



Sorptive removal of tetracycline from water by palygorskite

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ABSTRACT

Extensive use of pharmaceuticals and growth hormone in farm animal and live stocks has resulted in their frequent detection in soils, groundwater, and wastewater. The fate and transport of these compounds are strongly affected by their sorptive behavior to the soil minerals and humic materials. In this research, we conducted the sorption of tetracycline (TC), a common antibiotic, on palygorskite (PFL-1), a fibrous clay mineral of high surface area and high sorptivity towards organic compounds. The results showed that the sorption capacity of TC on PFL-1 was as high as 210 mmol/kg at pH 8.7. The sorption was relatively fast and reached equilibrium in 2 h. Solution pH and ionic strength had significant effects on TC sorption. The sorption of TC by palygorskite is endothermic and the free energy of sorption is in the range of -10 to -30 kJ/mol, suggesting a strong physical sorption. The X-ray diffraction patterns before and after TC sorption revealed no changes in *d*-spacing and intensity under different pH and initial TC concentrations, indicating that the sorbed TC molecules are on the external surface of the mineral in contrast to intercalation of TC into swelling clays, such as montmorillonite. The small positive value of entropy change suggested that TC molecules are in disordered arrangement on palygorskite surfaces. Surface sorption of TC on PFL-1 is further supported by the derivative of gravimetric analysis and by the calculation of the amount of TC sorption normalized to the surface area. The results suggest that palygorskite could be a good candidate to remove TC from wastewater containing higher amounts of TC.

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1. Introduction

A recent survey in 1999–2000 on 139 US streams revealed that among the 95 organic wastewater contaminants 82 were found [1]. Of these contaminants, antibiotics and growth hormones became more frequently detected. For example, tetracyclines (TCs), among others, were often detected in the final effluents after treatment from eight wastewater treatment plants (WWTPs) located in five Canadian cities [2]. An 80% frequency of detection with average influent concentrations of 48 ± 3 and 47 ± 4 $\mu\text{g/L}$ and average effluent concentrations of 3.6 ± 0.3 and 4.2 ± 0.4 $\mu\text{g/L}$ for TC and oxytetracycline (OTC) were reported from several WWTPs in Wisconsin [3].

To remove hydrophobic organic compounds from water, a sorbent with higher total organic carbon content will achieve a better effect. However, for ionizable compounds, their affinity to solid

surface is strongly affected by the solution pH and their hydrophobicity under different pH conditions. TCs are quite hydrophilic. Their water solubility is in the ranges of g/L [4], which resulted in a lower sorption to activated carbon [5]. Furthermore, TCs could have different charges on different site depending on solution pHs (Fig. 1). When solution pH is below 3.3, TCs exist as a cation, $+00$, due to the protonation of dimethylammonium group. At pH between pH 3.3 and 7.7, TCs exist as a zwitterion, $+−0$, due to the loss of a proton from the phenolic diketone moiety. At solution pH greater than 7.7, a monovalent anion, $+−−$ or a divalent anion $0−−$, from the loss of protons from the tricarbonyl system and phenolic diketone moiety will prevail [6].

Studies of TC sorption on soils and clays began as early as the 1950s [7], but are still limited [8]. Recent studies on TC removal were focused on using montmorillonite [6,9], less often on kaolinite, oxides, silica, and other soil components [9–12]. Palygorskite, formed in arid environment, is a special type of clay mineral made of periodic reversal of the building blocks so that the interlayer space is made of one dimensional channel, thus limiting its expandability. Even though, it is still a good sorbent for a variety of compounds due to its large surface area and moderate cation exchange capacity. Although most studies were focused on using palygorskite to

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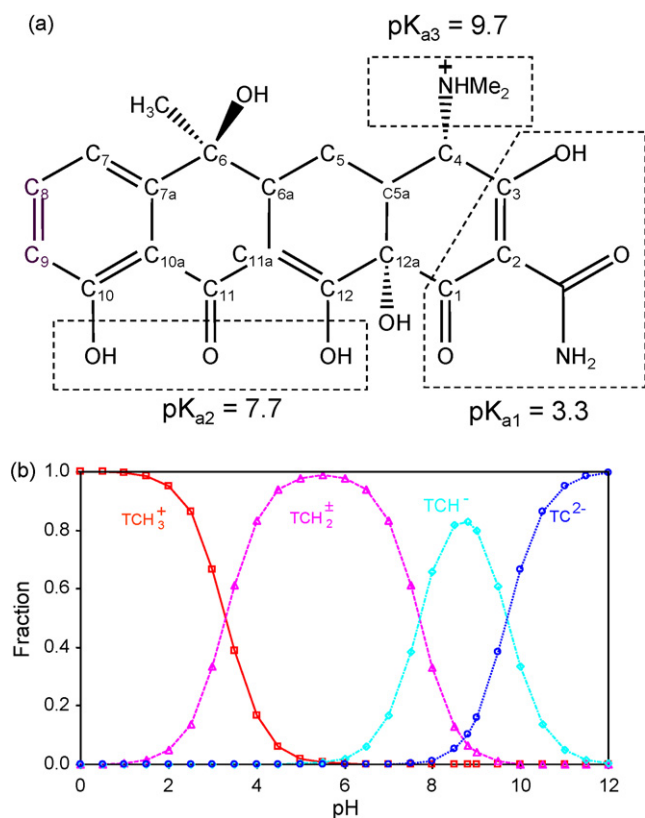


