Probing the interactions between chlorpheniramine and 2:1 phyllosilicates

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ABSTRACT

Interactions between chlorpheniramine (CP), an antihistamine drug used to treat allergy, and 2:1 phyllosilicates were studied under batch kinetic and different solution conditions to investigate the effect of charge density of the substrates on CP removal from solution. The CP removal by Na-montmorillonite was instantaneous, with a very large rate constant and a fast rate, reaching a capacity of 0.64 mmol/g, compared to its cation exchange capacity of 0.85 mmol/g. In contrast, CP removal by talc was 10 times lower at 0.06 mmol/g. Stoichiometric desorption of exchangeable cations accompanying CP removal by Na-montmorillonite confirmed cation exchange as the dominant interaction mechanism. Solution pH had a minimal effect on CP removal by Na-montmorillonite until pH 11. On the contrary, a slight increase in CP removal by talc was observed, due to increased negative charges on the pH-dependent surfaces of talc. Interactions between CP and Na-montmorillonite occurred on both external and interlayer sites, resulting in a d-spacing expansion from 12.5 Å to 15.2 Å. In contrast, interactions between CP and talc were only limited to the external surfaces. It was the charge density that ultimately controlled the amount of CP removal by 2:1 phyllosilicates. Thus, montmorillonite offers a superior option for the removal of cationic drugs from aqueous solution.

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1. Introduction

Many studies have been conducted recently to investigate the fate and transport of pharmaceuticals and personal care products (PPCPs) in the environment. Most of the PPCPs studied were limited to antibiotics, such as tetracycline, ciprofloxacin, and sulfa drugs [1–5]. Montmorillonite, a 2:1 phyllosilicate, and iron and aluminum hydroxide had great affinity for many of these cationic drugs [6,7]. The uptake of cationic antibiotics was mainly attributed to cation exchange; thus, minerals with high cation exchange capacities (CECs) were good candidates for the removal of cationic drugs [6]. Montmorillonite, a 2:1 phyllosilicate, and iron and aluminum hydroxide had great affinity for many of these cationic drugs [6,7]. The uptake of cationic antibiotics was mainly attributed to cation exchange; thus, minerals with high cation exchange capacities (CECs) were good candidates for the removal of cationic drugs [6].

Chlorpheniramine (CP), 3-(4-chlorophenyl)-N,N-dimethyl-3-pyridin-2-yl-propan-1-amine, is a first-generation alkylamine antihistamine used in the prevention of the symptoms of allergic conditions such as rhinitis and urticaria and is one of the most commonly used antihistamines in small-animal veterinary practice as well [12]. It is normally commercialized in a salt form with maleate because of the likelihood of protonation of both nitrogen atoms in the molecule. Although the presence of CP in wastewater treatment plants (WWTPs) was rarely reported, qualitatively identification was confirmed in samples collected from a WWTP in New York that had more than 20% inflow from pharmaceutical formulation facilities [13]. In addition, CP was identified as one of the pharmaceuticals with a priority for future study [2].

Most of the earlier studies on the interactions between CP and the solid surfaces were focused on drug adsorption in the presence of charcoal to be used as an antidote for the early treatment of acute accidental drug ingestions [14]. An almost 100% CP removal in the amount of 200 mg/g could be achieved by activated charcoal with a high surface area [15]. Separately, studies of drug interferences using montmorillonite in pharmacy were also conducted [16]. Adsorption of CP on montmorillonite resulted in an interlayer expansion, thus, was attributed to CP intercalation [17,18]. A two-step process including a cation exchange reaction followed by strong surface chemisorption was responsible for the binding of cationic drugs to montmorillonite [16].

Talc is a trioctahedral 2:1 phyllosilicate. In comparison with montmorillonite, it has limited isomorphic substitution, resulting in a minimal CEC. In addition, the interlayer space of talc does not contain any exchangeable cations or water molecules. A few studies were conducted to investigate interactions between drugs and talc surfaces. Adsorption of ciprofloxacin on talc reached a...
capacity of 740 µg/g, corresponding to 2.2 µmol/g [19] in comparison with 1.0 mmol/g on a Ca-montmorillonite [9]. Separately, adsorption of cimetidine, under the trade name Tagamet® approved by the FDA for inhibition of gastric acid secretion, on talc was found to be 290 µg/g, equivalent to 1.2 µmol/g [20].

