditions. As SDZ had a low K_{OW} value, the hydrophilic nature of the substrate prevented extensive uptake of SDZ, which could contribute to its extensive detection in the environment, including surface water and wastewater.

1. Introduction

The worldwide use of veterinary antibiotics poses a continuous threat to the environment. Used extensively in human and animal medicine, sulfonamide antibiotics (SAs) were highly stable towards hydrolysis, resulting in accumulations in the environment [1]. Neutral and cationic SAs interacted primarily with external surfaces, instead of intercalating into the swelling clay mineral montmorillonite [2]. However, conflicting results were reported on the stability of adsorbed SAs to solid surfaces. Adsorption of SAs to mineral soil colloids was weaker and resulted in a stronger desorption from clay-size fractions [3]. The distribution coefficients (K_d) of SAs were overall low, <10 L/kg on many types of soils, thus likely to be highly mobile in the environment [4–6]. Slightly high K_d values were reported for SAs sorption on pure clays, while organic matter had higher affinities for neutral SAs than smectite clays [7].

Sulfadiazine [SDZ, 4-amino-N-(2-pyrimidinyl)benzenesulfonamide] is a widely used potent antibacterial agent belonging to SAs. [8]. It was the second highest sold antibiotic in UK with a usage of 14 tons in 2000 [9]. Due to its

extensive use in veterinary medicine and frequent detection in the environment, a few studies were conducted on SDZ adsorption on soil materials and manure [3, 10]. In addition, a detailed literature review on the analysis, fate, and effects of SDZ on soil ecosystems indicated that, in applying manure from antibiotic-treated animals to arable soils, SDZ could reach the environment, but the fate and transformation processes and the consequences for soil microorganisms and soil functions were not studied adequately [11]. Therefore, little is known about the possible degradation of SDZ during its transport in the subsurface environment and its sorption behavior is not yet completely understood [12]. The irreversible adsorption of SDZ on two soils, silty loam and loamy sand, was still not well understood and required further investigations [12]. SDZ underwent a rapid and strong binding in soil on a time scale of minutes, resulting in an instantaneous loss in extractability [13]. On the other hand, slow reversible sorption into a residual fraction allowed low, but effective SDZ concentrations in the soil solution to be maintained over a long time period, which could be attributed to the development of microbial communities with increased resistance against the antibiotic over time [11].

SDZ adsorption onto four different acidic soils best followed the Freundlich isotherm and higher SDZ adsorption correlated to high organic carbon content and clay [14]. It was speculated that the adsorbed SDZ formed dimers inside the high silica zeolite as observed from the NMR findings and computational results from FTIR spectrum [15].

The goal of this study was to investigate the interactions between SDZ and clinoptilolite, a tectosilicate found in many volcanic soils with high external cation exchange capacity (ECEC) and total cation exchange capacity (TCEC), in order to better understand the fate and transport of SDZ in the environment and to understand the effect of solution chemistry on the removal of SDZ by high charged zeolite minerals. Ultimately, the possible mechanisms of SDZ uptake by the hydrophilic zeolite would be addressed.

2. Materials and Methods

The clinoptilolite zeolite, formed from alteration of volcanic ash, was obtained from St. Cloud Mine in Winston, NM, USA. The aggregated particle size was less than 0.4 mm, while individual crystal size was in the micrometer range. The zeolite was used as received without further treatment. It contained 74% clinoptilolite, 12% feldspar, 12% quartz and cristobalite, and trace amounts of clay minerals based on quantitative X-ray diffraction analysis [16]. Its specific surface area (SSA) was 15.7 m²/g as determined by N₂ adsorption [17]. The ECEC was between 90 and 110 mmol_c/kg and the TCEC was more than 1 mol_c/kg [16].