Fig. 1. Molecular structure of TC on a planar view (a) and speciation of TC under different pHs (b).

remove heavy metals from water such as Cd [13], Cu [14], Pb, Ni, and Cr (VI) [15], tests on using palygorskite to remove organic compounds were also reported. Spectroscopic studies indicated that most of the sorbed 2,2'-bipyridyl molecules are coordinated to Lewis acidic centers of attapulgite as bidentate ligands [16]. Interaction of nicotinamide with palygorskite originated from coordination of nicotinamide molecules to surface hydroxyls and/or to Lewis acidic centers by hydrogen bonding interaction through the ring nitrogen lone pairs [17]. The most important example of using palygorskite as sorbent is Maya Blue. Sorption of indigo in the palygorskite channel resulted in the longevity of the blue dye [18]. Although extensive studies of using palygorskite as sorbents have been carried out, and palygorskite is also used as additives to pharmaceuticals, there has been no report on the sorptive interaction between TCs and palygorskite.

The goal of this research is to study the sorption of TC on palygorskite under different physical and chemical conditions in conjunction with X-ray diffraction (XRD), Fourier transform infrared (FTIR), and thermogravimetric (TG) analyses in order to evaluate the feasibility and applicability of using palygorskite as a potential sorbent to treat wastewater containing higher amounts of TCs.

2. Experimental

2.1. Materials

The palygorskite used is a reference clay PFL-1 obtained from the Source Clay Minerals Repository, Purdue University, West Lafayette, IN, and was used as received. X-ray powder diffraction revealed trace amount of smectite in it. Scanning electron microscope showed short fibers for palygorskite (~0.1 μm wide and 1–2 μm

long). The CEC measured by an ammonia electrode method is 165 meq/kg compared to 175 meq/kg as reported for reference clay [19]. The surface area measured by single point BET was 126 m^2/g .

Tetracycline hydrochloride was purchased from Calbiochem (Darmstadt, Germany). It has a formula weight of 480.9 g/mol, $\text{pK}_{\text{a}1}$, $\text{pK}_{\text{a}2}$, $\text{pK}_{\text{a}3}$ values of 3.3, 7.7, 9.7, respectively [6], and $\log K_{\text{ow}}$ value of -2.2 to -1.3 [20,21].

2.2. Batch experiment

For all batch experiments, the amount of PFL-1 used was 0.10 g, while the volume of solution used was 20 mL. They were combined in 50 mL centrifuge tubes and mixed on a reciprocal shaker at 150 rpm. For batch kinetic study, the initial TC concentration was 200 mg/L while pH was maintained at 5–6. The mixtures were shaken for 0.25, 0.5, 1.0, 2.0, 4.0, 8.0, and 24.0 h. For pH sorption edge experiment, the initial TC concentration was 200 mg/L, while the pH varied from 3.5 to 11 with a 0.5 increment. For ionic strength experiment, the initial TC concentration was 200 mg/L, while the ionic strength of the solution was adjusted with 0.001, 0.01, and 0.1 M of NaCl. For temperature dependent sorption, the initial TC concentration was 200 mg/L, the pH was 5–6, while the temperature was maintained at 298, 313, and 328 K. For batch sorption study, the initial concentrations were 50, 100, 200, 400, 600, and 800 mg/L, while the pH was adjusted to pH 1, 5–6, 8.7, and 11 with either HCl or NaOH. Under these pHs, the TC will be a cation, +00, a zwitterion, +–0, an anion, +– –, and a divalent anion 0– – (Fig. 1).

During mixing and storage processes, the centrifuge tubes were wrapped with aluminum foils to prevent light induced decomposition. After mixing, samples were centrifuged at 7600 rpm for 20 min and the supernatant analyzed for equilibrium TC concentrations by an HPLC method. All experiments were run in duplicate. The amount of TC sorbed was determined by the difference between initial and equilibrium concentrations.

2.3. Methods of analyses

The TC was quantified by an HPLC method. A GBC 1202 pump was used for mobile phase delivery, a GBC LC1205 UV–vis detector at a wavelength of 254 nm was used for TC detection, while an Asahipak ODP-50 4E column (Shodex) was used for species separation. The mobile phase is made of 0.01 M phosphoric acid/acetonitrile (75:25) with a final pH of 2.5. At a flow rate of 1.5 mL/min, the retention time of TC is 6 min. The standards were adjusted to the same pH as the experiments. Calibration was made with 5 standards between 5 and 100 mg/L with an r^2 no less than 0.99.

The metal cations desorbed were analyzed by ion chromatography (Dionex 100) with an IonPac Cs12A column (4 mm \times 250 mm) and a mobile phase made of 1.922 mL of 20 mM methanesulfonic acid in 1 L of water. At a flow rate of 1 mL/min, the retention time for Na^+ , K^+ , Mg^{2+} , and Ca^{2+} was 3.2, 4.4, 5.2, and 6.0 min, respectively.

