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Q1 **Formation process and mechanism of humic acid-kaolin**
 2 **complex determined by carbamazepine sorption experiments**
 3 **and various characterization methods**

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A B S T R A C T

To explore the formation process and mechanism of organic matter and organic-mineral 16
 complex under humification and mineralization conditions, a series of samples including humic 17
 acid, kaolin, and humic acid-kaolin complex were prepared using a subcritical water treatment 18
 method (SWT) under specific temperature, pressure and reaction time conditions. HA was used 19
 as a surrogate for natural organic matter because it has a similar abundant pore structure, 20
 variety of carbon types, and chemical components. These samples were used in carbamazepine 21
 (CBZ) sorption experiments and characterized by a variety of techniques. The polymerization of 22
 humic acid under the conditions of increased temperature and pressure resulted in an increase 23
 in specific surface area and molecular quantity. In addition, the degree of aromaticity rose from 24
 59.52% to 70.90%. These changes were consistent with the transformation from 'soft carbon' to 25
 'hard carbon' that occurs in nature. The results of sorption experiments confirmed the 26
 interaction between humic acid and kaolin from the difference between the predicted and 27
 actual Q_e values. The conceptual model of humic acid-kaolin complex could be deduced and 28
 described as follows. Firstly, the aromatic components of humic acid preferentially combine 29
 with kaolin through the intercalation effect, which protects them from the treatment effects. 30
 Next, the free carboxyl groups and small aliphatic components of humic acid interact on the 31
 surface of kaolin, and these soft species transform into dense carbon through cyclization and 32
 polymerization. As a result, humic acid-kaolin complex with a mineral core and dense outer 33
 carbonaceous patches were formed. 34

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49 **Introduction**

50 Organic matter and clay minerals are the most important
 51 components of geosorbents found in nature in various forms,
 52 such as soil, sediment, vadose and aquifer mediums. They
 53 usually form an organic whole and commonly experience

changes in geological conditions, such as mineralization and 54
 humification. Organic-mineral complex are the product of 55
 mineralization and humification. In the natural state, with 56
 changes in burial conditions, temperature, and geological time, 57
 mineralization and humification often change the structure, 58
 composition, content, and stability of organic matter, and the 59

Abbreviations: HA, humic acid; KL, kaolin; CBZ, carbamazepine; SWT, subcritical water treatment; SSA, specific surface area analysis; FT-IR, Fourier transform infrared; XRD, X-ray diffraction; ¹³C-NMR, ¹³C nuclear magnetic resonance.

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specific surface area, crystallinity, and crystal spacing of clay minerals (Schmidt et al., 2011; Theng et al., 1993). In addition, these geosorbents play an important role in the migration, transformation and fate of pollutants, including organics, radioactive elements, and so on. (Yu et al., 2016; Wang et al., 2016). Previous studies described the overall sorption of organic pollutants on geosorbents as the sum of the different sorptive components (McCarty et al., 1981), i.e., the combination of the mineral and organic matter components (Stenzel et al., 2013; Endo and Goss, 2014; Zhao et al., 2014). Thus, the interaction between organic matter and clay minerals was ignored in the complicated complex systems. However, recent studies confirmed that a complex interaction occurs between these two components within soil, which is influenced by the structures and properties of the components as well as the environment (Lahlou et al., 2000; Leone et al., 2002; Pronk et al., 2012). Previous studies have led to the development of a widely accepted interaction mechanism between organic matter and clay minerals, as summarized below. The primary mode of interaction involves the sequestration or protection of organic matter by microporous minerals (Mayes et al., 2013), where organic matter inserts into the expandable silicate intercalation layers (Kennedy et al., 2002) or other pores within minerals (Kaiser and Guggenberger, 2003). The second mode of interaction involves patches of surface functional groups, with organic matter containing various active groups adhering to the surface of minerals through coordination (Torn et al., 1997), ion-bridge (Ellerbrock and Kaiser, 2005) and electrostatic interactions. The third mode of interaction, on the basis of patch expression (Ransom et al., 1998), involves inner associated organic matter combining with the outer molecules via hydrophobicity and accumulation (Kleber et al., 2007; Petridis et al., 2014). However, if the formation of complex comes solely from the selective combination of minerals with some components of organic matter, with no accompanying changes to the properties of the organic matter, then the sorption capacity of complex should be less than or equal to the sum of the capacity of the two components. Therefore, it will be difficult to explain the phenomena that the sorption capacity of trichloroethylene on organic-mineral complex was bigger than the sum of minerals and organic matter components at several mass ratios (Zhu et al., 2016). For this reason, researchers have become interested in investigating the properties of the organic matter in complex. Gunasekara and Xing (2003) reported that amorphous organic carbon rearranges on the surface of clay minerals, resulting in denser structures when the complex are formed. Sparks and Chen (2013) discovered that spatially distinct regions within soil clay particles have highly variable carbon functional group compositions. Additionally, these researchers determined that polysaccharides preferentially attach to thin and small particles or on the outer region of clay particles, while aromatic structures and carboxyl groups mainly distribute along the inner surface of the mineral, in dense and thick deposits. For this reason, it is necessary to explore the structure and property changes of organic matter and clay minerals separately, while also taking environmental factors into account. In addition to numerous geological conditions, the critical factors that affect the properties and structures of the organic matter (Kenji et al., 2009) and clay minerals (Junet et al., 2013; Larissa et al., 2014) include, the buried depth (pressure) (Theng and Hashizume,