Even with the above-mentioned studies on interactions between cationic drugs and 2:1 phyllosilicates, the influence of solution pH on CP removal from solutions, the desorption of exchangeable cations accompanying CP removal due to cation exchange reaction as well as the charge density effect on CP removal from solutions were not investigated in detail. The goal of this study was focused on the interactions between CP and Na-montmorillonite, an important soil and sediment component, and t alc, a phyllosilicate with limited surface charge, in order to enrich further understanding of the fate and transport of PPCPs in the environment on one hand, and to understand the effect of surface charge on the removal of cationic drugs by 2:1 phyllosilicates on the other hand.

2. Materials and methods

The montmorillonite used was SWy-2 obtained from the Clay Mineral Repositories in Purdue University (West Lafayette, IN) and was used without further purification. It is made of 95% of smectite, 4% quartz, and 1% feldspar + gypsum + mica [21]. It has a chemical formula of (Ca0.12 Na0.32 K0.05)[Al3.01 Fe(III)0.41 Mg0.54][Si5.38 Al0.62]2O20(OH)4, a CEC of 85±3 mmol/100 g [22], a layer charge of 0.32 eq/mol per (Si,Al)4O10 [23], and an external surface area (ESA) of 23 m2/g, respectively [24], and a mean particle size of 3.2 µm with a d50 to d75 in the range of 3–10 µm. The talc used was purchased from Acros (Geel, Belgium) with a particle size less than 200 mesh (<0.075 µm) and an ESA of 2.3 m2/g measured by a multi-point BET method. It has a general formula of Mg3Si4O10(OH)2. Although t alc was listed as 100% pure by the supplier, the XRD analysis did show some impurities of chlorite, quartz, and dolomite. However, the ratio of peak heights of (001)chlorite/(002) talc was less than 2, suggesting that the amount of chlorite present was no more than 2%. Due to low isomorphic substitution in tetrahedral and octahedral sites, talc had an essential no permanent surface charge [25] and extremely low CEC due to its pH-dependent surface charge.

The chlorpheniramine maleate (CAS #: 23095-76-3), also called chlorphenamine, was provided by Wei Li Pharmaceutical Co. Ltd. (Tainan, Taiwan). It has a molecular weight of 390.9 g/mol, a water solubility of 1–5 g/100 mL at 21 ºC with a logKOW value of 3.38 [26]. Protonation of both nitrogen atoms (Scheme 1) in the molecule [27] resulted in pKa values of 9.2 and 4.0 [28]. In comparison, maleic acid is a diprotic acid with pKa values at pH 1.9 and 6.6. Under pH 1.9–4, maleic acid is the dominant form for the counterion while CP is a divalent cation. In pH 4–6.6, both maleate and CP are monovalent. When solution pH is between 6.6 and 9.2, divalent maleate is the dominant counterion maleate while CP and Na+ are monovalent. When solution pH is between 6.6 and 9.2, divalent maleate is the dominant counterion while CP is a monovalent cation.

The initial CP concentrations varied from 50 to 2000 mg/L for the adsorption isotherm study, while a fixed concentration of 1000 mg/L was used for the kinetic study and pH effects on CP removal. To each 50-mL centrifuge tube, 20 mL of CP solution and 0.1 g of SWy-2 or 1.0 g of talc were mixed and shaken for 24 h at 150 rpm room temperature. For the kinetic study, the equilibration time varied from 0.25 to 24 h. After the mixtures were centrifuged at 7600 rpm for 20 min, the supernatants were filtered through 0.45 µm syringe filters before being analyzed for CP concentrations and the amount of exchangeable cations desorbed.

The CP concentrations were measured using a UV–Vis spectrophotometer (Model T6 New Century 1650, made by General Instrument, Inc. LLT, Beijing China) with a 0.5% error in transmissivity at the wavelength of 264 nm, corresponding to its maximal absorbance [29,30]. Calibrations were made using standards of 10, 20, 30, 40, 50, and 60 mg/L with regression coefficients all greater than 0.999. The amount of CP adsorbed was calculated from the difference between the initial and final concentrations.

The exchangeable cations desorbed were determined by atomic absorption on a Perkin Elmer AAnalyst-100 Atomic Absorption Spectrometer (Waltha, MA, USA). The calibration was made using seven standard solutions with concentrations from 0.2 to 3.0 mg/L for K+, Na+, and Mg2+, and 1.0 to 25.0 mg/L for Ca2+. The detection wavelengths were 765.6, 589.0, 285.2, and 422.7 nm with a detection limit of 0.01, 0.006, 0.06, and 0.4 mg/L for K+, Na+, Mg2+, and Ca2+, respectively. The relative standard deviation is 0.2%.