Powder XRD analyses were performed on a Rigaku D/Max-IIIa diffractometer with Ni-filtered Cu K α radiation at 35 kV and 20 mA. Samples were scanned from 2 $^\circ$ to 30 $^\circ$ 2 θ at 1 $^\circ$ /min with a scanning step of 0.01 $^\circ$ /step. A 1 $^\circ$ divergent slit and scatter slit and 0.3 mm receiving slit were used.

The FTIR spectra were acquired on a Spectrum GX spectrometer (PerkinElmer) using KBr pressing method. The spectra were obtained by accumulating 256 scans at a resolution 4 cm^{-1} in the range of 4000–400 cm^{-1} .

The TG analyses were performed on a Prys Diamond TG/DTA (PerkinElmer). The heating rate was 10 $^\circ\text{C}/\text{min}$ under air condition. The initial sample weight was between 5 and 9 mg.

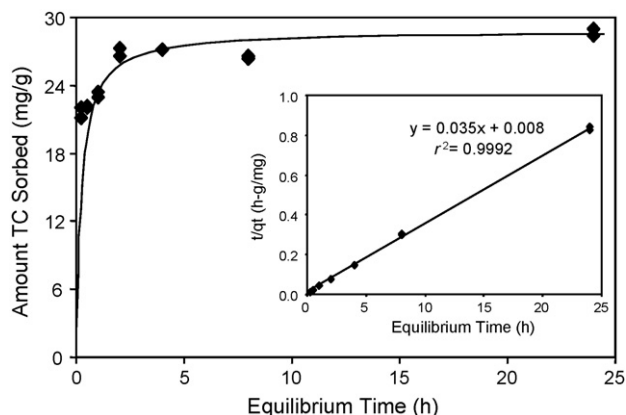


Fig. 2. Sorption kinetics of TC on palygorskite. The solid line is pseudo-second-order fit to the observed data. Insert is the linear plot of Eq. (1).

3. Results and discussion

3.1. TC sorption kinetics

Previous results of TC sorption on rectorite showed that 24 h were needed to reach equilibrium [22]. For this reason, TC kinetic study was conducted first. The results are plotted in Fig. 2 and fitted to several kinetic models. The pseudo-second-order kinetics model, which was used to describe chemisorption and has been widely applied to the sorption of pollutants from aqueous solutions in recent years, fits the experimental data best. The integrated rate law of the pseudo-second-order kinetics model is [23]:

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

where k (g/mg-h) is the rate constant of sorption, q_e (mg/g) the amount of TC sorbed at equilibrium, and q_t (mg/g) is the amount of TC sorbed on the surface of the sorbent at any time, t . Eq. (1) can be re-arranged into a linear form [24,25]

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

where kq_e^2 is the initial rate (mg/g-h). The coefficient of determination r^2 is 0.9992, the initial rate is 120 mg/g-h, the rate constant is 0.145 g/mg-h, and the q_e is 29 mg/g, when the kinetic data are fitted to Eq. (2). By just visualize the data in Fig. 2 one could see that the sorption reached equilibrium in 2 h, which is much faster than TC sorption on rectorite [22]. Although an equilibrium could be established quickly, in subsequent experiments the equilibration time was set for 24 h.

3.2. TC sorption isotherm

Sorption of TC on PFL-1 under pH 1.5, 5–6, 8.7 and 11 are plotted in Fig. 3. The experimental data were fitted well by the Langmuir type isotherm:

$$S = \frac{K_L S_m C_L}{1 + K_L C_L} \quad (3)$$

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

$$\frac{C_L}{C_S} = \frac{1}{K_L S_m} + \frac{C_L}{S_m} \quad (4)$$

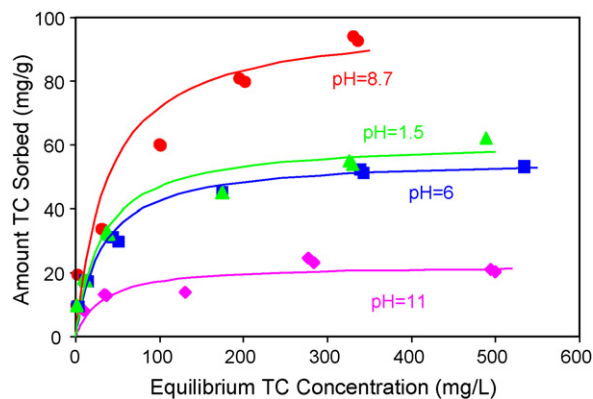


Fig. 3. Sorption isotherm of TC on palygorskite. The lines are Langmuir fit to the observed data.

Table 1

Langmuir sorption coefficient and TC sorption capacity on PFL-1.

pH	K_L (L/mg)	S_m (mg/g)	Area occupied/molecule (\AA^2)	r^2
1.5	0.033	61	162	0.98
5–6	0.032	56	170	0.997
8.7	0.027	99	100	0.96
11	0.033	23	417	0.97

so that K_L and S_m can be determined by a linear regression. The Langmuir sorption parameters together with the regression coefficient r^2 are listed in Table 1. TC sorption maxima are 61, 59, 99, and 23 mg/g, corresponding to 130, 120, 210, and 50 mmol/kg at pH 1.5, 5–6, 8.7 and 11. The first two values are slightly less than the CEC, the third value is greater than the CEC, while the last one is much smaller than the CEC of the mineral.

