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Adsorption of tetracycline on montmorillonite: influence of solution pH, temperature, and ionic strength

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ABSTRACT

The adsorption of tetracycline (TC) from aqueous solution by different types of montmorillonite (MMT) was studied under varying pH, temperature, and ionic strength conditions. The adsorption data obeyed the Langmuir isotherm with maximum TC adsorption at 468, 404, and 243 mg/g on SAz-1, SWy-2, and SYn-1 at pH 1.5, and at 375 mg/g on SHCa-1 at pH 8.7, corresponding to 0.86, 1.07, 0.78, and 1.28 of their cation exchange capacities, respectively. The kinetics of TC adsorption was very fast and reached equilibrium in almost 2 h and the results followed the pseudo-second-order kinetic model. In general, lower solution pH facilitated TC adsorption except for SHCa-1. Ionic strength had minimal influences on TC adsorption. The adsorption of TC on MMTs was endothermic, suggesting a strong physical adsorption. Under a weak alkaline condition, the TC adsorption resulted in extensive MMT delamination or exfoliation. Because of its high TC adsorption capacity, the results suggested that MMT could be a very good candidate to remove TC from wastewater containing high amounts of TC.

Keywords: Adsorption; Isotherm; Kinetics; Montmorillonite; pH; Tetracycline

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are an important and emerging group of contaminants that have increasingly raised concerns due to their health effects on organisms and potential risks to ecosystems, even at low concentrations [1]. Pharmaceuticals could be released into surface water via a number of routes with the most important being through the excretion of pharmaceuticals partly metabolized by the body or their pharmacologically-active metabolites, and their incomplete removal with conventional wastewater treatment plants [2]. Among these PPCPs, antibiotics make an important group. Antibiotics may appear in the environment when manure, sewage sludge, and wastewater effluents were used in different agricultural applications, which would result in concerns of their residual concentration in agricultural soils that may lead to the development of bacterial resistance [3]. Moreover, antibiotics

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can lead to the generation of antibiotic resistance genes that can be translated among different bacteria [4]. Therefore, many efforts were put to investigate interactions between antibiotics and environmental solids and to explore cost-effective ways to remove antibiotics from drinking water, groundwater, and wastewater. Activated alumina and coal fly ash showed excellent removal of an antibiotic ciprofloxacin hydrochloride from aqueous solution with an adsorption capacity as high as 71 mg/g under an optimal pH at 4 [5].

Although studies of tetracycline (TC) adsorption on soils and clays began in the 1950s [6], more researches were conducted recently to investigate the interactions between TC and many types of clay minerals, such as montmorillonite (MMT) [7–12], rectorite [13], palygorskite [14], kaolinite [15], and other materials such as silica [16], aluminum, and iron hydrous oxides [17]. As MMT is a group of swelling clay minerals, besides Ca-MMT and Na-MMT, other commonly encountered MMT should also be taken into consideration when investigating the interactions between antibiotics and soil components. In this study, four smectitic materials SAz-1, SWy-2, SHCa-1, and SYn-1 were chosen as the adsorbents. The interactions between these MMTs and TC were studied under different physico-chemical conditions, such as the types of interlayer cations, solution pH and ionic strength, and temperature.

2. Experimental procedures

2.1. Materials

Smectite is the name for a group of minerals, both dioctahedral and trioctahedral, while montmorillonite refers to dioctahedral smectites with the origin of the layer charge primarily in the octahedral sheet. The general formula for MMT is $R^{+}_{0.33}(\mathrm{Al}_{1.67}\mathrm{Mg}_{0.33})\mathrm{Si}_4\mathrm{O}_{10}(\mathrm{OH})_2\cdot n\mathrm{H}_2\mathrm{O}$, where R is the exchangeable cations in the interlayer [10]. The MMTs were obtained from the Source Clay Minerals Repository (Purdue University, West Lafayette, IN). SAz-1 is a high-charge Ca-MMT containing 98% smectite, 1% quartz, 1% other; SWy-2 is a low-charge Na-MMT containing 95% smectite, 4% quartz, 1% feldspar + gypsum; SHCa-1 is a low-charge Li-bearing trioctahedral smectite (layer charge mainly from the octahedral sheet) containing 97% smectite, 2% calcite, 1% dolomite + kaolinite; while SYn-1 is a synthetic mica-MMT containing 95% mica-MMT and 5% boehmite [18]. They were used as received without further purification. Their reported cation exchange capacity (CEC) values were 1,230, 850, 660, and 700–1,400 $\mathrm{mmol_c/kg}$, respectively [19], and their specific surface areas (SSA) were 65, 23, 36, and 118 m^2/g, respectively [20].

TC hydrochloride was obtained from Calbiochem (Darmstadt, Germany) and was used as received. It has a molecular weight of 444.43 g/mol. With different functional groups (Fig. 1), its $\mathrm{p}K_{a1}$, $\mathrm{p}K_{a2}$, and $\mathrm{p}K_{a3}$ values were 3.3, 7.7, and 9.7, respectively [8]. It had a log K_{ow} value of −2.2 to −1.3 [8,21]. This extremely hydrophilic nature makes it hardly have any affinity on hydrophobic surfaces.

2.2. Batch experiment and methods of analyses

To each 50 mL centrifuge tube, 0.1 g of MMT and 20 mL of TC solution were combined. The initial TC concentration was 1,000 mg/L for all experiments except the isotherm study. For the kinetic study, the mixing time was 0.25, 0.5, 1.0, 2.0, 4.0, 8.0, and 24.0 h. For pH adsorption edge experiments, the equilibrium solution pH varied between 2 and 11 with an increment of 1, which was achieved by adding 2 M NaOH or 2 M HCl drop-wise every a few hours over the

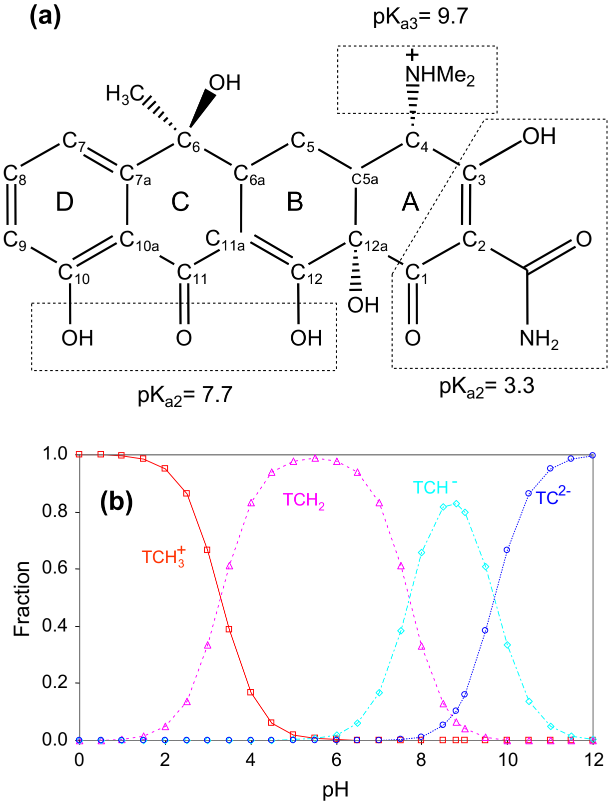

Fig. 1. Molecular structure of TC (a) and speciation of TC under different pHs (b).