The sulfadiazine (CAS no. 68-35-9) was purchased from Alfa Aesar (Ward Hill, MA, USA). It has a pK_{a1} value at 2.28–2.71 corresponding to the protonation of the NH₂ group and a pK_{a2} value at 6.45–6.52 due to the deprotonation of the sulfonamido group [18, 19]. The equilibrium constant between the neutral and zwitterionic form of SDZ is 10^{2.17} [18], suggesting a dominant species of SDZ⁰ instead of SDZ[±], when solution pH was between 2.7 and 6.4 (Figure 1). It has a molar mass of 250.28 g/mol and a log K_{OW} value of –0.09 [3]. The reported water solubility varied from 265 mg/L at pH 5.5 and 25°C to 5690 mg/L at pH 8 and 37°. A solubility value as low as 77 mg/L was also reported [3].

For the adsorption study, 0.2 g of zeolite was combined with 10 mL of SDZ solutions at initial SDZ concentrations of 0.01 to 0.08 mmol/L in 50 mL centrifuge tubes. The mixtures were shaken at 150 rpm for varying amounts of time for the kinetic study and for 24 h for all other tests. Then the mixtures were centrifuged at 3500 rpm for 10 min and the supernatants filtered through 0.45 μm syringe filters before being analyzed for equilibrium SDZ concentrations. The solution pH was adjusted a few times over a 24 h period to reach equilibrium values of 2–11 using 1 M HCl or NaOH for the pH-dependent study. Under these pH conditions, the clinoptilolite was stable [20]. Temperature was set at 296, 306, 316, and 326 K for the temperature-dependent study. Duplicate samples were run for each experimental condition.

The SDZ concentration in the supernatant was measured using a UV-Vis spectrophotometer at the wavelength of 275 nm, the optimum for UV absorption [1]. Calibrations

were made using standards of 0.002, 0.01, 0.02, 0.05, and 0.08 mmol/L with regression coefficients all greater than 0.9998. For the pH-dependent study, the pH variation between the standards and the samples was less than 2. The amount of SDZ adsorbed was calculated from the difference between the initial and equilibrium concentrations.

The desorption of exchangeable cations was tested using an HPLC system with a mobile phase of 3.5 mM cupric sulfate and a PRP-X200 cation chromatographic column. At a flow rate of 2.0 mL/min, the retention time was 1.4, 1.9, 2.9, and 3.9 min for Na⁺, K⁺, Mg²⁺, and Ca²⁺, respectively. The detection limit was 0.05 mM for the cations, and the linear range was from 0.1 to 1 mM.

A Jasco FT/IR-4100 spectrometer equipped with a ZnSe attenuated total reflection accessory was used to record the FTIR spectra of zeolite after SDZ uptake. The spectra were obtained from 650 to 4000 cm^{–1} by accumulating 256 scans at a resolution 4 cm^{–1}. A cosine apodization function was used for data processing.

3. Results and Discussion

3.1. Kinetics of SDZ Uptake on Zeolite. The data of SDZ uptake by zeolite were fitted to several kinetic models, but only the pseudo-second-order kinetics fitted the data well (Figure 2). The integrated rate law of the pseudo-second-order kinetics is

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

where k (kg/mmol-h) is the rate constant of adsorption, q_e (mmol/kg) is the amount of solute adsorbed at equilibrium, and q_t (mmol/kg) is the amount of solute adsorbed on the surface of the adsorbent at any time, t . Equation (1) can be rearranged into a linear form as

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

where kq_e^2 is the initial rate (mmol/kg-h). Fitting the experimental data to the pseudo-second-order kinetic model resulted in a coefficient of determination r^2 of 0.98, an initial rate of 4 mmol/kg-h, a rate constant of 2 kg/mmol-h, and a q_e of 1.3 mmol/kg. The initial rate was only 1/4 of that for SDZ adsorption on hydrophobic talc. Although the q_e was 5 times higher than that for SDZ uptake by talc, the rate constant was two orders of magnitude less than that for SDZ uptake by talc [21]. The much slower rate reflected slow diffusion of SDZ into the internal pore space of the zeolite in comparison to surface adsorption of SDZ on talc, as the zeolite used was aggregated. The higher amount of SDZ uptake by zeolite could be attributed to a larger surface area of 15.7 m²/g in comparison to 2.3 m²/g for talc [21].