At pH 1.5, TC is in its cationic form of TCH_3^+ . If cation exchange is the only mechanism for TC sorption by PFL-1, the TC sorption maximum should be the highest at low pH. At pH 5–6, the TC is in its zwitterionic form TCH_2^0 . Even though, the amount of metal cations desorbed is positively correlated to the amount of TC sorbed (Fig. 4). The amount of K^+ , Na^+ , and Mg^{2+} released are low and are almost invariable with respect to the amount of TC sorbed. The major cation desorbed is Ca^{2+} and the amount of Ca^{2+} desorbed is much larger than that of TC sorbed (Fig. 4). The desorption of exchangeable cations with TC uptake confirms that cation exchange still played an important role even if the TC molecules are in zwitterionic form [22]. On the other hand,

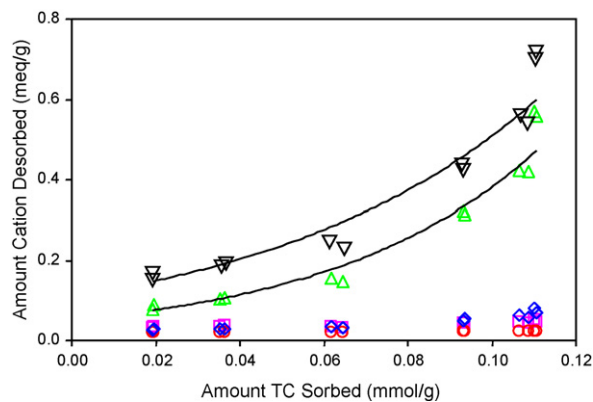


Fig. 4. Amount of Na (□), K (○), Mg (◇), Ca (△), and total cation (▽) desorbed as affected by TC sorption on palygorskite.

the extra Ca^{2+} desorption associated with TC sorption could be attributed to the replacement of H^+ for Ca^{2+} as the TC used is in HCl form. At pH 8.7, although the TC is in its anionic form TCH^- , its sorption reached a maximum of 210 mmol/kg, much higher than the CEC of the clay minerals. Due to the presence of positively charged functional group of dimethylammonium (Fig. 1), cation exchange may still play a role. However, the two negative charges need to be balanced by the metal cations in solution or could be interacting with the Lewis acid sites on palygorskite surfaces. At pH 11, the positively charged dimethylammonium group is no longer present. Therefore, the sorption maximum is reduced to 50 mmol/kg.

A search using tetracycline and palygorskite on Scopus returned zero result. Thus, these values cannot be compared to the same sorbate on the same sorbent. However, they are much lower than 800 mg/g determined for OTC sorption on montmorillonite [6], but slight higher than 27 mg/g for OTC sorption on a similar montmorillonite [9]. These values are also lower than TC sorption on rectorite that is made of a regular 1:1 interstratification of an illite layer and a montmorillonite layer [22]. TC sorption on PFL-1 reached the highest at pH 8.7 compared to pH 5 on montmorillonite [9] and pH 4–5 on rectorite [22].

3.3. Effect of pH on TC sorption edge

The amount of TC sorbed varied from 17 to 27 mg/g or 42 to 93% at an initial concentration of 200 mg/L and a liquid/solid ratio of 200, and reached maximum at pH 8–9.5 (Fig. 5). The trend in TC sorption as affected by pH agrees well with the TC sorption isotherm study. The pH effect on TC sorption on PFL-1 is completely different from TC sorption on Na-bentonite, on which higher amounts of TC sorption is associated with low pH [9,26]. On the other hand, a similar observation was found for OTC sorption on iron oxide with the contaminant distribution coefficient (K_d) maximized at pH 8 [10].

3.4. Effect of ionic strength on TC sorption

The amount of TC sorbed is inversely proportional to the logarithmic concentration of the background ionic strength as indicated by the NaCl concentration (Fig. 6). At an ionic strength of 0.001 M NaCl, 82% of the input TC was removed from water. On the contrary, only 56% of input TC sorbed on PFL-1 at an ionic strength of 0.1 M NaCl. The competing of present ion against TC for sorption sites shows that part of the TC sorption was due to ion exchange mechanism, same as that observed for TC sorption on other clays [6,9,22].

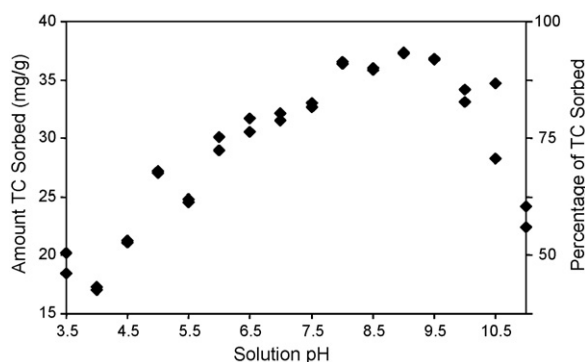


Fig. 5. Sorption of TC on palygorskite as affected by solution pH.

