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Probing the interactions between lucigenin and phyllosilicates with different layer structures

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ABSTRACT

The incorporation of organic fluorescent dyes into inorganic matrixes could greatly improve the luminous properties of organic dyes. In this study, we investigated the effect of three different types of layered mineral clays on the luminous properties of lucigenin (bis-*N*-methylacridinium nitrate, BNMA). Attempts were made to fit the isothermal data using Langmuir and Freundlich equations. The adsorption of BNMA onto montmorillonite and kaolinite were fitted well by Langmuir isotherm equation while that of BNMA onto rectorite was fitted by Freundlich equation. The results indicated that the adsorptive behavior, which was resulted from the different layer structures, had a direct impact on the luminous properties of the composites.

1. Introduction

Organic fluorescence materials have been one of the most important research fields in many subjects, such as chemistry and materials chemistry [1,2]. Compared with traditional inorganic fluorescence materials, organic fluorescence materials has the following advantages: high quantum efficiency, good flexibility, bright colors and easy to product in large-scale [3], which enables them to show broad prospects in the development of multi-color display and lighting device and has attracted much attention. However, the application of organic luminescent dyes was limited because of low intensity and fluorescence quenching induced by aggregation [4,5]. Therefore, much effort was focused on the fabrication of hybrid materials to improve the stability of organic dyes [6,7]. SiO_2 [8], TiO_2 [9] and other porous inorganic [10–12] matrixes were applied to reduce the fluorescence quenching by establishing covalent bonds between dye molecules and the surfaces of inorganic matrixes. Whereas, the methods listed above are not universal for many other luminous dyes, not to mention the complexity of some of the processes. Using charged inorganic layered materials as a carrier to prepare organic/inorganic materials is getting more and more attention [13,14] The incorporation of photoactive organic dyes into inorganic matrixes such as montmorillonite (MMT), phyllosilicate and layered double hydroxide has been reported as well [15,16]. To avoid aggregation and fluorescence self quenching of the dyes, a hydrophobic surfactant was introduced that suppressed the aggregation of the dyes [17]. Dye aggregation could be reduced by adsorbing fluorescent dye into C12TMA modified laponite films and the fluorescence ability of the dye could be enhanced [18].

Kaolinite (KLN), MMT, and rectorite (REC) are three typical layered silicate clays. KLN has a 1:1 layer structure, with the basic unit made up of a tetrahedral sheet of SiO_4 and an octahedral sheet with Al^{3+} as the octahedral cation. MMT is composed of units of two silica tetrahedral sheets with a central alumina octahedral sheet. REC is a 1:1 regular interstratification of a dioctahedral mica and a dioctrahedral MMT [19]. Isomorphic substitution within the layers (e.g., Al^{3+} usually replaced by Mg^{2+} or Fe^{2+}) generates a negative charge, and the excess of negative charge is balanced by hydrated cations (Na^+, K^+ and Ca^{2+}) in the interlayer region [20]. The exchangeable cation in the interlayers is defined by the cationic exchange capacity (CEC), the common order of CEC of these three clays is as follow: KLN < REC < MMT. Large specific surface areas (SSA), chemical and mechanical stability, layered structure, high CEC (especially for MMT and REC) have made the clays excellent adsorbent materials [21,22]. In spite of the numerous studies during the past decades, the main focus was on the environmental aspects that the clays played [23–25], such as adsorption of heavy metal ions [26,27] and other organic pollutants [28].

As an organic fluorescent dye, the application of BNMA was restricted by fluorescent quenching. In one of our previous works [29],

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we observed that tunable layer charges of a certain phyllosilicate could inhibit the fluorescence quenching of BNMA in different degrees. Nevertheless, the role of silicate layers that could be an important part for the inhibition of fluorescence quenching was not mentioned yet. The purpose of this study is to investigate the adsorption of BNMA onto three different types of phyllosilicates KLN, REC and MMT and the relationship between layer structures and fluorescence quenching. The isotherm, kinetics as well as thermodynamic parameters for the adsorption of BNMA onto the clays were studied in detail. The relationship between adsorption and fluorescent intensity was discussed as well.