course of experiment till the desired pH was stabilized. The purpose of using high concentrations of NaOH or HCl was to minimize the change in total liquid volume. For ionic strength experiments, the solution concentrations were adjusted by NaCl at 0.01, 0.1, and 1.0 M. The pH values were maintained close to its pK_{a2} value. For temperature experiments, the pH was 4–5, while the temperature was maintained at 298, 313, and 328 K. For TC adsorption isotherm studies, the initial concentrations were 100, 200, 400, 600, 800, 1,000, 1,500, 2,000, 2,500, and 3,000 mg/L for SAz-1 and SWy-2 and 100, 200, 400, 600, 800, 1,000, 1,500, and 2,000 mg/L for SHCa-1 and SYn-1 at pH 1.5, 6, 8.7, and 11. Although the concentrations used in this study were much higher than its anticipated environmental concentration, the objective of this study was mainly focused on finding the relations between TC adsorbed and other physico-chemical parameters such as solution pH and ionic strength, SSA and CEC of the sorbents in order to simultaneously decipher TC adsorption mechanism on MMTs.

The mixtures were shaken on a reciprocal shaker at 150 rpm for 24 h for all experiments other than kinetic studies. After equilibration, the mixtures were centrifuged at 10,000 rpm for 5 min, the supernatants passed through 0.45 m filters before analyses by an UV/VIS spectrophotometer. All experiments were run in duplicate. All tubes were wrapped with aluminum foils to prevent light-induced decomposition. Control experiments [13] showed no degradation or adsorption of TC on centrifuge tubes during mixing.

The equilibrium TC concentrations were analyzed by a UV/VIS spectrophotometer (SmartSpec 3000, Bio-Rad Corp.) at a wavelength of 254 nm. Calibration was made with five standards between 5 and 50 mg/L with an R^2 no less than 0.99. In order to minimize the influence of solution pH on the absorbance of TC, four sets of standards were prepared under the solution pH of 3, 6, 8.7, and 11. For pH adsorption edge study, the TC concentrations were determined using the standards whose pH was close to that of the unknown solutions.

Powder XRD analyses were performed on a Rigaku D/Max-IIIa diffractometer with Ni-filtered Cu Kα radiation at 30 kV and 20 mA. Samples were scanned from 2° to 20° 2θ at 1°/min with a scanning step of 0.01°/step. A 1° divergent slit, scatter slit, and 0.3 mm receiving slit were used.

Selected samples were coated with Au for electron microscopic observations. A FEI Quanta 250 FEG (Netherland) scanning electron microscope was operated at an accelerating voltage of 6.5–8.5 kV and various low-beam currents for optimal imaging.

3. Results and discussion

3.1. TC adsorption kinetics

Previous research showed that 24 h was sufficient for TC adsorption to reach equilibrium on clays such as illite [22] and palygorskite [14]. The kinetics of TC adsorption were tested to confirm fast TC sorption on MMTs. As expected, TC adsorption reached equilibrium in 2 h (Fig. 2). Even though, we still fixed equilibrium time to 24 h in subsequent experiments.

The pseudo-second-order kinetic model was used to characterize chemisorption and cation exchange, and was widely applied to the adsorption of pollutants from aqueous solutions in recent years [23]. The integrated rate law was:

$$q_t = \frac{kq_e^2 t}{1 + kq_e t} \tag{1}$$

where k (g/mg h) is the rate constant of adsorption, q_e and q_t (mg/g) are the amount of TC adsorbed on the surface of the adsorbent at equilibrium and at any time, t, respectively. Eq. (1) could be re-arranged into a linear form:

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

where kq_e^2 is the initial rate (mg/g h). The pseudo-second-order kinetic model was used to describe TC adsorption on sludge-derived adsorbents in aqueous phase [24]. When the kinetic data were fitted using the pseudo-second-order model (Fig. 2), the coefficients of determination R^2 were never less than 0.999. The initial rates for TC adsorption on SAz-1, SWy-2, SHCa-1, and SYn-1 were 5,000, 557, 50,000, and 909 mg/g h, respectively (Table 1). The fast initial rates and large rate constants indicated that MMTs would be a fairly good adsorbent for TC.

3.2. Equilibrium TC adsorption isotherm

The TC adsorption on MMTs was fitted using the Langmuir adsorption model (Fig. 3), in contrast to a linear isotherm for TC adsorption on SWy-2 reported previously [25]. The Langmuir isotherm can be described as:

$$S = \frac{K_L S_m C_L}{1 + K_L C_L} \tag{3}$$

where C_S is the amount of TC adsorbed on solid at equilibrium (mg/g), C_L is the equilibrium solute concentration (mg/L), S_m is the apparent adsorption capacity or adsorption maximum (mg/g), and K_L is the Langmuir coefficient (L/mg). Eq. (3) can be reorganized to a linear form

$$\frac{C_L}{C_S} = \frac{1}{K_L S_m} + \frac{C_L}{S_m} \tag{4}$$

so that K_L and S_m can be determined by a linear regression.

When the experimental data were fitted using the Langmuir model the R^2 values were high than 0.99 except for SHCa-1 at pH 11 (Table 2). At pH 1.5, TC exists as TCH_3^+. Under this pH value, the highest TC adsorption was found on SAz-1, SWy-2, and SYn-1 (Fig. 3(a), (b), and (d)), suggesting that cation exchange was the main adsorption mechanism. Furthermore, the TC adsorption maxima were 468, 404, 243 mg/g, respectively, corresponding to 0.86, 1.07, and 0.78 of their CEC. These results were different from TC adsorption on rectorite [13], in which, H^+ competed against TC for the adsorption sites of clay minerals under extremely low pH conditions, triggering a decrease in TC adsorption [11]. At pH 8.7, TC exists as TCH^-, its adsorption capacity on SAz-1, SWy-2, and SYn-1 decreased to 302, 220, and 126 mg/g, respectively. These amounts are still very high, suggesting that the positive charge of dimethylammonium functional group was still likely to continue act as a cation to promote TC adsorption via electrostatic interactions. At pH 11, TC is in the form of TC^{2-} instead, cation exchange would not occur as the positively charged functional group in TC is no longer present. This resulted in a drastic reduction in TC adsorption on SAz-1, SWy-2, and SYn-1 to 86, 143, and 86 mg/g, respectively (Table 2). The gradually reducing trend of TC adsorption as solution pH increased was confirmed by the experiments involving pH effect (Fig. 4(a), (b), and (d)).