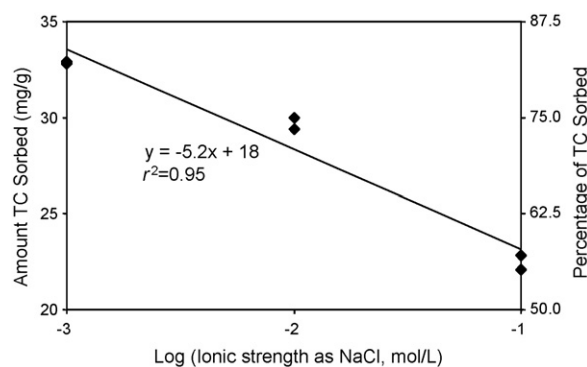


Fig. 6. Sorption of TC on palygorskite as affected by solution ionic strength. The line is a linear fit on a semi-log scale showing reverse relationship between TC sorbed and solution ionic strength.

3.5. Effect of temperature on TC sorption

The sorption of TC on PFL-1 under different pH and temperature conditions can be seen in Fig. 7. The relationship between K_d , which is the ratio of the amount of TC sorbed to the equilibrium TC concentration, and the thermodynamic parameters of sorption 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 sorption can be determined by

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

The calculated thermodynamic parameters are listed in Table 2. The negative ΔG value indicates attractive interaction between TC and PFL-1, thus the sorption of TC on PFL-1 is spontaneous. The positive ΔH value suggests that TC sorption on PFL-1 is an endothermic process. Therefore, increases in temperature should facilitate the sorption of TC onto PFL-1. As the K_d value for TC sorption on palygorskite is much greater than 1 and the ΔH is positive, which will result in a positive ΔS . The small positive ΔS indicates that the sorption is spontaneous due to an increase in system randomness as TC molecules remove themselves from water onto solid surfaces. It may also suggest that the sorbed TC molecules might adopt a randomly oriented manner instead of arranging themselves in an orderly pattern on the external surface of palygorskite. Compared

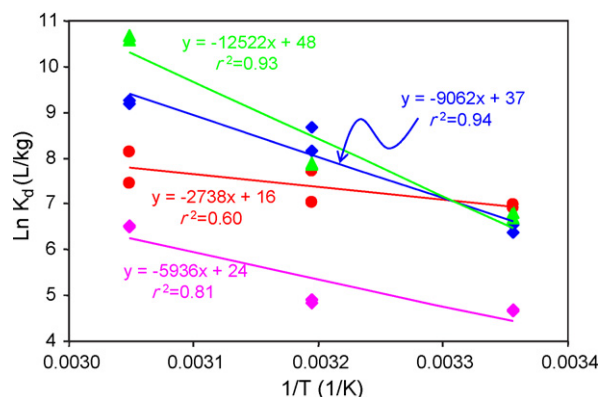


Fig. 7. Influence of temperature on TC sorption on palygorskite. The lines are fitted to the observed data based on Eq. (5).

Table 2
Thermodynamic values of TC sorption on PFL-1 at different pHs.

pH	ln(K_d) (L/kg)			ΔG (kJ/mol)			ΔH° (kJ/mol)	ΔS° (kJ/mol-K)
	298 K	313 K	328 K	298 K	313 K	328 K		
1.5	6.75	7.88	10.62	-16.0	-22.1	-28.1	104.1	0.40
6	6.45	8.42	9.21	-16.4	-21.0	-25.6	75.3	0.31
8.7	6.95	7.38	7.79	-17.2	-19.2	-21.2	22.8	0.13
11	4.67	4.88	6.51	-11.0	-14.0	-17.1	49.4	0.20

to the ΔG value of -8 kJ/mol for TC sorption on silica [11], the more negative values of ΔG for TC sorption on PFL-1 indicate that TC had stronger affinity for PFL-1 than for silica.

3.6. XRD analyses

The XRD patterns of PFL-1 after sorbing TC at an input concentration of 800 mg/L are plotted in Fig. 8. The most important character is the location of the first strong peak at 8.4° (2θ), which has a d_{110} spacing of 10.53 Å. This peak showed no shift in peak location after sorbing 30–90 mg/g of TC. Not only this peak, but also other peaks at 6.39, 5.38 and 4.46 Å all remained at the same location after TC sorption. Furthermore, the amount of TC sorbed had no effect on the locations of PFL-1 diffraction peaks (Fig. 9). These results are completely different from those of TC sorption on montmorillonite [6,27], on soils [12], and on rectorite [22], in which the d -spacing expanded after sorbing TC or OTC, indicating that TC or OTC intercalated into the interlayer position of these minerals. The invariability of d -spacing after sorbing different amounts of TC at different pH conditions suggest that the uptake of TC by palygorskite is on the external surface.