Powder XRD analyses were performed on a Rigaku D/max-llla diffractometer (Tokyo, Japan) with a Ni-filtered Cu Kα radiation at 30 kV and 20 mA. Orientated samples of SWy-2 were scanned from 2° to 10° 2θ at 1°/min with a scanning step of 0.01°/step. Talc was scanned from 3° to 70° 2θ at 5°/min with a scanning step of 0.02°/step.

Fourier transform infrared (FTIR) spectra were acquired on a Spectrum 100 spectrometer equipped with a mercury cadmium telluride detector made by Perkin Elmer (Waltha, MA, USA) using the KBr pressed-disk method at a sample to KBr ratio of 1:20. The spectra were collected by accumulating 256 scans at a resolution of 4 cm⁻¹ in the range of 450–4000 cm⁻¹.

Molecular simulation was performed under the module Force of Materials Studio 5.0 software to investigate the CP conformation in the interlayer of montmorillonite. The montmorillonite model was constructed, and the atomic coordinates were derived from the space group of C2/m with a = 5.18 Å, b = 8.98 Å, c = 15.0 Å, α = γ = 90°, β = 99° [31]. The supercell of the model was made of eight montmorillonite unit cells at 4a × 2b × 1c. On the surface of XOY, the area was 20.72 Å × 17.96 Å. It was assumed that the layer charge came from the substitution of aluminum by magnesium in the octahedral sheets and the total layer charge was −5 balanced by Na⁺ in the interlayer [32]. The substitution resulted in a CEC of 0.85 mmol/g and a formula of Na0.625Si4Al3.375Mg0.625O20(OH)4 with a formula weight of 732.5 g/mol. From the CP adsorption capacity of 0.66 mmol/g, determined by the batch adsorption study, four of the five Na⁺ ions would be substituted by CP.

The established model was optimized geometrically. The temperature was set at 298 K, and time was 1 ns with a time step of 1 fs. Universal force field was used during simulation. The Ewald summation method was used to calculate the electrostatic interaction. After the system reached equilibrium, the NVT kinetic simulation was performed under the same time constant and temperature conditions. The data were collected on the last 500 ps for later analyses.

3. Results and discussion

3.1. Kinetics of CP removal

The kinetic study was intended to investigate the time needed to reach equilibrium for CP removal so that future studies could be unified into a fixed time by which equilibrium would be
established. Removal of CP by SWy-2 was instantaneous (Fig. 1). The experiment data were fitted to several kinetic models (See supplementary material for detail) and the pseudo-second-order kinetic was the only model fitted the experimental data well with a coefficient of determination $R^2 = 1.000$ for both SWy-2 and talc. For CP removal by SWy-2, an initial rate of 1000 mmol/h, a rate constant of 4500 g/mmol-h, and $q_e$, the amount of CP adsorbed at equilibrium, of 0.47 mmol/g were obtained. The instantaneous removal of CP by SWy-2 suggested a great affinity of CP for montmorillonite surfaces. For CP removal by talc, the initial rate was 0.7 mmol/h, the rate constant was 230 g/mmol-h, and the $q_e$ was 0.05 mmol/g. In comparison with montmorillonite, talc had a much lower initial rate and rate constant. Thus, for the removal of cationic drugs such as CP from water, swelling clays like montmorillonite offer a great advantage due to its larger initial rate and rate constants as well as higher capacity for contaminant removal.

The patterns of $(t/q_e)$ vs. $t$ (Fig. 1 inserts) could be used to assess the surface heterogeneity of the adsorbent and the plot of $(t/q_e)$ vs. $t$ would fall into two segments if the surface was heterogeneous [33]. In this study, both plots followed a perfect straight line, suggesting that the adsorption site was homogeneous for both minerals. As the adsorption of CP on SWy-2 involved in intercalation, the indication of homogeneous adsorption sites suggested that both the external surfaces and the interlayer spaces were equally accessible by CP.

Confirmations of the pseudo-second-order kinetics suggested that the removal of CP was mass transfer limited, and the mass transfer coefficient can be determined by [34]:

$$K_f = \frac{mkq^2}{(C_0A)}$$

(1)

where $mkq^2$ is the initial rate (mg/kg-h), $m$ is the mass of adsorbent, $C_0$ is the initial concentration of CP, and $A$ is the external surface area. As the CP adsorption involved in both interlayer spaces and external surfaces, using the total specific surface areas of 725 m$^2$/g for SWy-2 [35] and 2.3 m$^2$/g for talc as determined in this study, the calculated mass transfer coefficients were $1.5 \times 10^{-6}$ and $3.3 \times 10^{-8}$ cm/s, for CP adsorption on SWy-2 and talc, respectively. These values confirmed that the transfer of CP from solution onto montmorillonite was much facilitated in comparison onto talc due to the higher charge density of montmorillonite and lower charge density of talc.