Desorption of metal cations Ca^{2+} or Na^+ showed a positive correlation with the amount of TC adsorbed, suggesting a cationic exchange mechanism for TC adsorption on SAz-1, SWy-2, and SHCa-1, and surface complexation for SYn-1 [12]. The TC adsorption capacity on SAz-1 at pH 1.5 was 468 mg/g, equivalent to

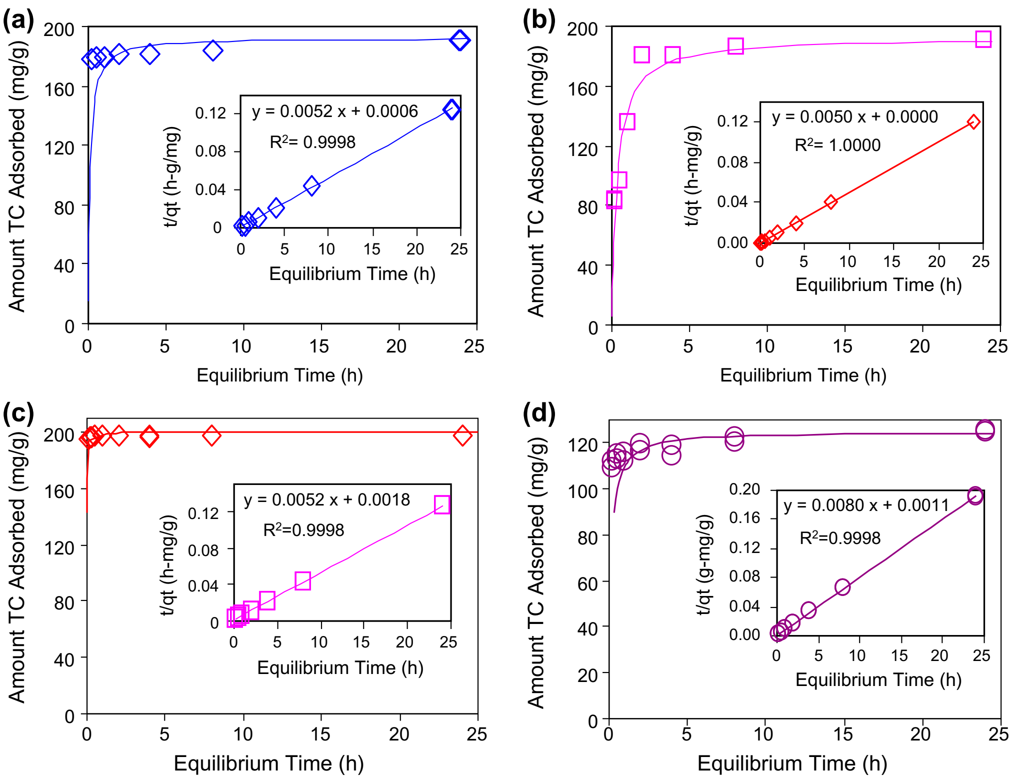

Fig. 2. TC adsorption kinetics on SAz-1 (a), SWy-2 (b), SHCa-1 (c), and SYn-1 (d), respectively. The solid line is pseudo-second-order fit to the observed data. Insert is the linear plot of Eq. (2).

Table 1
The kinetic parameters of TC adsorption on montmorillonite

Clays	Initial concentration (mg/L)	Initial rate (mg/g h)	Rate constant (g/mg h)	q_e (mg/g)	R^2	Equilibrium time (h)
SAz-1	1,000	5,000	0.140	192	0.999	2
SWy-2	1,000	557	0.015	192	0.999	2
SHCa-1	1,000	50,000	1.25	198	1	2
SYn-1	1,000	909	0.058	125	0.997	2

Table 2
Langmuir sorption coefficients and TC adsorption maxima on montmorillonite

	pH 1.5	pH 6	pH 8.7	pH 11	pH 1	pH 6	pH 8.7	pH 11
SAz-1 (CEC = 1,230 mmol$_c$/kg)					SWy-2 (CEC = 850 mmol$_c$/kg)			
K_L (L/mg)	0.08	0.01	0.01	0.003	0.06	0.02	0.01	0.01
S_m (mg/g)	468	462	302	86	404	355	222	143
S_m (mmol/kg)	1,053	1,040	680	194	910	800	500	322
R^2	0.998	0.997	0.997	0.99	0.996	0.997	0.998	0.998
SHCa-1 (CEC = 660 mmol$_c$/kg)					SYn-1 (CEC = 700–1,400 mmol$_c$/kg)			
K_L (L/mg)	0.004	0.163	0.3	0.007	0.01	0.03	0.02	0.001
S_m (mg/g)	38	357	375	263	243	173	126	86
S_m (mmol/kg)	86	803	844	592	547	389	284	194
R^2	0.998	1	0.992	0.994	0.98	0.998	0.999	0.99

1.05 mmol/g. It is slightly less than the CEC of the mineral, again confirming the cation exchange mechanism. The amount of TC adsorbed in this study is much higher than 124 mg/g on a Ca-montmorillonite [7], 140 mg/g on rectorite [13], 99 mg/g on a palygorskite [14], 32 mg/g on illite [22], and 4 mg/g on a kaolinite [15], but lower than 800 mg/g in a study for oxytetracycline (OTC) adsorption on SWy-2 [8]. The major cause of these differences was due to use of different clay minerals of different CEC values.

For SHCa-1, it is possible that competition between H^+ and TC significantly affected its adsorption (Fig. 3(c)), and the TC adsorption capacity was only 38 mg/g at pH 1.5 in comparison to 263 mg/g at pH 11 (Table 2). The pH adsorption edge experiment also confirmed this trend (Fig. 4(c)). At pH 8.7, TC exists as TCH^-; the amount of TC adsorbed was 375 mg/g. Under this pH, the positive charged dimethylammonium group would still be present, suggesting that cationic exchange may still function as adsorption mechanism, similar to TC adsorption on palygorskite [14]. At pH 11, although no positive functional group, TC adsorption was as high as 227 mg/g on SHCa-1 (Table 2), suggesting mechanisms other than cation change or electrostatic interactions to control the adsorption. Possible mechanisms include surface complexation or cationic bridging.