1996; Funatsu et al., 2004), temperature and time. Thus, a method to simulate natural effects was required in this experiment. Previous studies reported the use of subcritical water treatment (SWT) for the preparation of real and artificial soil samples (Hawthorne et al., 1994; Miller and Hawthorne, 2000; Tavakoli and Yoshida, 2005). Johnson et al. (2001) kept peat and shale at various temperatures and pressures and found that the samples changed significantly after treatment, as revealed by spectral analysis. Therefore, it seems that subcritical water acts as not only a solvent but also as a reaction agent and catalyst (Lopez-Sangil and Rovira, 2013).

Humic acid (HA) is a macromolecular polymer formed by plants and animals through long-term physical, chemical, biological processes. It is one of the most active multiphase components in soil, with a complex chemical structure including carboxyl, phenolic, ketone and other active groups (Song et al., 2017). Kaolin (KL) is a kind of clay and clay rock. The main component is kaolinite group clay minerals. The structure of KL is composed of interlinked silicon-oxygen tetrahedra and aluminum-oxygen octahedra, with high porosity and SSA. It is representative of clay minerals found in soil. Consequently, a series of samples containing commercial HA, KL and their complex were prepared by controlling the conditions of the SWT. Carbamazepine (CBZ), a typical organic contaminant used in current studies, was chosen as the sorbate for all samples in this experiment. The differences between the predicted value of the sorption capacity, based on components theory, and the actual value for each organic-mineral complex, were determined. The mechanism of formation of organic-mineral complex as well as the changes in the properties of the two components were determined under the conditions of SWT via measurement of sorption parameters and various characterization methods.

1. Materials and methods

1.1. Materials

HA and KL were used as the organic matter and mineral components of the geological adsorbent to prepare the organic-mineral complex. HA used in this experiment was commercial chemically pure grade, purchased from Sinopharm Chemical Reagent Co., Ltd. The material is a black powder containing aromatic rings and alicyclic rings in its basic structure. KL in this experiment was in the form of white powder or fragments (chemically pure). The main component was kaolinite group clay minerals with 2.54–2.60 g/cm³ density. KL was also purchased from Sinopharm Chemical Reagent Co., Ltd. The type of pressure kettle used in this experiment was model CJ-1/15.0-S30408 (effective volume, 1000 mL; designated temperature, 400°C; designated pressure, 15 MPa; nickel plated walls), customized from Xinyuan Chemical Mechanical Reagent Co., Ltd. CBZ (C₁₅H₁₂N₂O; 5H-dibenzo[b,f]azepine-5-carboxamide) was acquired from Beijing Chemical Works (purity ≥ 99.0%). CBZ is a drug commonly used in the treatment of epilepsy and neuropathic pain as well as of schizophrenia and bipolar disorder. The accumulation of CBZ in food crops grown on soils or groundwater poses a significant risk to human health. Ultra-pure water with very low conductivity, dissolved colloidal

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