3.2. Thermodynamics of SDZ Uptake on Zeolite. Although the log K_{OW} value was –0.09 [3], suggesting some hydrophilicity

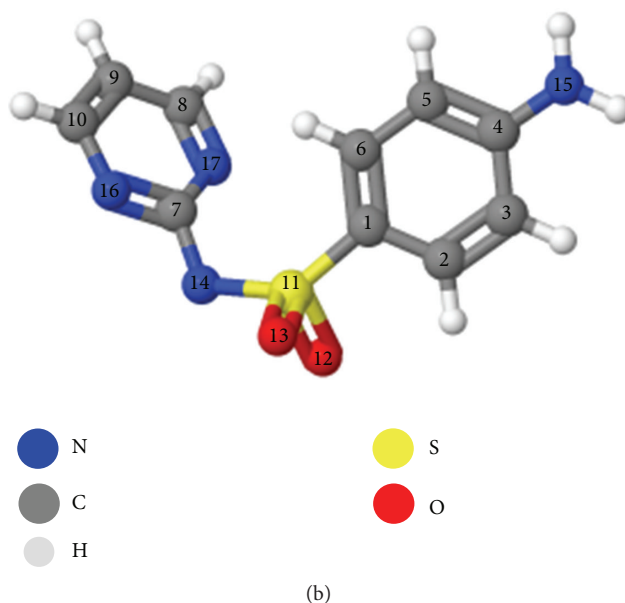
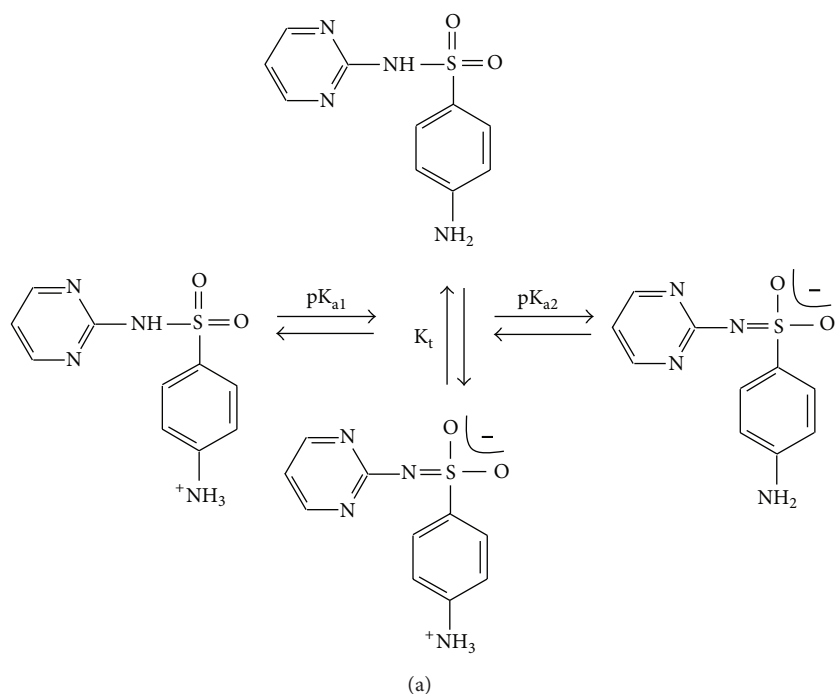


FIGURE 1: Speciation of SDZ (a) and its 3d arrangement of C, N, and S (b).

of the solute, the SDZ uptake on zeolite followed a linear type isotherm

$$C_S = K_d C_L, \quad (3)$$

where C_S and C_L are the solute concentrations on solid (mmol/kg) and in solution (mmol/L) and K_d is the solute distribution coefficient (L/kg), a measure of the affinity of a solution to the solid surface.

The coefficient of determination r^2 was 0.99, and the K_d value was 24 L/kg (Figure 3). This value is comparable to the K_d values for some SAs adsorption on montmorillonite and kaolinite [1], one to two orders of magnitude larger than

the K_d of 1.4 to 2.8 L/kg for SDZ adsorption on soil [3], 1.8 and 0.9 L/kg for sulfachloropyridazine adsorption on a clay loam and sandy loam soil, respectively [4], 0.2 to 4.0 L/kg for sulfamethazine (SMZ) sorption on five different soils of varying organic carbon contents and solution pH [5], and to 0.07 to 0.91 L/kg for sulfadimethoxine and sulfamethoxazole adsorption on soils [6].