3.7. FTIR analyses

The FTIR spectra of raw PFL-1 and PFL-1 with absorbed TC under different pH conditions are shown in Fig. 10. The vibration of the backbone of the silicate structure of PFL-1 before and after TC sorption showed no apparent change, indicating that the sorbed TC did not alter the structure (Table 3), similar to that of XRD observation. The most characteristic peaks of TC are those in 1200–1700 cm^{-1} with their vibration frequencies listed in Table 4. The TC vibrations

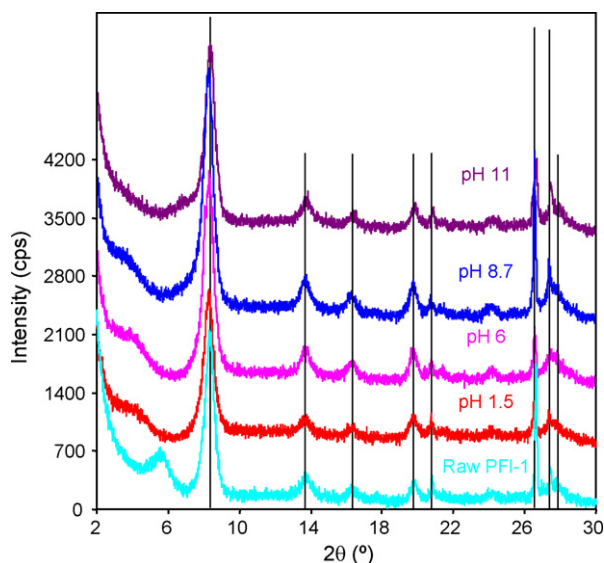


Fig. 8. X-ray diffraction patterns of palygorskite after treated with TC at an initial concentration of 800 mg/L at different pHs.

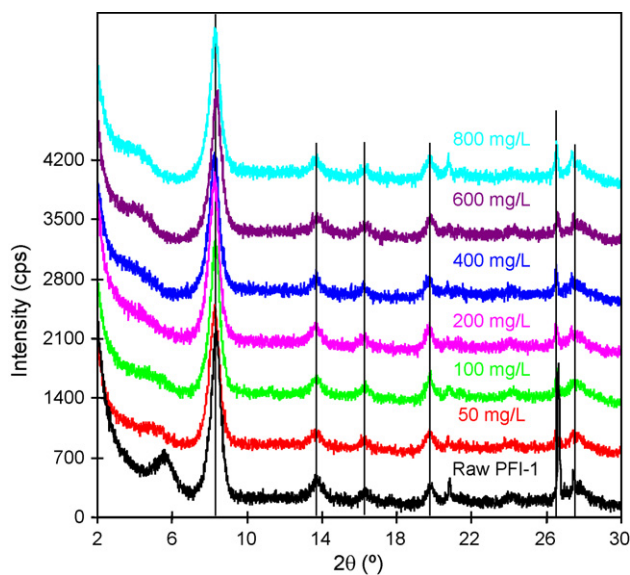


Fig. 9. X-ray diffraction patterns of palygorskite after treated with TC at different initial concentrations at neutral pH.

were much weaker compared to those sorbed to montmorillonite [6] and rectorite [22], indicating that less amount of TC sorbed on PFL-1. At a solution pH of 1.5, the bands at 1311, 1456, 1524, 1579 and 1616 cm^{-1} all shifted about 10–15 cm^{-1} to higher frequencies (Fig. 11), in contrast to shifting to lower frequencies as reported for montmorillonite [6,27]. A shift to higher frequencies resulted from

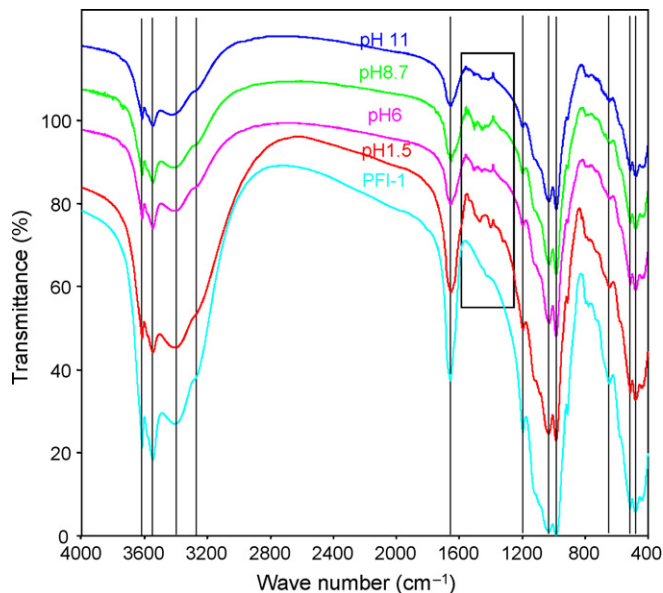
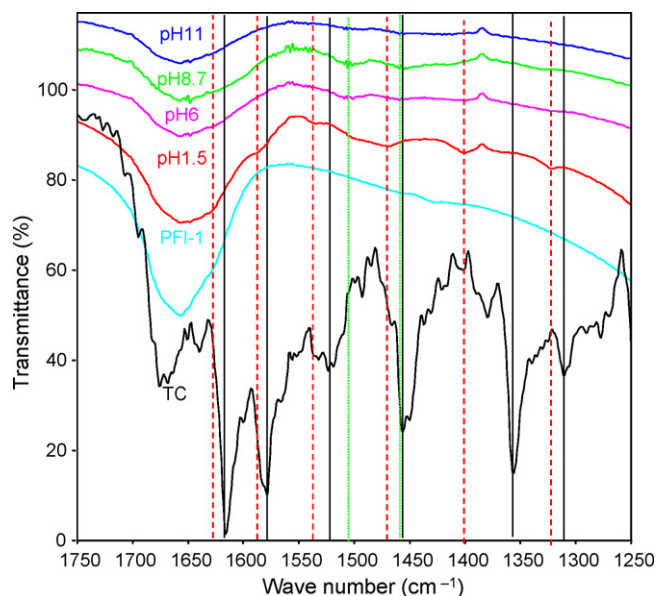