3.3. Effect of pH on TC adsorption edge

The pH of a solution is an important factor that can affect the form and the quantity of TC in water. Under the action of electrostatic attraction, the TC adsorbed on the clay surface was mainly by cation exchange [9,12,15,26]. Between pH 2 and 7, the adsorption of TC on SAz-1 and SWy-2 showed a similar trend, decreasing slightly from 197 to 180 mg/g and from 195 to 175 mg/g, respectively (Fig. 4(a), and (b)). Maximum TC adsorption on a bentonite obtained from La Pampa province, Argentina, was found at pH 3 [27]. Similar trend was found for TC adsorption on illite and kaolinite [3]. The adsorption of TC on marine sediments decreased with an increase of pH and salinity [28].

Theoretically, high concentration of H^+ could compete against TC for adsorption at low pH. The similar adsorption in the pH range of 2–pK_{a2} suggested that TC had higher affinity for the surface of SAz-1 and

SWy-2 than H^+, no matter whether it was in a cationic or a zwitterionic form [22], resulting in a minimal pH effect as influenced by the H^+ concentration. Similar observation was noticed for TC adsorption on rectorite [13], kaolinite [15], and illite [22]. Above pK_{a2} until pH 11, the TC adsorption diminished quickly to 56 and 33 mg/g which were attributed to cation bridging on illite [9].

For SHCa-1 (Fig. 4(c)), the TC adsorption capacity decreased at low pH values, implying that high concentrations of H^+ competed against TC for the adsorption sites. The more plausible explanation would be attributed to the presence of 2% calcite in the sample [18]. The dissolution of calcite at low pH increased the aqueous concentration of Ca^{2+} significantly [12]. The binding between TC and Ca^{2+} in aqueous solution would facilitate the formation of TC-Ca^{2+} aqueous complex, which would prevent TC adsorption on SHCa-1 surfaces. The TC adsorption peaked at pH 7–8 (Fig. 4(c)). From pK_{a2} to pH 11, the TC adsorption was reduced to 135 mg/g. The same trend was found for OTC adsorption on iron oxide [29] and TC on palygorskite [14]. The effect of pH adsorption edge on TC adsorption agreed well with the batch TC adsorption on SHCa-1 (Fig. 3(c)).

For SYn-1, TC adsorption decreased significantly as solution pH increased (Fig. 4(d)). The trend of TC adsorption on SYn-1 as influenced by solution pH was similar to a previous study and was attributed to surface complexation [7]. However, this study showed the electrostatic interaction also played an important role for TC adsorption on SYn-1.

3.4. Effect of ionic strength on TC adsorption

For SAz-1 (Fig. 5(a)), a slight decrease in TC adsorption from 187 to 178 mg/g was observed as the ionic strength of the solution increased from 0.001 to 1 M. For SWy-2 and SHCa-1, the influence of ionic strength on TC adsorption was even minute (Fig. 5(b), and (c)). The influence of ionic strength on TC adsorption onto SYn-1 was similar to that onto SAz-1 (Fig. 5(d)). Previous results showed that TC adsorption on this MMT was at the mineral surface without any intercalation [11]. The influence of additional ion on adsorption for intercalated clay was very weak, as the variation of TC adsorbed on SWy-2 and SHCa-1 was 0% for both, and that for SAz-1 was only 5%, while that for SYn-1 was 18% (Fig. 5). The same phenomena were also found for palygorskite [14] and illite [22] on which TC adsorption was on the external surfaces only. The variations of TC adsorbed on palygorskite and illite were 26 and 50% under the Na^+ concentrations of 0.1 and 1 M, respectively. It implied that due to intercalation, most of the adsorbed TC resided in the interlayer space. The competition of added ionic species against TC was much weaker compared to surface adsorption. The weak influence of ionic strength on TC adsorption and removal may imply that MMTs could be well utilized with small quantities in wastewater treatment facilities to remove minute amounts of cationic antibiotics.

3.5. Effect of temperature on TC adsorption

The relationship between K_d (L/kg), the TC distribution coefficient between the solid and the liquid, and the thermodynamic parameters of adsorption is expressed as:

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (5)$$

where ΔH is the change in enthalpy, ΔS is the change in entropy, R is the gas constant, and T is the reaction temperature in K. The free energy of adsorption can be determined by:

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

The negative ΔG values indicated mutual attractive interaction between TC and MMTs when solution pH was between pK_{a1} and pK_{a2} (Table 3). The ΔG values

Table 3
Thermodynamic values of TC adsorption on montmorillonite at pH 6

	Ln (K_d) (L/kg)			ΔG (kJ/mol)				
Clays	298 K	313 K	328 K	298 K	313 K	328 K	ΔH (kJ/mol)	ΔS (kJ/mol K)
SAz-1	4.13	6.66	7.22	−4.6	−13.3	−21.9	167.7	0.58
SWy-2	1.38	8.86	9.23	−6.1	−17.2	−28.4	215.6	0.74
SHCa-1	3.20	9.72	9.97	−10.3	−20.1	−30.0	185.8	0.66
SYn-1	6.39	6.51	6.85	−15.7	−17.1	−18.6	12.5	0.09

became more negative as temperature increased, suggesting an endothermic adsorption process. Generally considered ΔG value was within the ranges of −400 to −80 kJ/mol for chemisorption. For van der Waals interaction, the ΔG values would be between 0 and −20 kJ/mol. The ΔG values in this study suggested that the adsorption was mainly via physical processes, such as electrostatic interaction or cation exchange [30]. These values were similar in magnitude to TC adsorption on illite and kaolinite [3]. The positive ΔH values confirmed endothermic processes of TC uptake by the MMTs (Fig. 6). The ΔS values suggested an increase of disordered arrangement of TC on MMT surfaces.

3.6. X-ray diffraction analyses and SEM observations

The XRD patterns of MMTs after adsorption from an initial 2,000 mg/L TC solution under different pH conditions are depicted in Fig. 7. The raw MMT matched with the published data well [18]. The lower diffraction angles for samples at low pHs indicated larger interlayer spacings due to intercalation, especially in the case of SAz-1 and Swy-2. This is another evidence to support a cation exchange mechanism. One striking feature in this study was the disappearance of (001) peak under certain pH conditions. For SAz-2 and SWy-2, the disappearance of (001) peak occurred at solution pH 8.7 (Fig. 7(a), and (b)), at which the TC is in its monoanionic form TCH^-. As for SHCa-1 and SYn-1, the (001) peak disappeared under all pH conditions except pH 11 (Fig. 7(c), and (d)).