The adsorption of most ionizable antibiotics such as tetracycline (TC) and ciprofloxacin (CIP) on charged mineral surfaces fitted the Langmuir isotherm well and was attributed to a surface-limited or charge-limited adsorption, such as cation exchange [22, 23]. Fitting to the linear sorption

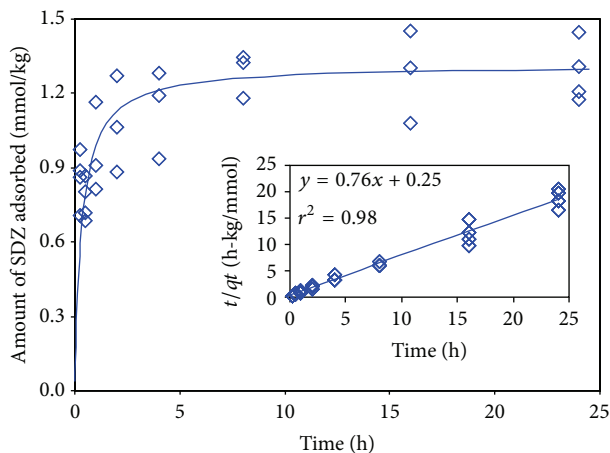


FIGURE 2: Kinetic study of SDZ adsorption on zeolite. The line is the pseudo-second-order fit to the observed data and the inset is the plot of (2).

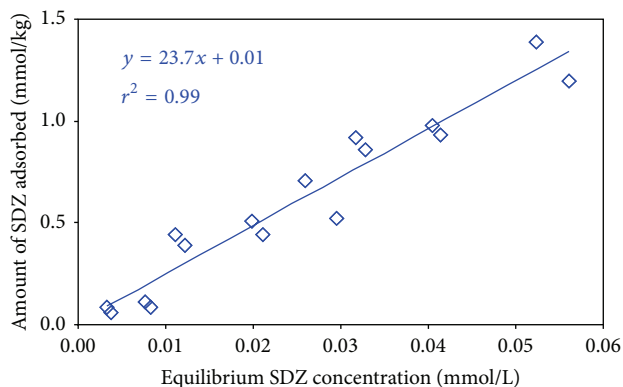


FIGURE 3: Adsorption of SDZ on zeolite. The solid line is the linear fit to the observed data.

isotherm rather than the Langmuir isotherm suggested a different sorption mechanism for SDZ uptake on the zeolite, even though its surface is negatively charged. In comparison to the ECEC of 90–110 mmol/kg [16], the amount of SDZ uptake was no more than 1.3 mmol/kg under the given experimental condition (Figure 3). This amount is almost two orders of magnitude lower than the ECEC and even three orders of magnitude lower than the TCEC of the mineral. Although multiple adsorption cycles could be performed to increase the amount of SDZ adsorbed, with the solubility limit of 77 mg/L [3], the highest amount of SDZ adsorbed based on the extension of the straight line fit in Figure 3 would be no more than 10 mmol/kg. These analyses suggest that cation exchange may not be the major mechanisms for SDZ uptake by the zeolite.

The K_d values can be used to determine the thermodynamic parameters for SDZ uptake by zeolite by

$$\ln K_d = -\frac{\Delta G}{RT}, \quad (4)$$

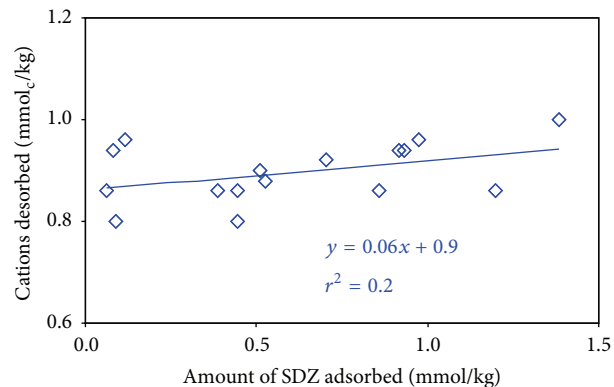


FIGURE 4: Desorption of metal cations as affected by SDZ adsorption.

