



# Concept model of the formation process of humic acid–kaolin complexes deduced by trichloroethylene sorption experiments and various characterizations



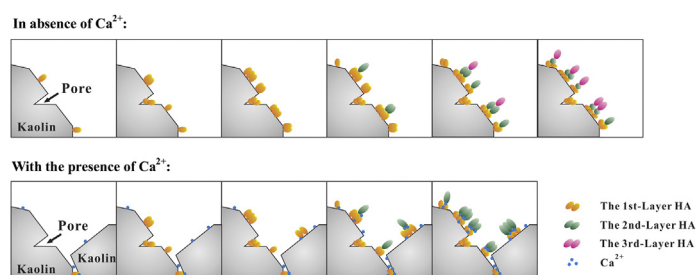
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## HIGHLIGHTS

- Interactions between humic acid (HA) and kaolin during the formation of their complexes were confirmed.
- $\text{Ca}^{2+}$  could enhance HA and kaolin self-aggregations and impact HA-kaolin interactions.
- HA would first patch onto charged kaolin surface sites and filled the pores, and subsequently form a multilayer loading on kaolin.

## GRAPHICAL ABSTRACT



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## ABSTRACT

To explore the interactions between soil organic matter and minerals, humic acid (HA, as organic matter), kaolin (as a mineral component) and  $\text{Ca}^{2+}$  (as metal ions) were used to prepare HA-kaolin and Ca-HA-kaolin complexes. These complexes were used in trichloroethylene (TCE) sorption experiments and various characterizations. Interactions between HA and kaolin during the formation of their complexes were confirmed by the obvious differences between the  $Q_e$  (experimental sorbed TCE) and  $Q_{e,p}$  (predicted sorbed TCE) values of all detected samples. The partition coefficient  $k_d$  obtained for the different samples indicated that both the organic content ( $f_{om}$ ) and  $\text{Ca}^{2+}$  could significantly impact the interactions. Based on experimental results and various characterizations, a concept model was developed. In the absence of  $\text{Ca}^{2+}$ , HA molecules first patched onto charged sites of kaolin surfaces, filling the pores. Subsequently, as the HA content increased and the first HA layer reached saturation, an outer layer of HA began to form, compressing the inner HA layer. As HA loading continued, the second layer reached saturation, such that an outer-third layer began to form, compressing the inner layers. In the presence of  $\text{Ca}^{2+}$ , which not only can promote kaolin self-aggregation but can also boost HA attachment to kaolin, HA molecules were first surrounded by kaolin. Subsequently, first and second layers formed (with inner layer compression) via the same process as described above in the absence of  $\text{Ca}^{2+}$ , except that the

**Abbreviations:** HA, humic acid; KL, kaolin; TCE, trichloroethylene; HA-KLs, HA-kaolin complexes; Ca-HA-KLs, Ca-HA-kaolin complexes; Ca-KL, Ca-kaolin complex; SEM, scanning electron microscopy; FT-IR, Fourier translation infrared; ECD, electron capture detector.

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second layer continued to load rather than reach saturation, within the investigated conditions, because of enhanced HA aggregation caused by  $\text{Ca}^{2+}$ .

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## 1. Introduction

The sorption behavior of organic pollutants in geological environments is an important factor that directly affects the migration, the transformation, and even the fate of organic pollutants. The soil sorption of organic pollutants depends on both the organic matter as well as the mineral components of the soil (Mader et al., 1997). As a matter of fact, organic matter and mineral components always bind and form organic-mineral complexes, thereby changing the properties of the resulting mineral surfaces as well as the structures of the associated organic matter, which could theoretically affect the soil sorption capacities of organic pollutants. In this regard, scholars represented by Karickhoff (1981) proposed the theoretic partition model. McCarty et al. (1981) maintained that the overall geosorbent adsorption could be calculated by adding the contributions of all individual sorption domains. Later in the 1990s, Huang et al. (1997) and Weber et al. (2002, 1992) presented a distributed reactivity model, Xing and Pignatello (1996; 1997) and Pignatello and Xia (2000) proposed the dual-mode model, researchers represented by Abraham put forward poly-parameter Linear Free Energy Relationships (Abraham, 1993; Abraham et al., 2004; Goss, 2005), and Gunasekara et al. (2003) proposed that, during the process by which organic matter and minerals interact and form complexes, organic matter near the mineral surfaces would transform into a condensed structure that affect their adsorption behavior.