3.2. CP adsorption isotherm

The adsorption of CP on SWy-2 was fitted to several adsorption models. The Freundlich fit resulted in a big discrepancy between the observed and predicted data (Fig. 2). Although the initial part of the Langmuir fit deviated from the ideal slightly, the better fit to the Langmuir model suggested a surface-limited or charge-limited adsorption (Fig. 2). Sorption of other organic cations, such as tetracycline and ciprofloxacin, on montmorillonite was also well described by the Langmuir isotherm [8–10]. Assuming that there was a capacity for adsorption sites available on the surface of solid and all the sites were equally accessible, the Langmuir isotherm has the form:

$$C_s = \frac{K_sS_mC_f}{1 + K_sC_f}$$

(2)

where $C_s$ is the amount of CP adsorbed on solid at equilibrium (mmol/g), $C_f$ the CP solution concentration (mmol/L), $S_m$ the apparent sorption capacity or adsorption maximum (mmol/g), and $K_s$ the Langmuir coefficient (L/mmol). Eq. (2) can be re-arranged into a linear form:

$$\frac{C_s}{C_f} = \frac{1}{K_sS_m} + \frac{C_f}{S_m}$$

(3)

so that $K_s$ and $S_m$ can be determined by a linear regression. The fitted $K_s$ and $S_m$ values were 10 L/mmol and 0.64 mmol/g, respectively, comparable to CP adsorption of 0.76 mmol/g on a similar montmorillonite [17,18], and on a pharmaceutical acrylic resin used to formulate oral controlled-release delivery system to coat on small particles and tablets [29]. However, no $K_s$ values were available in the literature [17,18]. In comparison, a high charge Ca-montmorillonite SAz-1 resulted in a slightly higher CP adsorption capacity of 0.72 mmol/g [36]. Compared to montmorillonite, the adsorption of CP on talc was much lower, with a capacity of 0.06 mmol/g and a $K_s$ of 0.22 L/mmol (Fig. 2). The capacity value was much larger than 2.2 mmol/g for adsorption of ciprofloxacin on talc [19] and 1.2 mmol/g for adsorption of cimetidine, an H2-receptor antagonist used for the treatment of duodenal ulcers and gastric hypersecretion, on talc [20]. The CEC of talc was <0.01 mmol/g [37], much smaller than that of 0.85 mmol/g for SWy-2 [22], resulting in a much lower CP adsorption capacity.

The $K_s$ value could be related to the free energy of adsorption by [38]:

$$\Delta G_{ads} = -RT \ln(K_s \times 55.5)$$

(4)

where the value 55.5 corresponded to the molar concentration of water for dilute solutions with units of mol/L. The calculated values of free energy of adsorption $\Delta G_{ads}$ of CP on SWy-2 and talc were $-15.8$ and $-6.2$ kJ/mol, respectively, indicating that montmorillonite surface was more favorable than talc for CP adsorption, although both values fell into a physical adsorption category, as intercalation does not necessarily mean formation of chemical bond. Thus, chemisorption may not be necessarily the dominant mechanism. For example, the adsorption of water in the interlayer results in

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**Fig. 1.** Kinetics of CP adsorption on SWy-2 (a) and talc (b). The solid line is pseudo-second-order fit to the observed data. Inserts are plot of $(t/q_e)$ against $t$ for SWy-2 (a) and talc (b).

**Fig. 2.** CP adsorption on SWy-2 (a) and talc (b). The solid and dash lines are the Langmuir and Freundlich fits to the observed data.
interlayer expansion, which is termed as intercalation, and it is a kind of physical adsorption.

3.3. Cation desorption accompanying CP adsorption

The major desorbed cation was Na⁺, confirming that the montmorillonite was indeed in Na form. Overall, there was a strong linear correlation between the amount of CP adsorbed and total exchangeable cations desorbed (Fig. 3). The near-unit slope suggested that cation exchange was mainly responsible for CP adsorption, similar to the desorption of other cationic drugs on montmorillonite [8–10]. However, a nonzero intercept was observed in this study and in a previous study for the TC adsorption on the same mineral [8]. Forcing the regression through the origin resulted in a slope of 1.76 with a lower r² (Fig. 3). Thus, the nonzero slope suggests more cations desorbed in comparison with CP adsorbed. As the equilibrium solution pH was close to 7.5 at lower initial CP concentrations and 6 at higher initial CP concentrations, at this pH range, the maleate is a divalent anion, while the CP is a monovalent cation. A plausible explanation to the nonzero slope could be attributed to the second deprotonation of maleic acid, which would add an access proton to solution. As the solution pH was not decreased proportionally, the excess cation desorption could be attributed to cation exchange between the proton provided by the maleic acid and the exchangeable cations on montmorillonite.