where ΔG is the free energy of SDZ adsorption, R is the gas constant, and T is the absolute temperature. The calculated ΔG value was -7.8 kJ/mol. This value was much less than adsorption of cationic drugs on charged particles such as -20 to -30 kJ/mol for TC adsorption on palygorskite [24]. But the value is similar to -8 kJ/mol for TC sorption on silica [25] and larger than SDZ adsorption on hydrophobic talc [21]. Considering the linear sorption isotherm and lower ΔG values for SDZ adsorption on zeolite, it could be inferred again that cation exchange may not play a major role for SDZ uptake.

3.3. Monitoring Desorption of Exchangeable Cations Accompanying SDZ Uptake. A plot of the amount of the exchangeable cations releases against the amount of SDZ adsorbed showed essentially no relationship. If a forced linear regression is applied, the slope was only 0.06 and an intercept close to 0.9 mmol/kg with an r^2 of only 0.2 (Figure 4). The greater intercept suggests spontaneous release of exchangeable cations even under negligible initial SDZ concentrations. The results are completely different from CIP adsorption on montmorillonite in which a plot of the exchangeable cations desorbed against CIP adsorbed resulted in a slope of 0.99, an intercept of -0.05 , and an r^2 of only 0.994, and the uptake of CIP by the montmorillonite was attributed to cation exchange [24]. Thus, the release of exchangeable cations accompanying SDZ uptake further confirmed that cation exchange may not be the major mechanism for SDZ uptake by the zeolite even though it has a high ECEC value.

3.4. Influence of Solution pH on SDZ Uptake on Zeolite. With the pK_{a1} and pK_{a2} values of SDZ at 2.7 and 6.4, respectively [18], the dominant species would be SDZ^+ at $pH < 2.7$, SDZ^0 between $pH 2.7$ and 6.4, and SDZ^- when $pH > 6.4$ (Figure 5). Higher SDZ uptake was found when solution pH was lower than the pK_{a1} or higher than the pK_{a2} values when the SDZ was either in cationic or anionic forms (Figure 5). The K_d values followed a similar trend, varying from 1 to 33 L/kg, with the lowest one found at pH 4, suggesting that the minimal SDZ uptake occurred for SDZ^0 (Figure 5). A similar trend on SDZ uptake on talc was also noticed [21].

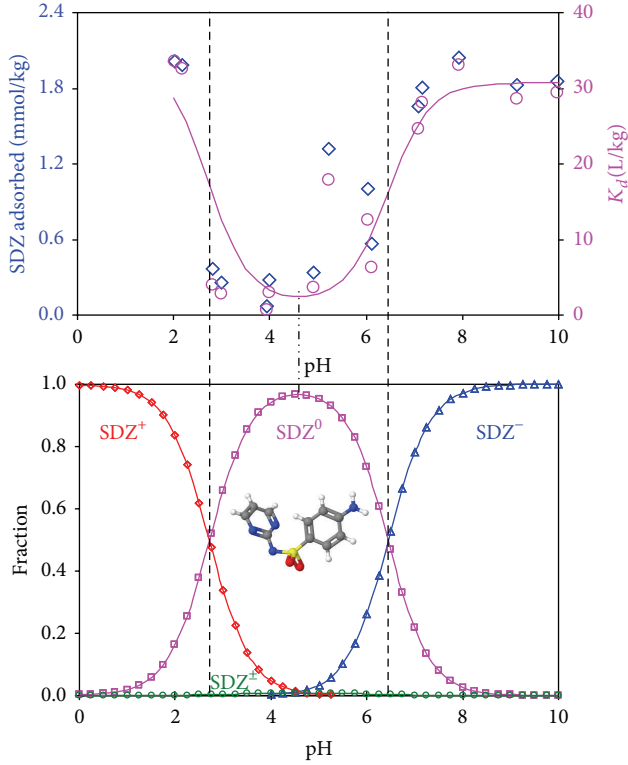


FIGURE 5: SDZ adsorption on zeolite as affected by equilibrium solution pH (\diamond with left y-axis) and K_d as affected by solution pH (\square right y-axis). The solid line is the fitted K_d as a function of pH.