To further assess TC adsorption under pH 8.7, SAz-1 was equilibrated with different amounts of TC for 24 h. The XRD pattern of the raw SAz-1 was identical to that from an aqueous suspension with pH 8.7 (Fig. 8). At a lower amount of TC adsorption, the (001) spacing expanded slightly, but was well preserved. It almost disappeared at the TC adsorption of 187 mg/g, equivalent to 0.43 CEC of the mineral. At TC adsorption of 340 mg/g, or 0.77 CEC, the (001) peak disappeared completely (Fig. 8). Recrystallization of TC from solutions with pHs of 1.5 and 8.7 resulted in identical XRD patterns (Fig. 9), suggesting that TC

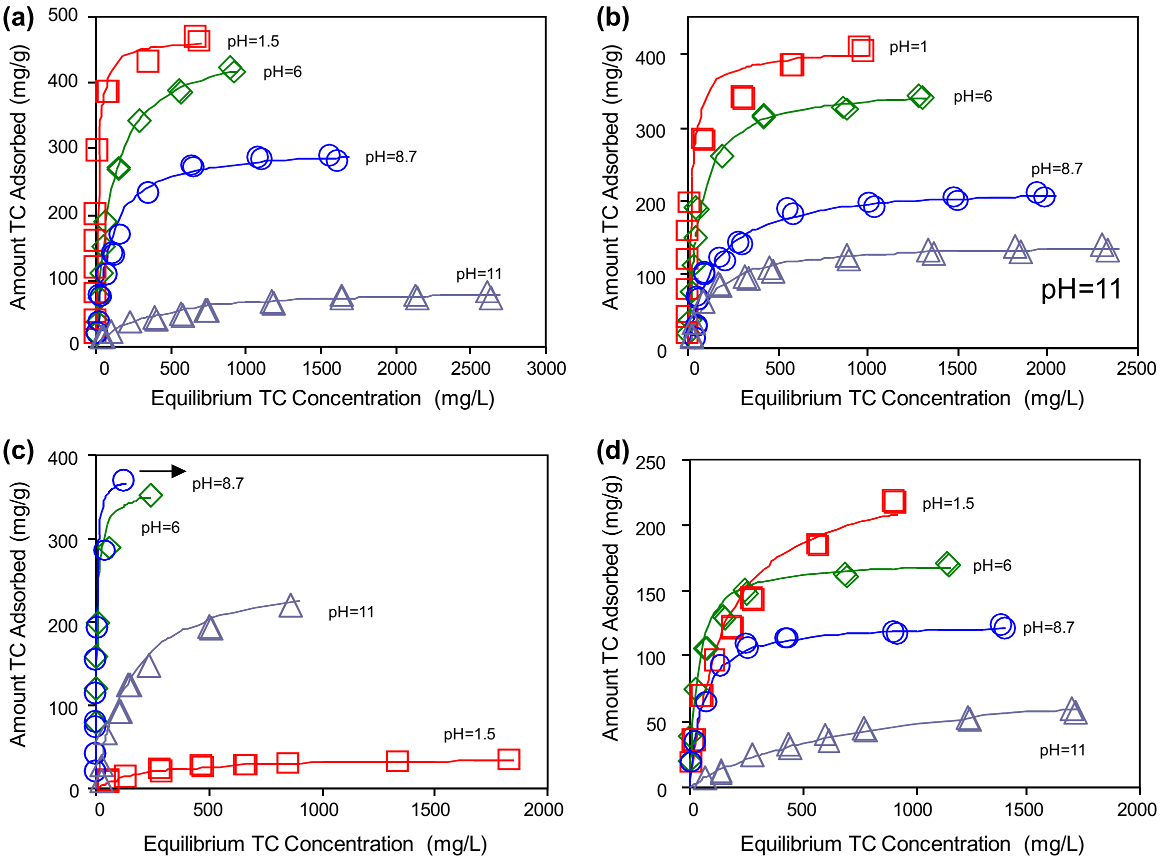

Fig. 3. TC adsorption on SAz-1 (a), Swy-2 (b), SHCa-1 (c), and Syn-1 (d) at pH 1.5 (□), 6 (◇), 8.7 (○), and 11 (△), respectively. Lines are the Langmuir fit to the observed data.

was not destructed under these pH conditions. In addition, the reflections of crystalline TC were absent in the patterns of TC-adsrobed MMTs (Figs. 7 and 8), suggesting that the removal of TC from solution was purely due to adsorption instead of precipitation.

In comparison to the delamination of Na-montmorillonite layers by OTC which was incomplete at neutral and high pH values [31], the disappearance of (001) diffraction peak of MMT after adsorption of TC at pH 8.7 suggested that TC could be a good chemical agent to exfoliate MMT at higher initial concentrations at pH 8.7. Exfoliation of the MMT was further evidenced by SEM observation which showed that after going through weak alkaline condition, the MMT plates were relatively thin and curly compared to those in the raw material and exhibited opening features (Fig. 10).

3.7. Discussion

The point of zero charge (PZC) is an important parameter to assess the surface charge properties of pH-dependent surfaces, such as kaolinite [15,32]. The PZC values of SAz-1, SWy-2, and SHCa-1 were 8.44, 8.35 [33], and 8.3 [34], respectively, while the PZC value for SYn-1 was not available. When the solution pH < PZC, surface had positive charge due to protonation of clay minerals; while for solution pH > PZC, surface becomes negatively charged. At solution pH = PZC, the surface is without charges. From the PZC point of view, its values are insufficient to explain the change of the adsorption quantity under different pH values (Figs. 3 and 4). Instead, TC adsorption may largely depend on their CECs as MMTs contain permanent surface charges due to isomorphic substitution. Although significant electrostatic interactions between

