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Binding sites of chlorpheniramine on 1:1 layered kaolinite from aqueous solution

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ABSTRACT

Interactions between chlorpheniramine (CP), an antihistamine drug used to treat allergy, and kaolinite in aqueous solution were investigated under batch studies and molecular simulations. The CP adsorption was relatively fast with a large rate constant. The CP adsorption capacity on kaolinite was 25 mmol/kg, about the same magnitude of the cation exchange capacity of kaolinite. Molecular dynamic simulation showed that the edges of kaolinite were responsible for the uptake of CP, while a net repulsive interaction between the basal plane and CP molecules was obtained. As the broken bond effect of kaolinite was strongly affected by solution pH via protonation–deprotonation of kaolinite edges, a higher CP adsorption was achieved under neutral to weak alkaline solution. It was the charge density, rather than the surface area, that ultimately controlled the amount of CP adsorption on kaolinite.

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Introduction

Emerging organic contaminants (EOCs) detected in groundwater may have adverse effects on human health and aquatic ecosystems [1]. Among the EOCs, frequent detection of residues of pharmaceuticals and personal care products (PPCPs) in final effluents of wastewater treatment plants (WWTPs) throughout many countries in the world [2–6] resulted in great attention on renewed study of their interactions with solid substrates. A more recent report [7] documented numerous PPCPs found in the Great Lakes region in US. In addition to the detection in the final effluent of WWTPs, concentrations from nanogram to microgram per liter are present in groundwater for a large range of EOCs as well as their metabolites and transformation products [1].

By far, EOCs have not been widely studied compared to other anthropogenic contaminants, and there is a paucity of information on their occurrence and fate in the aquatic environment [1]. In addition, fundamental research on the sorption and degradation of EOCs in soil and aquifer material is required to develop predictive modeling capabilities for EOCs in the subsurface environment [1]. For these reasons, many studies were conducted to investigate interactions between model sorbents and different types of PPCPs [8–10]. Often montmorillonite was used as the representative solid and antibiotics such as tetracycline (TC) and ciprofloxacin (CIP) as model PPCPs [9,11,12]. Adsorption and interaction between antibiotics and other natural occurring materials include iron and aluminum hydroxide were also investigated [13,14]. At a larger scale, a lysimeter study was performed to investigate the fate of sulfonamide, tetracycline, and macrolide groups in a clay soil, and soil analyses at the end of the experiment showed almost no antibiotic residues remained [15].

Most of the earlier studies on the interactions between chlorpheniramine (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 [16]. A two-step process including a cation exchange reaction followed by strong surface chemisorption was attributed to binding interactions between CP and montmorillonite [17]. An expansion of *d*-spacing after CP adsorption on montmorillonite confirmed interlayer adsorption and intercalation of CP [18,19].

Kaolinite, as a major soil mineral component, is widely distributed in soils of tropical to subtropic climate regions. It has a pH-dependent surface charge and limited cation exchange capacity (CEC). Thus, it has the benefit of being used as the model sorbent to study the interactions between ionic molecules and pH-dependent sorbents, since ionic molecules can have more complex behaviors as their fate varies with pH conditions [1]. In the presence of kaolinite for drug formulation, the amounts of the active

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drugs, such as chloroquine and CP tablets, amoxycillin/clavulanic acid, and ampicillin/cloxacillin powder, released into the dissolution medium from the formulations was greatly reduced [20]. Cation exchange and the electrostatic interaction between kaolinite and the tertiary amine of amitriptyline, the most commonly prescribed tricyclic antidepressant, was attributed as the dominant mechanism for the uptake of amitriptyline on kaolinite [21]. Furthermore, modeling to quantitatively determine the structure-activity relationship is increasingly used as a tool for environmental toxicological studies and the large number of potential compounds and lack of fundamental properties for many EOCs make this approach with obvious future applications for understanding the fate of EOCs in the environment [1]. For these reasons, we selected kaolinite as the model clay and CP as the model ionizable drug to investigate their sorption and interaction in aqueous solution and to determine the dominant sorption sites and sorption mechanism.

Materials and methods

Materials

The kaolinite used was KGa-1b, a well crystallized reference kaolinite obtained from the Clay Mineral Repositories in Purdue University (West Lafayette, IN). Its physico-chemical properties were well documented. To facilitate comparison with numerous previous studies on this mineral, it was used without further purification. It contained 96% of kaolinite, 3% of anatase, and 1% crandallite [22]. It has a CEC of 30 $mmol_c/kg$ with Mg^{2+} and Ca^{2+} as the major exchangeable cations [23], and a specific surface area (SSA) of 10 m^2/g determined using polyvinylpyrrolidone sorption [24], as well as 12 and 13 m^2/g measured by a N_2 BET method [25,26]. The edge surface area was about 30% of the SSA [27]. Scanning electron microscopic observation showed pseudohexagonal kaolinite plates dominating the matrix with about 58% particles less than 2 μm [25]. A mean particle size of 2.3 μm and mean area-based particle size of 1.5 μm were determined using a BT-9300S laser particle size analyzer (Dandong Baite Instrument Co. Ltd., China).