Literature data of K_d for SDZ were scarce and were restricted to a narrow pH range (6.9–7.5) [26], resulting in a small variation of the observed K_d of 1.4 to 2.8 L kg⁻¹ [5]. In general, the amphoteric sulfonamides behave as weak acids and form salts in strongly acidic or basic solutions [27]. This salt-forming tendency might be responsible for the higher K_d values at high solution pH conditions. At low pH values, forces between the protonated antibiotic and negative charges of clinoptilolite due to isomorphous substitutions would result in more SDZ uptake. In comparison, adsorption of SDZ on activated carbon was relatively insensitive to pH [28], due to lack of surface charge.

The K_d value is collectively contributed by the mass fraction (α) and the K_d of each species by

$$K_d = K_d^{SDZ^+} \alpha^+ + K_d^{SDZ^0} \alpha^0 + K_d^{SDZ^-} \alpha^-, \quad (5)$$

where the superscripts SDZ+, SDZ0, and SDZ- refer to cationic, molecular, and anionic forms of SDZ, respectively. The α values for each species are a function of solution pH and the pKa values of the solute. A multivariable regression using α^+ , α^0 , and α^- under different pH conditions against K_d values experimentally obtained resulted in 34, 1.6, and 31 L/kg for $K_d^{SDZ^+}$, $K_d^{SDZ^0}$, and $K_d^{SDZ^-}$, respectively, with an r^2 of 0.94 (Figure 5). In comparison to SDZ uptake on talc, the $K_d^{SDZ^0}$ values were similar, while $K_d^{SDZ^+}$ and $K_d^{SDZ^-}$ values were 4 times larger than those for SDZ uptake on talc [21]. In a separate study, the $K_d^{SMZ^+}$ value was two orders of magnitude

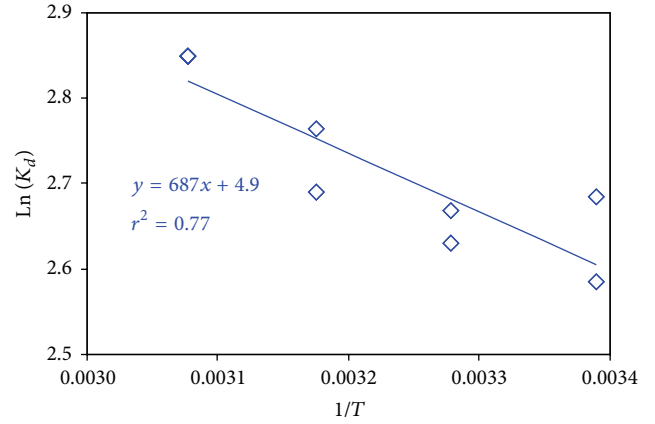


FIGURE 6: SDZ adsorption on zeolite as affected by equilibrium temperature.

larger than the $K_d^{SMZ^0}$ for sorption of SMZ on montmorillonite and kaolinite [2]. The $K_d^{SDZ^0}$ value was higher than $K_d^{SDZ^+}$ and much higher than $K_d^{SDZ^-}$ for SDZ adsorption on some commercial available resins [28]. In contrast, the variations of $K_d^{SMZ^+}$, $K_d^{SMZ^0}$, and $K_d^{SMZ^-}$ values were within one order of magnitude at 0.3 to 9 L/kg for SMZ sorption on five soils of different organic contents [5]. Avisar et al. [6] noticed that SA adsorption on montmorillonite decreased as solution pH increased, but detailed pH range was not provided. At pH 7.2, removal of SAs by montmorillonite was only 15% in comparison to close to 100% removal of TC [6].