Fig. 10. FTIR spectra of palygorskite after equilibrated with TC at an initial concentration of 800 mg/L at different pHs.

Table 3
FTIR band positions (cm^{-1}) for palygorskite without and with TC sorption.

PFL-1	pH 1.5	pH 6	pH 8.7	pH 11	Possible band assignment [36]
3616	3615	3616	3615	3614	OH stretching of structural hydroxyl groups
3548	3547	3547	3547	3547	OH stretching of water coordinated to Al, Mg
3409	3409	3412	3412	3409	OH stretching of adsorbed and zeolitic water
1658	1656	1658	1658	1658	OH deformation of water
1198	1196	1196	1197	1197	Si–O stretching
1033	1034	1030	1030	1030	Si–O stretching
986	984	984	984	983	Si–O stretching

**Fig. 11.** FTIR spectra of palygorskite after equilibrated with TC at an initial concentration of 800 mg/L at different pHs in the range of 1250–1750 cm^{-1} .

strong interaction between rectorite surface and the intercalated TC molecules [22].

3.8. Derivative of thermogravimetric (DTG) analyses

The DTG curve of PFL-1 has three decomposition temperatures at 83, 220, and 420 °C [28]. The first two corresponded to dehydration temperature while the third one is dehydroxylation temperature [29]. They represent the temperature of removal of superficial water, zeolitic water from fiber channels, and water linked to octahedral ions and water from hydroxyl groups [30].

The DTG curve of pure TC showed a peak decomposition temperature (T_{peak}) at 230 °C with a mass loss of 25% (Fig. 12). Thereafter

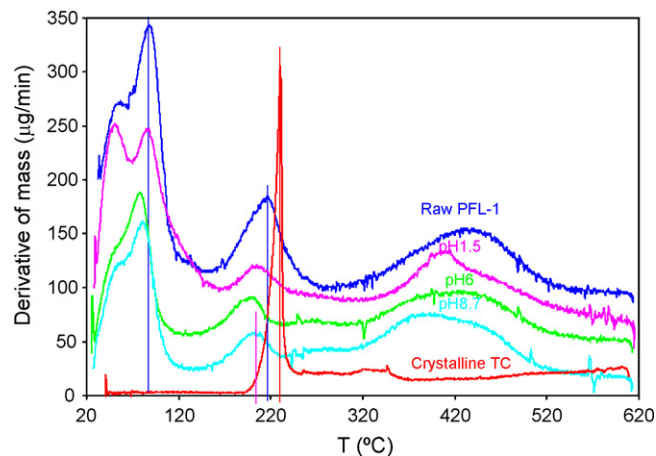
Table 4
FTIR band positions (cm^{-1}) for crystalline TC and TC sorbed on PFL-1 at pH 1.5.

Crystalline TC	pH 1.5	Possible band assignment [37]
1616	1630	$\nu(\text{CO1})$, $\nu(\text{amid-CO})$, $\delta(\text{amid-NH})$, $\nu(\text{CO3})$, $\nu(\text{C2C3})$, $\delta(\text{OH10,12})$
1579	1588	$\delta(\text{Amid-NH})$, $\delta(\text{amine-NH})$, $\nu(\text{Amid-CO})$, $\nu(\text{C2C3})$, $\nu(\text{CO3})$
1524	1538	
1456	1473	$\delta(\text{OH10,12})$, $\delta(\text{CH7,8,9})$, $\nu(\text{D})$, $\nu(\text{CO10,CO11})$, $\nu(\text{C11C11a, C11aC12})$, $\delta(\text{OH12a})$, $\delta(\text{CH36})$
1356	1400	$\nu(\text{Amid-C,C2})$, $\nu(\text{C3,C4})$, $\delta(\text{CH4a,5})$, $\delta(\text{CH36})$, $\delta(\text{OH12a})$, $\delta(\text{amid-NH})$, $\nu(\text{amid-CN})$, $\delta(\text{OH10})$, $\nu(\text{C6aC10a,C6aC7})$
1311	1322	$\delta(\text{OH10,12})$, $\delta(\text{CH4,4a,5,5a})$, $\nu(\text{C5aC11a})$, $\nu(\text{C1C2})$, $\nu(\text{C9C10, C10C10a, C10aC11})$, $\nu(\text{CO11,12})$, $\nu(\text{CO3})$, $\delta(\text{CH7,8,9})$

slow but gradual weight loss lasted until 600 °C, at which 55% of the initial mass had lost. The results are in agreement with a previous report [31], in which a mass loss of 20.3% at 235 °C and a total loss of 36% at 350 °C were obtained.