The chlorpheniramine maleate (CAS #: 23095-76-3), also called chlorphenamine, was obtained from Wei Li Pharmaceutical Co. Ltd. (Tainan, Taiwan). It has a formula weight of 390.9 g/mol, a water solubility of 1–5 g/100 mL at 21 °C with a log K_{OW} value of 3.38 [8], and pK_a values of 9.2 and 4.0 due to protonation of both nitrogen atoms (Fig. 1) [28]. On the other hand, the counterion maleic acid is a diprotic acid with pK_a values of 1.9 and 6.6. Thus, 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, maleate is a monovalent anion and CP is a monovalent cation, resulting in a charge balance. When solution pH is between 6.6 and 9.2, divalent maleate is the dominant counterion while CP is a monovalent cation. Above pH 9.2, CP became a neutral molecule while maleate is a divalent anion.

Batch experiments

The initial CP concentrations varied from 80 to 4000 mg/L for the adsorption isotherm study and were fixed at 1000 mg/L for the kinetic study and pH dependency study. The mass of kaolinite used was 1 g while the volume of solution used was 10 mL for all studies except the kinetic study, in which 25 ml of solution was used. The solid and solution were combined in each 50-mL centrifuge tube and shaken for 24 h at 150 rpm and room temperature for all studies except the kinetic study, in which the shaking time was 0.5, 1, 1.5, 2, 4, 6, and 8 h. After the mixtures were centrifuged

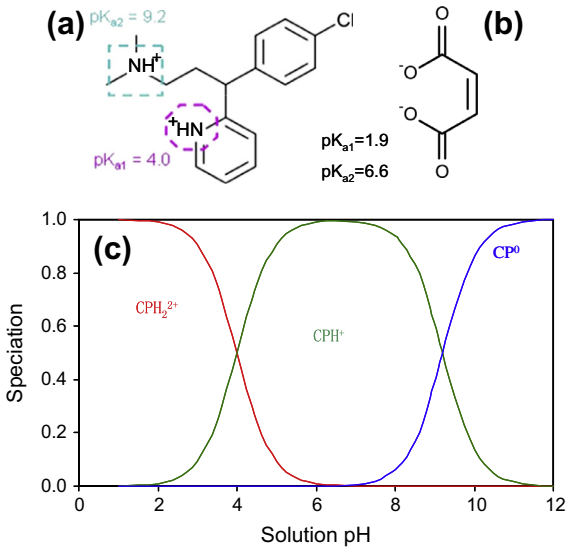

Fig. 1. Molecular structure of chlorpheniramine (a), counterion maleate (b), and speciation of CP under different pHs (c).

at 7600 rpm for 20 min, the supernatants were filtered through 0.45 μm syringe filters before being analyzed for equilibrium CP concentrations. All experiments were performed in duplicates for each experimental condition.

Instrumental analyses

The equilibrium CP concentrations were analyzed with a UV–Vis spectrophotometer (Model T6 New Century 1650, made by General Instrument, Inc. LLT, Beijing China) at the wavelength of 264 nm, corresponding to its maximal absorbance [29–31]. Calibrations were made using standards of 10, 20, 30, 40, 50, and 60 mg/L with a regression coefficient of 0.9998. The amount of CP adsorbed was calculated from the difference between the initial and final concentrations.

Powder XRD analyses were performed on a Rigaku D/max-IIIa diffractometer (Tokyo, Japan) with a Ni-filtered Cu Kα radiation at 30 kV and 20 mA. Orientated samples were 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

Molecular simulation was performed using the module Forcite of Materials Studio 5.0 software to investigate the sorption sites of CP on kaolinite. Kaolinite is a dioctahedral 1:1 phyllosilicate. Each layer consists of a tetrahedral SiO_4 sheet and an octahedral $Al(O,OH)_6$ sheet bound to each other via inner vertex oxygen centers with a unit cell $Al_4Si_4O_{10}(OH)_8$. These two sheets are connected via hydrogen bonds [32]. The kaolinite model was constructed and the atomic coordinates were derived from the space group of C1 with a = 5.15 Å, b = 8.93 Å, c = 7.38 Å, α = 91.93°, β = 105.04°, γ = 89.79° [33]. The supercell of the model was made of 64 kaolinite unit cells at $8a \times 4b \times 2c$. On the surface of XOY, or the (0 0 1) surface, the area was 41.19 Å × 35.72 Å. while for the surface of XOZ, or the (0 1 0) surface, the area was 41.19 Å × 14.76 Å.

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