3.4. Effect of solution pH on CP removal

As the pH ranges of CP were 9.2 and 4.0 [28], it would be dominated by a divalent cation CPH²⁺ when solution pH was 4 or lower, by a monovalent cation CPH⁺ between pH 4 and 9, and in a neutral form at pH > 9.2. The CP removal by SWy-2 increased slightly from 0.41 to 0.47 mmol/g as solution pH increased from 2 to 8–9, where it peaked (Fig. 4). Although most of the CEC of montmorillonite was originated from isomorphic substitution, the pH-dependent CEC may contribute slightly to the total CEC. Thus, the steady increase could be attributed to a slight increase in pH-dependent CEC as solution pH increased. A further increase in solution pH beyond 9 resulted in a slightly decrease in CP removal from 0.47 to 0.44 mmol/g. This could be attributed partially due to the neutral charge of the CP species, thus reduced electrostatic interaction, and partially to possible dissolution of Al³⁺ from montmorillonite, thus affecting CP adsorption. Overall, the amount of CP removal was greater than 0.4 mmol/g in all pH ranges tested, suggesting that the final solution pH had a much less effect on CP removal by SWy-2, similar to an early study of CP adsorption on a similar montmorillonite [17,18].

For talc, there was a slightly monotonic increase in CP removal in the pH ranges of 4–12 (Fig. 4), suggesting a slight different mechanism of CP removal by talc. Guar gum adsorption on talc was affected significantly by changes in solution pH and ionic strength, ruling out electrostatic force as the controlling factor [39]. The isoelectric point of talc was 2.5 [40], above which the talc surface would be negatively charged due to deprotonation. As the solution pH increased, the pH-dependent surface of talc would be more negatively charged, resulting in an increase in electrostatic interaction between the negatively charged mineral surfaces and the positively charged N group, thus an elevated CP uptake by talc.

For both minerals, significant amounts of CP removal occurred when solution pH was greater than the pKₐ value, suggesting that electrostatic interaction still played a major role even though the CP molecules are in neutral form. This could be interpreted as the effect of partial positive charges associated with both N in the molecule.

3.5. X-ray diffraction (XRD) analyses

The XRD patterns of SWy-2 adsorbed with different amounts of CP, adsorbed at different time and different solution pH were plotted in Fig. 5. The raw SWy-2 and SWy-2 equilibrated with 2000 mg/L of CP were further analyzed from 3° to 70° (Fig. 5a). Previous results showed disappearance of crystalline CP peaks after intercalation into Ca-montmorillonite [36]. However, the d-spacing remained at 15.2 Å before and after CP intercalation [36]. It was hypothesized that the dimension of intercalated CP would be the same as that of Ca²⁺ plus 2 layers of water. In this study, the d₀₀₁-spacing of Na-montmorillonite was 12.5 Å, and a progressive shift to 14.3 Å at a CP adsorption of 0.01 mmol/g, and to 15.2 Å at the CP adsorption capacity of 0.64 mmol/g could be observed (Fig. 5b), in contrast to 16–17 Å in a previous study when CP was intercalated into a similar Na-montmorillonite at pH 5.5–7 [18]. Thus, results from this study confirmed the speculation made in the precious study [36].

There was no measurable change in the d₀₀₁-spacing when CP and SWy-2 were equilibrated at different time (Fig. 5c) and different pH conditions (Fig. 5d) as the input CP concentration was 1000 mg/L, resulting in a near constant CP adsorption of 0.41–0.47 mmol/g.

Previous results suggested that the adsorbed CP adopted a special orientation in the interlayer of SAZ-1 so that the d-spacing remained the same at 15.5 Å after the CP molecules replaced Ca²⁺ with two layers of water. The results of this study further confirmed the 15 Å d-spacing after CP intercalation into Na-montmorillonite at different solution pH, different time, and different initial CP solution concentrations. In comparison with CP adsorption on montmorillonite, the d-spacing remained constant at 9.3 Å after CP adsorption on talc at different amounts and different solution pH conditions, suggesting surface adsorption instead of intercalation on talc (Fig. 6). After CP adsorption, the position of the (001) chlorite peak at 14.2 Å remained constant, suggesting that
3.6 FTIR analyses

The FTIR spectra of CP and CP-intercalated montmorillonite are illustrated in Fig. 7. The band assignments for montmorillonite and CP are tabulated in Tables 1 and 2. Overall, the vibration bands of SWy-2 before and after equilibrated with 2000 mg/L CP and that of the crystalline CP (a); at different contact time in min with an initial concentration of 1000 mg/L (c); and at different equilibrium pH with an initial concentration of 1000 mg/L (d).