In this study, the T_{peak} for the removal of zeolitic water from raw PFL-1 is at 214 °C. It decreased to about 205 °C after sorbing TC at an initial concentration of 800 mg/L (Fig. 12). In the study of TC sorption on rectorite, it was found that the TC intercalated into the interlayer of the montmorillonite component of the rectorite had a higher decomposition temperature compared to crystalline TC [22]. If the T_{peak} at 205 °C is thought as a composite peak made of 214 °C for the removal of zeolitic water and the decomposition of TC at a slightly lower temperature, the thermal stability of the TC sorbed on PFL-1 is less stable compared to crystalline TC. This result is completely opposite to that of TC decomposition from the interlayer space of rectorite [22]. This opposite trend in TC thermal stability may again indicate that the sorbed TC is on the external surface of PFL-1 as revealed by XRD analyses, in contrast to the intercalation into rectorite [22].

TC can adapt different conformations through tautomerism in response to various chemical environments and 64 different possible tautomers can be considered [32]. However, generally accepted conformations for TC are extended and twisted ones. The former exists in basic solution, when the dimethylamino group lies below the plane spanned by the ring system [33], while the latter is present in acidic to neutral solutions, in which the dimethylamino group lies above ring system [32–34]. The dimension of totally protonated TC is 12.9 Å long, 6.2 Å high and 7.5 Å thick in twisted conformation [35]. On the other hand, the empty channel dimension of palygorskite is 7.3 Å × 6.3 Å [18]. Therefore, the TC molecules are slightly large to get into the internal channel of palygorskite, restricting the uptake of TC on external surfaces.

**Fig. 12.** Derivative of thermogravimetric analysis of raw PFL-1, and PFL-1 with TC adsorbed at an initial concentration of 800 mg/L at pH 1.5, pH 6, and pH 8.7. Also drawn is the DTG of crystalline TC, whose vertical scale is reduced by 50%.

When the ring is parallel to the surface, it occupies an area of 97 \AA^2 [35]. With the long axis of the molecule perpendicular to the surface, it would occupy an area of 47 \AA^2 . With a specific surface area of $126 \text{ m}^2/\text{g}$, at sorption maxima, the surface area occupied per molecules varied from 100 \AA^2 at pH 8.7 to 417 \AA^2 at pH 11 (Table 1). Therefore, the specific surface area is larger enough to accommodate any type of conformations. The results further confirm that the uptake of TC by PFL-1 is restricted only to the external surfaces in contrast to the intercalation of TC into montmorillonite interlayer [6,27]. For rectorite, at TC sorption maxima, the amount of TC sorbed corresponded to $6\text{--}15 \text{ \AA}^2$, suggesting that much of the sorbed TC is in the interlayer position of rectorite [22].

Previous studies showed that cation exchange was responsible for TC sorption at pH less than its $\text{pK}_{\text{a}1}$ value, when the TCs were in cationic form [6,9,12,27]. At neutral pH, surface complexation of zwitterion forms could be responsible for TC uptake [9,27]. FTIR study also revealed that hydrophobic interaction be responsible for the sorption of OTC in its zwitterion form by montmorillonite [6]. The positive correlation between the desorption of exchangeable cations and the sorption of TC confirmed that cation exchange is still responsible for part of the TC uptake by PFL-1. However, compared to the CEC value of $165\text{--}175 \text{ meq/kg}$, the amounts of TC sorbed are 130, 120, 210, and 50 mmol/kg at pH 1.5, 5–6, 8.7 and 11. Except at pH 8.7 the TC sorption maxima are less than the CEC of the clay, suggesting cation exchange may not be the major mechanism for TC uptake. Considering the larger specific surface area of PFL-1 and the XRD results, it is not surprised to conclude that sorption sites of TC on PFL-1 are on the external surfaces.

4. Conclusions

From the results of TC sorption on PFL-1 at different experimental conditions, we can draw the following conclusions:

1. Sorption of TC on palygorskite followed a pseudo-second-order kinetics. Sorption equilibrium could be reached in 2 h.
2. Sorption of TC on palygorskite followed a Langmuir sorption isotherm with the sorption maximum reached to 99 mg/g , or 210 mmol/kg at pH 8.7.
3. Solution pH and ionic strength had strong effects on TC uptake by palygorskite.
4. Sorption of TC on palygorskite is an endothermic reaction, and thus, increasing temperature will enhance the uptake of TC by palygorskite. The moderate negative ΔG indicates that physisorption or surface complexation may be the dominant mechanism. The small positive ΔS suggests that the sorbed TC molecules adopted a random arrangement on palygorskite surfaces.
5. XRD analyses showed no d -spacing changes at different pH values or different sorption amounts, further suggesting that the sorption is on the external surfaces.

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