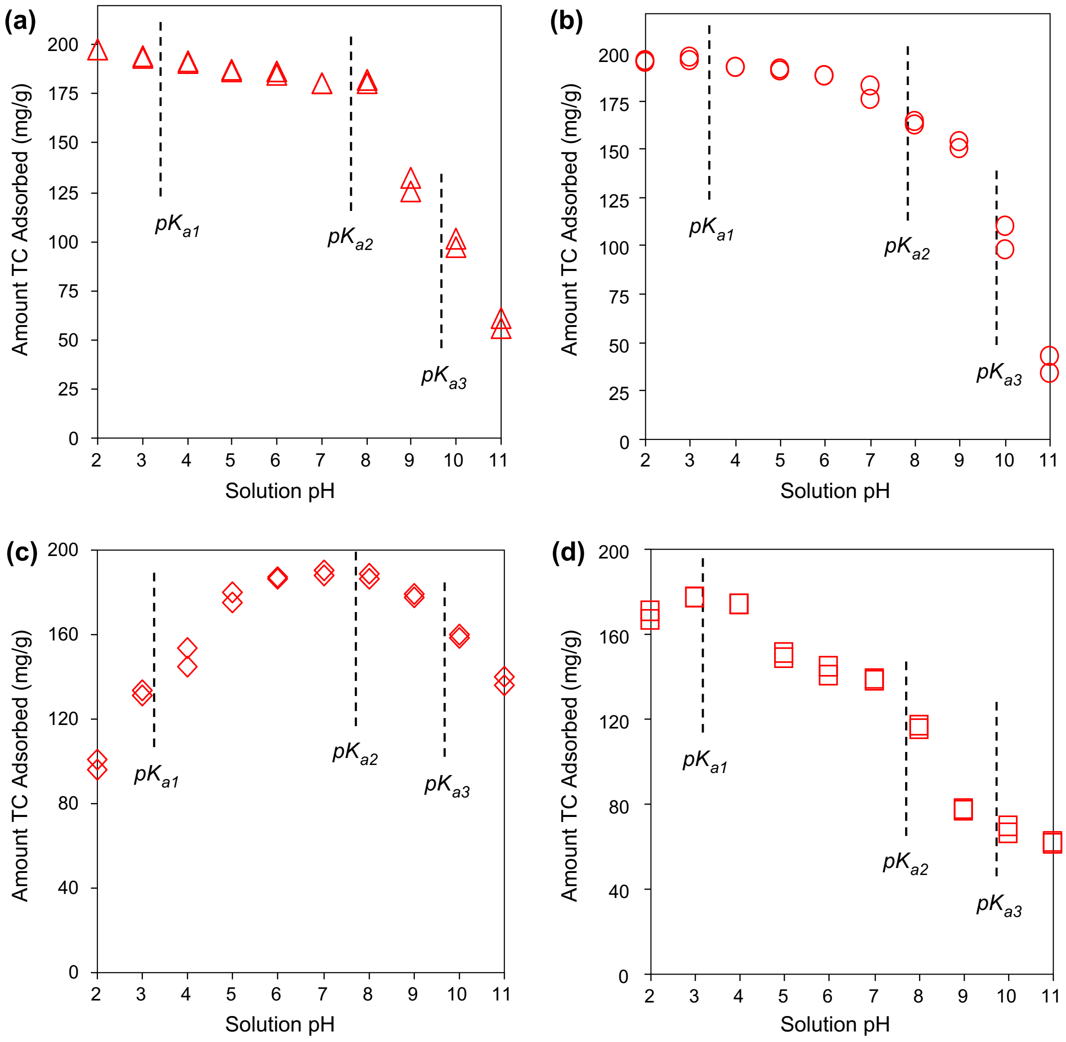

Fig. 4. Adsorption of TC on SAz-1 (a), SWy-2 (b), SHCa-1 (c), and SYn-1 (d), respectively, as affected by solution pH.

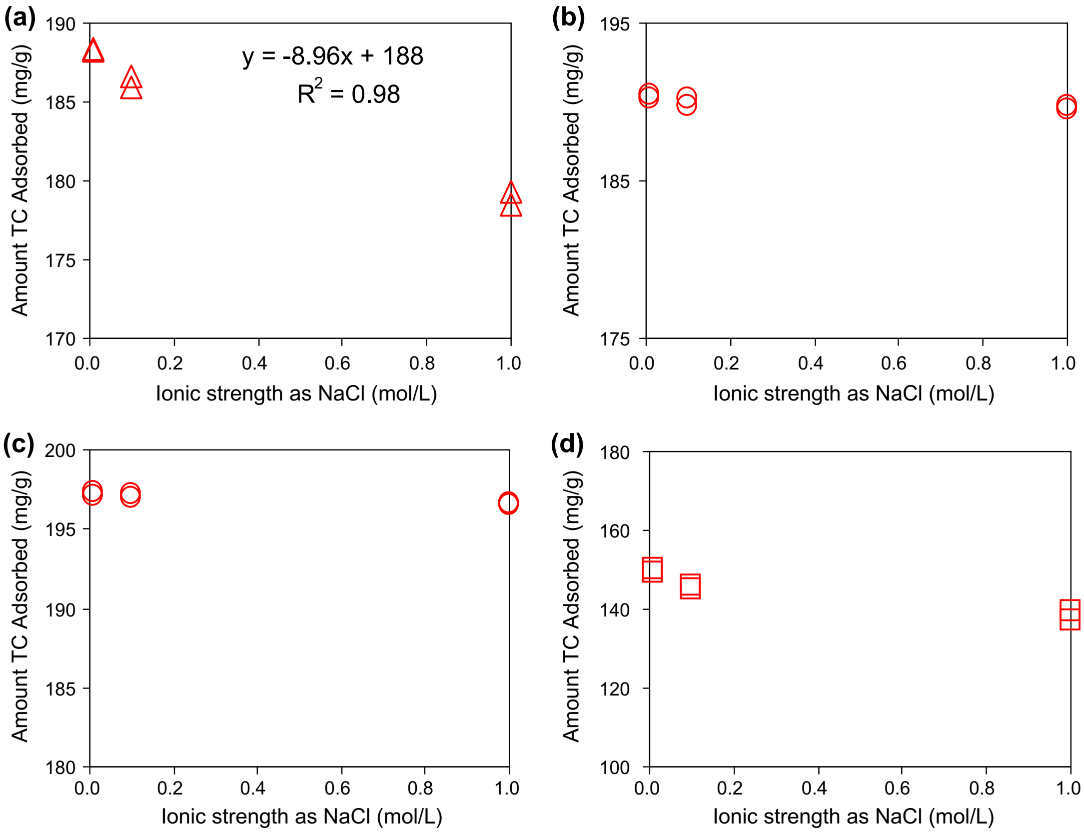

Fig. 5. Adsorption of TC on SAz-1 (a), SWy-2 (b), SHCa-1 (c), and SYn-1 (d), respectively, as affected by solution ionic strength.

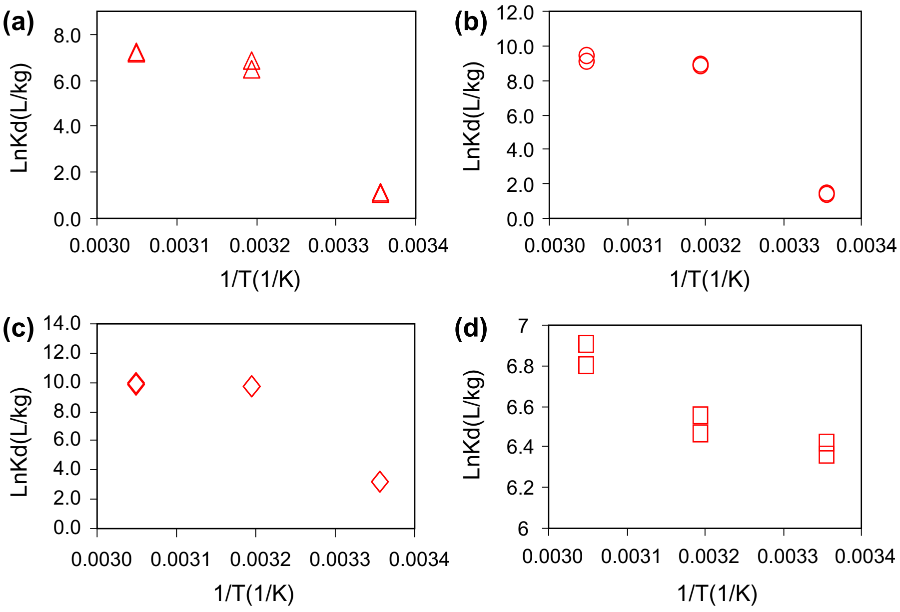

Fig. 6. Influence of temperature on TC adsorption on SAz-1 (a), SWy-2 (b), SHCa-1 (c), and SYn-1 (d), respectively.