Fig. 5. X-ray diffraction patterns of SWy-2 before and after equilibrated with 2000 mg/L CP and that of the crystalline CP (a); after equilibrated with different initial concentrations (mg/L) of CP (b); at different contact time in min with an initial concentration of 1000 mg/L (c); and at different equilibrium pH with an initial concentration of 1000 mg/L (d).

Fig. 6. X-ray diffraction patterns of talc after in contact with different initial concentrations of CP. The peaks labeled with the numbers 1, 3, 5, and 9 are chloride (001), (002), (004), and (005) peaks and numbers and 2, 4, 7, 11, and 12 are (002), (004), (006), (008), and (0010) peaks of talc. Peak 6 is from quartz and peak 8 is from dolomite.

However, in this study, the bands pertaining to maleate were not present after adsorption on talc or intercalated into montmorillonite, confirming that the adsorbed CP was not in ion pair form with maleate (Fig. 7). On the other hand, the bands at 1473 and 1488 cm⁻¹, assigned to C=O multiple bond stretching of aromatics [43], were present, suggesting the interactions of benzene rings. Moreover, the band at 1090 cm⁻¹, assigned to C–N vibration of the aliphatic tertiary amine [43], shifted to 1112 cm⁻¹ (Fig. 7), confirming strong interactions between the tertiary amine and the mineral surface.

The absence of spectral shifts in the FTIR spectra of adsorbed polymer was indicative of a hydrophobic interaction between the polycrylamides and the talc surface [38]. Thus, hydrophobic interaction may be partially responsible for CP removal by talc (data not shown). Furthermore, as the CP removal capacity by talc was 0.06 mmol/g, in comparison with its CEC of <0.01 mmol/g [37], other mechanisms, besides cation exchange, may also govern CP removal by talc.

Previous results showed that as the amount of CP increased, the amount of interlayer water gradually decreased as evidenced by a decrease in the intensity of the deformation band of water at 1630 cm⁻¹ [18] and the intensity of the OH stretching of water at 3373 cm⁻¹ for CP intercalation in Ca-montmorillonite [36]. For Na-montmorillonite under KBr pressed-disk method, the OH stretching of water was located at 3422 cm⁻¹ [41], which showed a decreasing trend as the amount of CP intercalation increased. The results of this study further confirmed the hypothesis that a progressive increase in CP adsorption would gradually remove all interlayer water from SWy-2.

3.7 CP adsorption sites and mechanism

Previous results showed that CP adsorption on Ca-montmorillonite was linearly correlated to the amount of total exchangeable cations desorbed [36]. The desorption of exchangeable cations from this study also supported this hypothesis. In addition, the good fit of the experimental data to the Langmuir isotherm further verified that the removal of CP by SWy-2 was capacity-limited or charge-limited.

Based on the ESA of 23 m²/g [24] and CEC of 0.85 mmol/g [22], the charge density calculated would be 4.5 Å² per charge if only external surface was considered. This area is much smaller than
the dimension of a CP molecule in any conformation. Therefore, interlayer adsorption, that is, intercalation, must have contributed significantly to the total CP removal by SWy-2.

The two pK$_a$ values of CP are 9.2 and 4.0 [28], corresponding to the protonation of both nitrogen atoms in the molecule. Under most experimental conditions, except the pH-dependent experiment, the pH of the equilibrium solution was 6–7.5, under which the CP will be a monovalent cation. The removal of CP by SWy-2 involved in the substitution of CPH$^+$ for Na$^+$ or Ca$^{2+}$. Adsorption of organic cations, such as methylene blue, tetracycline, and ciprofloxacin, often involved in intercalation, that is, adsorption in the interlayer positions resulting in an interlayer expansion [8–10].

On the other hand, a change in d-spacing was not observed after CP intercalation into on a Ca-montmorillonite, which was interpreted as a coincidence in interlayer dimensions due to intercalation of CP in comparison with Ca$^{2+}$ plus two layers of interlayer water [36]. In this study, the SWy-2 was in Na form with one layer of water, resulting in a d-spacing of 12.5 Å [44]. After intercalation of different amounts of CP, the d-spacing reached to 15.2 Å, similar to the d-spacing after CP intercalation into Ca-montmorillonite [36]. This result further confirmed that the adsorption of CP by montmorillonite indeed involved in intercalation and the gallery height was about 5.5 Å.