3.5. Influence of Temperature on SDZ Uptake on Zeolite. The adsorption of SDZ on the zeolite increased as the equilibrium temperature increased at initial SDZ concentrations of 0.08 (Figure 6), suggesting an endothermic adsorption process. The thermodynamic parameters of SDZ adsorption could be determined from the plot of $\ln K_d$ against reciprocal of temperature as

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}, \quad (6)$$

where ΔH is the change in enthalpy and ΔS is the change in entropy after adsorption. And the ΔG can be determined independently under different temperatures by

$$\Delta G = \Delta H - T\Delta S. \quad (7)$$

The calculated ΔG values were similar to those determined from isotherm study (Table 1). Again, the small negative ΔG values suggested that SDZ uptake on the zeolite was relatively weak, owing to physical adsorption such as hydrophobic or electrostatic interaction. The small positive ΔS values indicated spontaneous adsorption resulting in disorder of the adsorbed SDZ molecules on the zeolite surfaces. While the positive ΔH value suggested that SDZ uptake was an endothermic process, agreeing well with the ΔG value (Table 1).

TABLE I: Thermodynamic values of SDZ adsorption on zeolite at different temperatures.

C_{ini} (mM)	$\ln(K_q)$ (L/kg)				ΔG (kJ/mol)	ΔH (kJ/mol)			ΔS (kJ/mol-K)	
	295 K	305 K	315 K	325 K		295 K	305 K	315 K		325 K
0.08	2.60	2.76	2.93	3.10	-6.39	-6.80	-7.21	-7.62	5.7	0.04

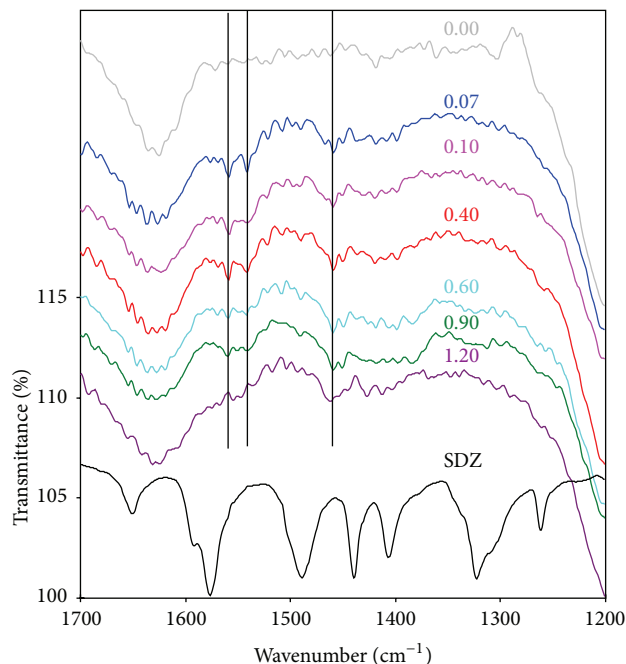


FIGURE 7: FTIR spectra of raw zeolite, solid SDZ and SDZ-adsorbed zeolite with different amounts of SDZ. The vertical lines are new peaks after SDZ adsorption on zeolite.

3.6. FTIR Analyses. The FTIR spectra of raw zeolite, crystalline SDZ, and zeolite with different amounts of SDZ uptake were plotted in Figure 7. Overall, the difference among the spectra of zeolites was minute. This might be due to the insensitivity of FTIR for detecting lower amounts of adsorbents as at the highest amount of SDZ adsorption, the SDZ accounted for only 300 mg/kg, or 0.03%.

For SDZ, the bending vibration of $-NH$ occurred at 1652 cm^{-1} [29]. In a study of interactions between SDZ and poly dendrimer, a new band at 1633 cm^{-1} appeared and was probably due to the bending mode of the $SDZ-NH_2$ group [29]. The presence of a band at 1622 cm^{-1} was attributed to the involvement of $-NH_2$ [30]. In this study, the band at 1630 cm^{-1} was attributed to water and the band at 1652 cm^{-1} was not resolved. Under an acidic condition, the calculated and experimental in-plane mode of sulfonamide $N-H$ was at 1499 and 1454 cm^{-1} , respectively, and it shifted from 1454 to 1477 cm^{-1} after adsorption onto zeolite Y [15]. In this study, a similar small band was found at 1460 cm^{-1} .