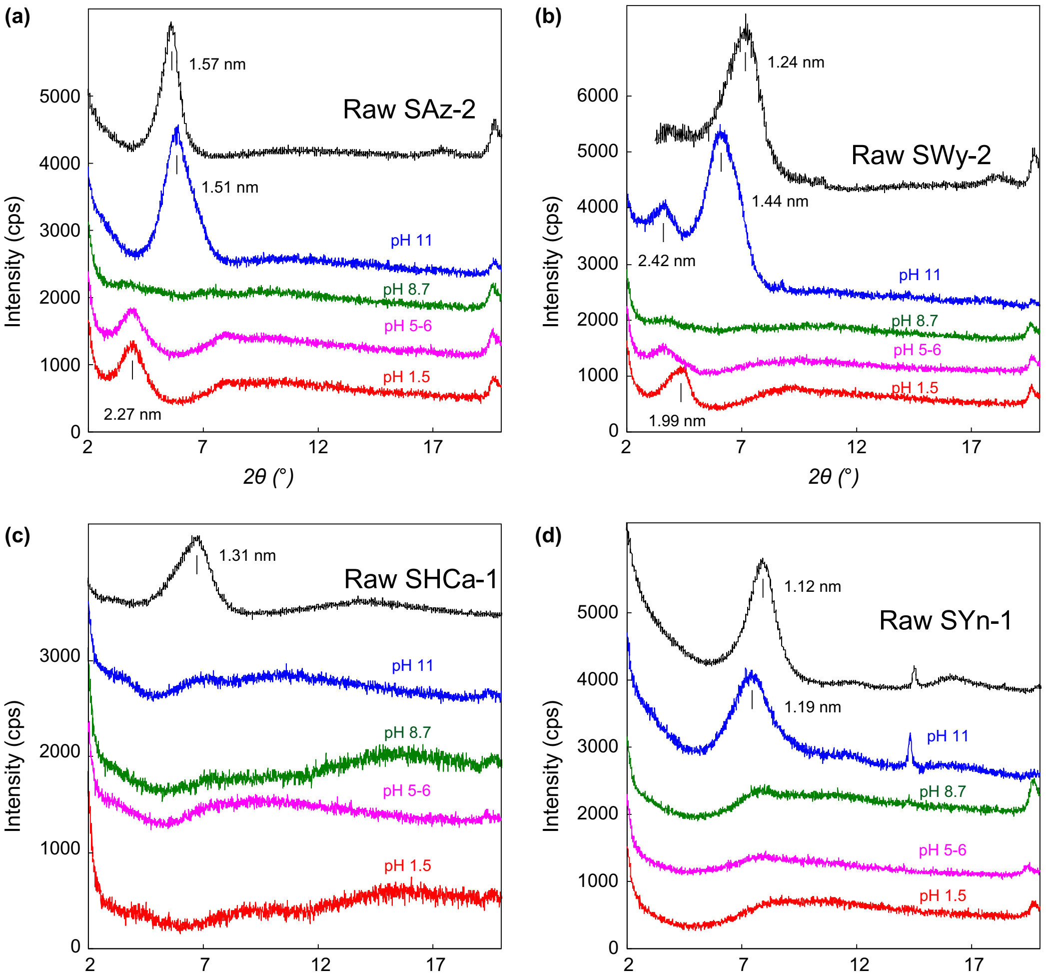

Fig. 7. XRD patterns of TC-adsorbed SAz-1 (a), SWy-2 (b), SHCa-1 (c), and SYn-1 (d) using an initial TC concentration of 2,000 mg/L under different pH conditions.

TC and MMTs were noticed, a rather strong non-electrostatic interaction was also present [26]. In addition, it was demonstrated using spectroscopic techniques that H-bonding and water-bridging interactions were also responsible for the binding of TC on MMT, in addition to cation-exchange [35]. Moreover, combination of van der Waals, complexation of polar functional groups and clays, and hydrophobic effect may also play a role [24]. In this study, the unusual behavior of TC adsorption on SHCa-1 could be attributed to stronger non-electrostatic interaction as noticed before [12].

Under pH from 4 to 6, the TC adsorption on MMTs was close to the minerals' CEC values, suggesting that the adsorption was more controlled by the CECs of the minerals than other factors. However, for SYn-1, TC adsorption only reached half of it CEC, suggesting that the charge density, surface area, or other factors might have strong influence than CEC to

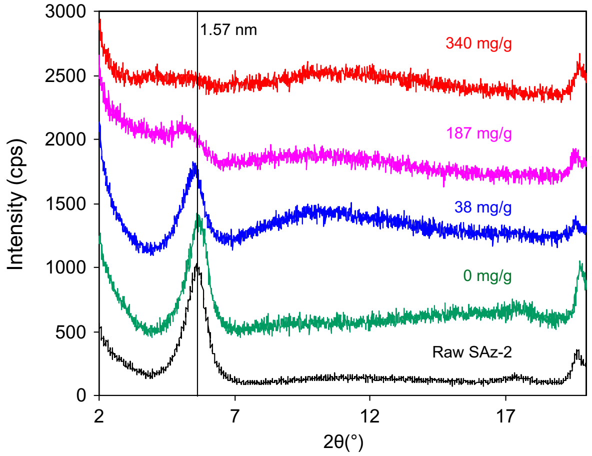

Fig. 8. XRD patterns of SAz-1 with different amounts of TC adsorption from solution at pH 8.7.

control TC adsorption on SYn-1 [12]. On the contrary, the TC adsorption was greater than the CEC value for SHCa-1, illustrating that other mechanisms may lead to an enhancement in TC adsorption.