Molecular dynamics simulation was performed to simulate the configuration of intercalated CP molecules in the interlayer. Previous results suggested that interlayer water was absent at the CP adsorption level of 0.38 mmol/g [36]. Thus, water molecules were excluded from the simulation. In addition, as the simulation was mainly for determining the interlayer configuration of intercalated CP and the possible location of the N atom, the d-spacing was fixed at 15.2 Å at the CP adsorption maximum. Moreover, as previous results showed no co-adsorption of counterion maleate accompanying CP adsorption on a Ca-montmorillonite [36], the influence of maleate was not considered in the simulation.

At 298 K, the system reached equilibration after 1 ns, confirmed the fast initial rate and rate constant determined in the kinetic study. The temperature and energy fluctuated around their set values, which remained almost constant over time. The results showed that at the initialization, the benzene rings were nearly parallel to the basal plane. After final energy minimization, the

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**Table 1**

Vibration bands (cm$^{-1}$) of montmorillonite and CP-intercalated montmorillonite at initial concentrations of 0, 100, 1000, and 2000 mg/L.

<table>
<thead>
<tr>
<th>Mont $^a$</th>
<th>Mont study</th>
<th>100 mg/L</th>
<th>1000 mg/L</th>
<th>2000 mg/L</th>
<th>Assignment</th>
</tr>
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<tr>
<td>3627 $^a$</td>
<td>3627</td>
<td>3627</td>
<td>3627</td>
<td>3627</td>
<td>OH stretching of structural hydroxyl groups $^a$</td>
</tr>
<tr>
<td>3422 $^a$</td>
<td>3433</td>
<td>3433</td>
<td>3433</td>
<td>3333</td>
<td>OH stretching of water $^a$</td>
</tr>
<tr>
<td>1634 $^a$</td>
<td>1634</td>
<td>1634</td>
<td>1633</td>
<td>1631</td>
<td>OH deformation of water $^a$</td>
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<td>1041 $^a$</td>
<td>1057</td>
<td>1043</td>
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<td>Si–O stretching $^a$</td>
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<td>AIOH deformation $^a$</td>
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<tr>
<td>798 $^a$</td>
<td>796</td>
<td>793</td>
<td>792</td>
<td>792</td>
<td>Si–O stretching of quartz and silica $^a$</td>
</tr>
<tr>
<td>778 $^a$</td>
<td>776</td>
<td>77</td>
<td></td>
<td></td>
<td>Si–O stretching of quartz $^a$</td>
</tr>
</tbody>
</table>

$^a$ From [41].

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**Table 2**

Vibration bands (cm$^{-1}$) of crystalline CP and CP intercalated in montmorillonite at initial concentrations of 100, 1000, and 2000 mg/L.

<table>
<thead>
<tr>
<th>CP</th>
<th>CP, this study</th>
<th>100 mg/L</th>
<th>1000 mg/L</th>
<th>2000 mg/L</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
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<td>3030 $^b$</td>
<td>3011</td>
<td>2847, 2920</td>
<td>2847, 2920</td>
<td>2847, 2920</td>
<td>C–H stretching aromatic vibration $^a$</td>
</tr>
<tr>
<td>2962–2853 $^b$</td>
<td>2847, 2920</td>
<td>1473, 1488</td>
<td>1473, 1488</td>
<td>1473, 1488</td>
<td>C–H stretching, alkane $^a$</td>
</tr>
<tr>
<td>1450 $^b$</td>
<td>1413, 1473, 1488</td>
<td>1112</td>
<td>1112</td>
<td>1112</td>
<td>C–C multiple bond stretching, aromatic $^a$</td>
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<tr>
<td>1400–1300 $^b$</td>
<td>1298</td>
<td>648</td>
<td></td>
<td></td>
<td>COOH carboxylate anion stretching</td>
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<tr>
<td>1350–1280 $^b$</td>
<td>1089</td>
<td>1585</td>
<td>1358 $^b$</td>
<td>865 $^b$</td>
<td>C–N vibration, aromatic Z$^+$ amine $^a$</td>
</tr>
<tr>
<td>1220–1020 $^b$</td>
<td>1089</td>
<td>1112</td>
<td>1356</td>
<td>864</td>
<td>C–O stretching of maleate $^a$</td>
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</tbody>
</table>

$^a$ From [43].