Recent research has focused predominantly on physical characteristics of geosorbents or the influences of organic components on sorption behavior, with only a few investigations regarding organic-mineral interactions and their effect on the sorption of pollutants. The modes of soil-occurring organic-mineral interactions that have been presented in recent years are summarized below. Leinweber and Schulten (1999) proposed that large particles of organic aggregates can combine with mineral surfaces via a variety of mechanisms. Ransom et al. (1998) put forward that organic matter can attach to mineral surfaces in patches. Wershaw (1993) asserted that the process by which organic matter loads onto mineral surfaces forms double molecular layers. And according to Kleber et al. (2007), electrostatic attraction and hydrophilic/hydrophobic interactions occur among these vertically oriented multi-molecular layers. Behera et al. (2010) noted the competitive sorption of organic compounds by organic matter on mineral surfaces and in solution. Mayes et al. (2013) illustrated that organic molecules can fill micro-pores in minerals. Although all of these studies explored the mechanisms of organo-mineral interactions, relatively few of them investigated these processes/interactions in detail or the effects of these processes/interactions on overall adsorption. The present study focuses on these issues.

In natural environments, metal cations present wildly and significantly affect the formation of organic-mineral complexes and their sorption of hydrophobic organic pollutants. Metal cations like  $\text{Ca}^{2+}$  not only can induce the aggregation of mineral particles (Leong et al., 2012; Zhong et al., 2011a, 2011b) but can also enhance interactions between organic matter to form aggregates (Kloster et al., 2013; Myneni et al., 1999; Tsang et al., 2009). HA is a type of diverse organic electrolyte found in soil and natural bodies of water (Myneni et al., 1999). A common organic pollutant in

groundwater, trichloroethylene (TCE), was chosen as the typical organic contaminant in the present study. Meanwhile, sample HA-kaolin and Ca-HA-kaolin complexes exhibiting various  $f_{\text{om}}$  values were prepared for TCE sorption experiments and several different characterizations, such that the interactions between organic matter and minerals during the formation of complexes as well as the impacts of  $\text{Ca}^{2+}$  on these interactions could be investigated and a theoretical basis for further investigations of organic-mineral interactions and mechanisms in naturally occurring soil could be obtained.

## 2. Materials and methods

### 2.1. Materials

HA and kaolin were used as the organic matter and mineral parts, respectively, of the geology adsorbent used to prepare samples of HA-kaolin complexes (HA-KLs) and Ca-HA-kaolin complexes (Ca-HA-KLs). CP-grade HA and kaolin were both purchased from Sinopharm Chemical Reagent Co., Ltd. AR-grade TCE was purchased from Beijing Chemical Works.

### 2.2. Samples preparation

HA (1.00, 2.00, 3.00, 4.00, 5.00, 6.00, 8.00, 10.00 and 12.00 g) was mixed with 50.00 g kaolin and added to 150 mL of ultrapure water at pH 9.0 to enhance HA dissolution. These suspensions were flat-laid and shaken for 7 d at 25 °C (Leone et al., 2002; Lahlou et al., 2000) at a speed of 200 rpm, after which they were freeze-dried, gently ground and filtered using a 250-mesh sieve, such that HA-KLs were obtained (C1, C2, C3, C4, C5, C6, C8, C10 and C12).

The preparation of Ca-HA-KLs (Ca1, Ca2, Ca3, Ca4, Ca5, Ca6, Ca8, Ca10 and Ca12) and Ca-kaolin (Ca-KL) complexes was the same as that used to prepare HA-KLs except that ultrapure water (in the latter) was replaced by 0.5 mol L<sup>-1</sup> CaCl<sub>2</sub> solution (in the former).

### 2.3. Characterization

Mineral composition analysis, elemental composition analysis, specific surface area and pore analysis, FT-IR spectra and scanning electron microscopy (SEM) were performed on HA, kaolin and all complexes considered herein (Table 1).

The mineral compositions of the samples were determined using an X-ray diffractometer (Rigaku Denki Co., Ltd, D/MAX 2500) under the following working conditions: 60 °C oven temperature, natural dried samples, 2.6°–45° scanning range (whole rock analysis), 6°·min<sup>-1</sup> scanning speed.

The elemental compositions (C, N and H) of the samples were determined using an Elementer Vario EL cube NHNS/O analyzer. The sample decomposition method employed dynamic combustion and exhibited a detection range of 0.004%–100%.

Specific surface area and pore analysis were performed on all samples using a Micrometer ASAP2010 specific surface & pore size distribution measuring instrument (BET nitrogen adsorption method). Samples were dried at 100 °C as pretreatment. The ambient temperature was 22 °C, the analysis bath temperature was approximately -196 °C, and the time required for the reaction to

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