Two small bands at 1541 and 1559 cm^{-1} appeared with the uptake of SDZ on the zeolite. The band at 1568 cm^{-1} assigned to the coupling of quadrant stretching modes of both phenyl and pyridazinyl rings remained in a similar position for the adsorbed SDZ on high silica mordenite [31], while a shoulder

at 1548 cm^{-1} , assigned to the heterocycle quadrant stretching coupled with the NH bending, was also found after SDZ adsorption onto high silica zeolite Y [15].

The interaction between SDZ and high silica zeolite Y was found involving multiple weak H-bond and van der Waals type interactions between the amine protons of SDZ and lattice oxygen atoms and hydrophobic interactions between the aromatic rings and zeolite cage walls [15]. An H-bond between mordenite silanol groups and pyridazine nitrogen atom of sulfachloropyridazine was clearly detected by FTIR [31].

The band at 1330 cm^{-1} was attributed to symmetric vibration of SO_2N [30, 32]. However, in a recent study, it was shown that SDZ contained no $S=O$ double bond, but instead it had two $S-O$ single bonds and the negative charges were observed at the pyrimidine nitrogen atom [33]. Analyses of geometrical structure and torsion angles showed that SDZ was very flexible and could be easily fitted to the sorbent [33]. The absence of this band suggested no involvement of this functional group on SDZ adsorption on the zeolite.

3.7. SDZ Adsorption Sites and Mechanism. At SDZ adsorption of 1.3 mmol/kg , using the SSA of $15.7\text{ m}^2/\text{g}$, the calculated SDZ adsorption density would be about 2000 \AA^2 per SDZ molecule on a monolayer coverage. Moreover, the amount of SDZ adsorbed at 1.3 mmol/kg was only 1% of the ECEC of the zeolite and 0.1% of the TCEC. Thus, neither the SSA nor the CEC of the zeolite was the limiting factor for SDZ adsorption. The highly dealuminated zeolite Y had an SSA of $750\text{ m}^2/\text{g}$ [15], compared to $15.7\text{ m}^2/\text{g}$ in this study. This may also attribute to a large difference in SDZ uptake by the hydrophobic zeolite in previous studies [15, 32] and hydrophilic clinoptilolite in this study.

At pH 1.35, a very high shift of the aniline protons was observed, and this was in accordance with decreased magnetic shielding of the aniline protons by an ammonium group ($R-NH_3^+$), favoring a conformation structure with ammonium group on N15 [33]. Due to the permanent negative charge of clinoptilolite, the higher SDZ uptake at lower pH could be attributed to stronger electrostatic interaction between the ammonium group and the negatively charged zeolite surfaces.

Under high pH conditions, due to the presence of N in SDZ, hydrogen bonding between N of the molecule and OH on the zeolite may be attributed more to adsorption of SDZ. In addition to the negative charges on oxygen, negative charges were also calculated for the nitrogen atoms N_{16} and N_{17} of the pyrimidine ring with values of -0.5 and -0.92 [33]. Neutral and deprotonated forms could act as a Lewis base in solution to form covalent coordinative bonds by donating a pair of electrons with metal cations on the surface of the zeolite.

As SDZ could easily adhere to heavy metal cations in solution or to bounded organic matter [33], it is no surprise to see ion-ion salt bridges and metal complexes for the uptake of SDZ under alkaline conditions. Moreover, the interactions between the benzene ring as well as the partially negatively charged O of SDZ and the Mg or Ca in the zeolite may also contribute to SDZ adsorption under high pH conditions.

4. Conclusions

The adsorption of SDZ on hydrophilic clinoptilolite was almost instantaneous and followed a linear adsorption isotherm with a K_d value of 23.7 L/kg. Neither the SSA nor the CEC was the limiting factor for the SDZ uptake. Higher K_d values were found at higher and lower pH conditions, suggesting that neutral SDZ molecules, that is, hydrophobic forces, had weak interactions with the hydrophilic surfaces of zeolite. Under acidic conditions, the electrostatic interaction between negatively charged zeolite surfaces and positively charged ammonium may contribute strongly to the overall SDZ uptake. Under strong alkaline conditions, the partial negative charged N and the mineral surface could be bound via ion bridging of Ca or Mg in the zeolite structure.

Acknowledgment

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