$^b$ From [42].
two benzene rings took nearly vertical position in the interlayer of montmorillonite (Fig. 8a). As the c dimension of a dehydrated montmorillonite is 9.6 Å, the distance from the origin of the coordination (center of the octahedral site) to the N on the alkyl chain is 8–9 Å, suggesting that the N on the alkyl chain was close to the basal plane of montmorillonite (Fig. 8b), confirming that the dimethylammonium was responsible for the interaction between the CP molecules and the mineral surfaces speculated in a previous study [36] as well as the band shift due to C–N vibration on the aliphatic tertiary amine as observed in FTIR spectra (Fig. 7a). There would be two locations where the N in the benzene rings was likely found: one close to the basal plane while the other stayed in the middle of the interlayer space (Fig. 8c).

The projected area occupied per CP was around 60 Å² based on crystallographic data [45]. Using the total surface area (TSA) of 725 m²/g determined by polyvinylpyrrolidone sorption [35] and the ESA of 23 m²/g [24], at the CP adsorption capacity of 0.64 mmol/g, the available surface area would be 190 and 6 Å² per CP molecule. Thus, the external surface area alone was too small to accommodate a monolayer adsorption of CP. When the TSA was accessible, the area available to a single CP molecule would be 190 Å², much larger than the CP molecule of 60 Å². Thus, it is the charge density, rather than the TSA that determined the CP adsorption capacity, another evidence to support charge-limited rather than surface area limited adsorption. For the high charge Ca-montmorillonite SAz-1, 170 Å² was available for each CP molecule [36].

Talc is quite hydrophobic. The hydrophilic part of the surface area could be estimated based on the amount of benzyltrimethylammonium adsorbed at the surface area occupied by 60 nm² per molecule [46]. Using this method, the amount of benzyltrimethylammonium adsorbed on talc was 5.3 μmol/g, resulting in a hydrophobic surface of 2 m²/g, that is, 20% of the total surface area [46]. Thus, the hydrophobic interaction may also play an important role in CP removal at high solution pH under which the CP would be a neutral molecule. Adsorption of naphthalene on talc in aqueous solution was strongly dominated by the hydrophobic surface of the talc and the major mechanism was due to van der Waals forces [47].

In a previous study, the surface charge of talc was determined to be \( -3 \mu\text{eq/g} \) [48], about the same magnitude of 5.3 μmol/g as determined by benzyltrimethylammonium adsorption [35]. It was proposed that the basal planes of talc carried a negative charge over a wide pH range while the edges of talc underwent a change from positive to negative when pH was above 7.7 [40]. Four talc samples studied by Charnay et al. [46] resulted in a BET surface area of 10 m²/g. Using this surface area and the amount of CP removed, the calculated adsorption density would be 30 Å² per CP molecule based on a monolayer coverage. Thus, for CP removal by talc, bilayer, or even multilayer adsorption due to hydrophobic interaction would be more likely.

Hydrophobic interaction was attributed to the adsorption of guar, a natural nonionic polysaccharide, onto hydrophobic sites, that is, the talc “face.” In the case of ionically modified guars, the electrostatic contribution to the overall thermodynamics of adsorption was weak [49]. On the other hand, hydrogen bonding rather than electrostatic or hydrophobic force was proposed as one of the main driving forces for guar adsorption on talc [39]. At alkaline pH values, polysaccharide could directly interact with the hydroxilated talc surface by hydrogen bonding; thus, it is not the hydrophobicity of the surface of talc, but the metallic sites of talc that contribute to enhanced adsorption [50].

This study showed that for the purpose of removal of cationic drugs from water, CEC plays an important role. For hydrophilic surfaces, such as those on montmorillonite, cation exchange reaction is the dominant mechanism of CP removal, while for hydrophobic surfaces, such as those on talc, hydrophobic interaction is more important in CP uptake. For the purpose of removal of cationic drugs from water, clays with higher CEC values offer the best option.

4. Conclusions

The removal of CP by montmorillonite was instantaneous with extremely large rate and rate constant. Adsorption of CP on montmorillonite followed a Langmuir isotherm with a capacity of 0.64 mmol/g. Cation exchange was responsible for CP removal by montmorillonite. The XRD and FTIR analyses showed that both external and interlayer adsorption sites were available for CP adsorption. On the contrary, CP adsorption on talc was much lower and was limited to external surfaces only, due to its low charge density. Hydrophobic interaction may also contribute significantly to CP adsorption on talc. Ultimately, it is the charge density of the
2:1 phyllosilicates that governed the removal of cationic organic molecules from water.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2012.01.029.

References