Generally, accepted conformations for TC were extended and twisted ones, with the former primarily existing in basic solution when the dimethylamino group lies below the plane spanned by the ring system [36], while the latter was present in acidic to neutral solutions when the dimethylamino group lies above the ring system [36–38]. In the twisted type, TC is 12.9 Å long, 7.5 Å wide, 6.2 Å high with the four rings lying on the same surface, occupying an area of 97 Å^2 [39]. The surface areas of SAz-1, SWy-2, SHCa-1, and SYn-1 were 65, 23, 36, and 118 m^2/g, respectively [20]. Take SAz-1 for instance. When TC adsorption reached the maximum adsorption capacity of 468, 462, 302, and 86 mg/g under the four pH conditions, the calculated area occupied by each TC molecule on the surface was 10, 10, 17, and 140 Å^2, respectively. These values were much smaller than 97 Å^2 except under strong alkaline conditions, indicating much of the TC adsorption was in the interlayer spaces, resulting in intercalation [12]. The higher amount of intercalation of solute would result in exfoliation [40], as observed under a weak alkaline condition in this study. Moreover, in comparison to twisted TC conformation under acidic condition, the extended TC conformation under alkaline condition, under which the dimethylamine was still protonated and bear a positive charge, would further increase the d_{001} spacing, result in much weaker interactions between layers, and thus, cause delamination or exfoliation. On the contrary, under a stronger alkaline condition, the TC adsorption density was 140 Å^2 per TC molecule, larger than 97 Å^2 for a flat-lying TC molecule. Moreover, the dimethylamine group of TC was deprotonated and there would be no more electrostatic interactions between the dimethylammonium and the negatively charged mineral surfaces. Intercalation would not be favored and the TC uptake was only limited to the external surfaces as observed by XRD analyses (Fig. 7).

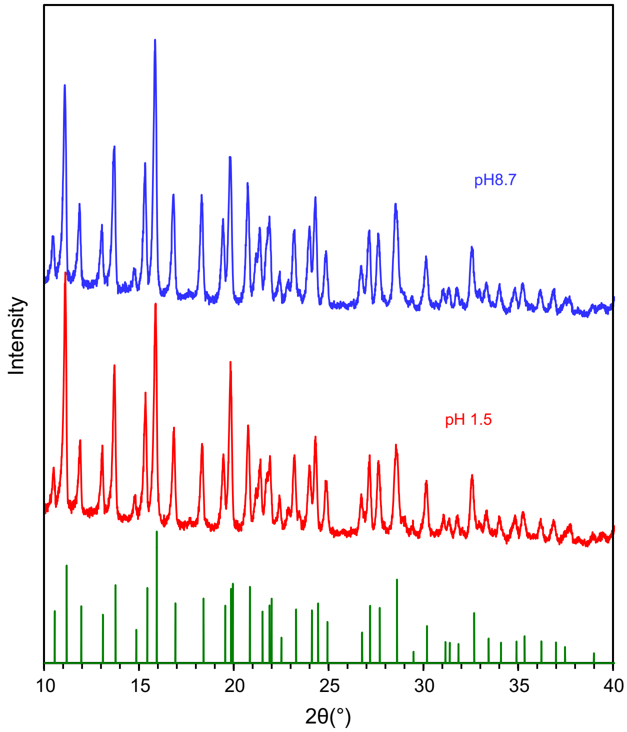

Fig. 9. XRD patterns of TC recrystallized from solutions at pHs of 1.5 and 8.7. Vertical lines are TC diffraction data reported in the literature [41].

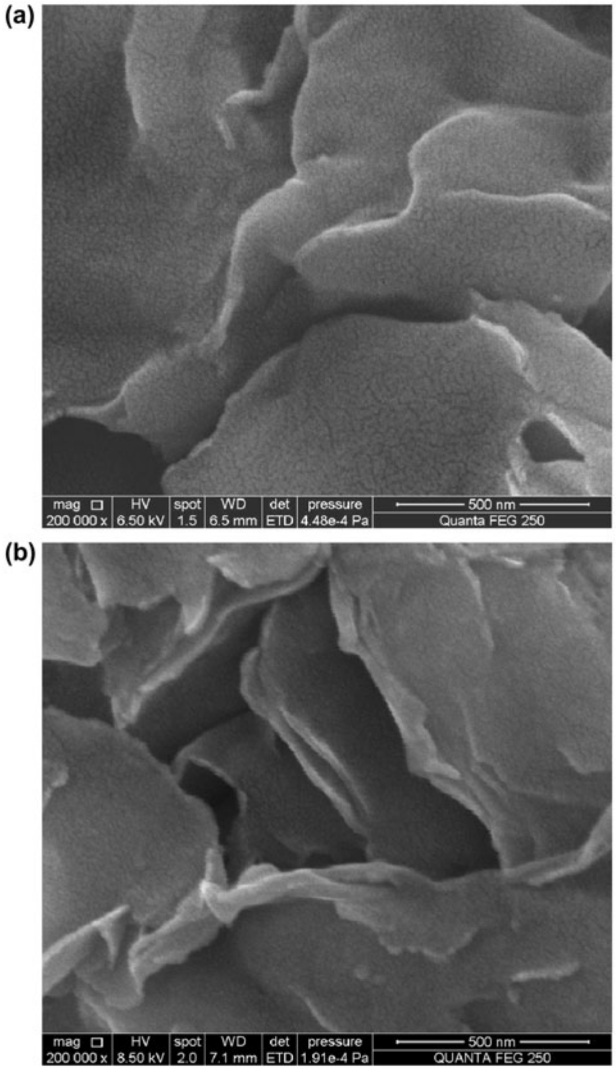

Fig. 10. SEM micrographs of SAz-1 from raw material (a) and suspension at pH 8.7 (b).

4. Conclusions

From the results of this study, the following conclusions can be drawn:

(1) The maximum TC adsorption was 468, 404, and 243 mg/g on SAz-1, SWy-2, and SYn-1, at pH 1.5, respectively, and 375 mg/g on SHCa-1 at pH 8.7. The adsorption data were better described by the Langmuir model.

(2) Solution pH had strong effects on TC adsorption by MMTs. Overall, increasing in solution pH resulted in a decrease in TC adsorption. Ionic strength had less pronounced effects on TC adsorption.

(3) TC adsorption on MMTs was an endothermic reaction, and thus, increasing temperature will enhance the adsorption of TC by MMTs. The small negative ΔG values indicated that physisorption may be the dominant mechanism. The small positive ΔS values suggested that the adsorbed TC molecules adopted a random arrangement on MMT surfaces.

(4) The CEC values had a dominant effect on TC adsorption under natural pH conditions, suggesting that cation exchange was the dominant mechanisms for TC uptake.

(5) The TC adsorption on SAz-1, SWy-2, and SHCa-1 occurred on both external surfaces and interlayer spaces due to cation exchange, while TC adsorption occurred only on the external surface of SYn-1 owing to surface complexation. Under a weak alkaline condition, extensive TC adsorption in combination with extended TC conformation resulted in exfoliation of MMT, which provide a new method to produce delaminated MMT plates.

(6) The results, in combination with previous studies, further confirmed that removal of cationic drugs, such as TC, by montmorillonite clays was via cation exchange under low pH and other mechanisms played more important role as solution pH increased. The higher adsorption capacity of montmorillonite towards cationic drugs, such as TC, will significantly affect their retention and transport in surficial and subsurface environment.

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