2. Materials and methods

2.1. Materials

The REC was obtained from Zhongxiang, Hubei, China. The MMT was from Nicheng, Inner Mongolia, China. The KLN was provided by China Kaolin Clay Co., Ltd. They were used without further purification. The SSA was 62.2 $m^2 \cdot g^{-1}$ for MMT, 26.6 $m^2 \cdot g^{-1}$ for KLN, and 22.3 $m^2 \cdot g^{-1}$ for REC. The BNMA was purchased from J&K, China, which has a pKa1 value of 3.3 and a pKa2 value of 5.1. Since the pH value of equilibrium solution was 3–5, most of the BNMA existed as monovalent cation during the adsorption.

2.2. Instruments and methods

A. UV–Vis spectrophotometer (T6) was used for the determination of BNMA at 368 nm. Calibration was made with 6 standards from 0.004 to 0.04 $mmol \cdot L^{-1}$ with the value of R^2 no less than 0.99.

Powder XRD analysis was performed on a Rigaku D/max-IIIa diffractometer (Tokyo, Japan) with a Ni-filtered CuKα radiation at 40 kV and 20 mA. Orientated samples were scanned from 3° to 70° with a scanning speed of 2°/min with a scanning step of 0.01°.

The FTIR spectra were acquired using a Nicolet-560 spectrometer (Thermal Nicolet Co. USA) from 500 to 4000 cm^{-1} with a nominal resolution of 4 cm^{-1} using the KBr pressing method.

The powders were added into the mould (provided by the equipment supplier), pressed with a slide, and then covered by a quartz plate. Put the mould together with quartz plate in the test chamber of the fluorescence spectrophotometer. The emission spectra of the samples were measured by a fluorescence spectrophotometer (F-4600, HITACHI, Japan) equipped with a photomultiplier tube and a 150 W Xe lamp used as the excitation lamp and the 370 nm pulse laser radiation was used as the excitation source. The life time was recorded on a spectrofluorometer (FS5, Edinburgh Instruments), and a 370 nm pulse laser radiation (nano-LED) was used as the excitation source.

Molecular simulation was performed under the module 'FORCITE' of Materials Studio 6.0 software to investigate the sorption of BNMA in the interlayers of MMT and REC, as well as the surface sorption of BNMA onto KLN. The primitive unit cell of the clays was characterized by the following parameters: a = 5.18 Å, b = 8.98 Å, c = 15.00 Å, α = γ = 90°, β = 99° for MMT; a = 5.14 Å, b = 8.91 Å, c = 7.26 Å, α = 91.76°, β = 104.67°, γ = 90° for KLN; and a = 5.189 Å, b = 8.996 Å, c = 23.096 Å, α = γ = 90°, β = 96.3° for REC. Based on the primitive unit cell, a series of 3 × 2 × 1 supercells were built for KLN, and 2 × 2 × 1 for REC and 2 × 2 × 2 for MMT. The constructed model was optimized geometrically. The simulation was performed at the temperature of 298 K and simulation time 1ns with a time step of 1 fs? Van der Waals force and electrostatic force were used during simulation.

2.3. Batch experiment

For all batch experiments (each repeated twice), the amount of clays used was 0.10 g, while the volume of solution was 25.00 mL. They were mixed in 50 mL centrifuge tubes in an air oscillator at 150 rpm at room temperature for a certain time and centrifuged at 8500 rpm for 5 min. The supernatant was then filtered through 0.22 μm syringe filters before being taken to a UV–Vis spectrophotometer for the analysis of equilibrium concentrations. For thermodynamic study, the initial concentrations were set differently based on the adsorption capacity of the clays, as shown in Table 1. For batch kinetic study, the initial concentration of BNMA was 1.8 $mmol \cdot L^{-1}$ for MMT, 1.6 $mmol \cdot L^{-1}$ for REC and 0.3 $mmol \cdot L^{-1}$ for KLN, respectively. The mixtures were shaken for 0.5, 1, 5, 15, 30, 60, 120 and 300 min at room temperature.

Table 1
Initial concentrations of BNMA for thermodynamic study of BNMA sorption on different clays.

Clay	Initial Concentrations ($mmol \cdot L^{-1}$)									
MMT	0.02	0.05	0.1	0.2	0.4	1.0	1.6	1.8	2.0	
REC	0.05	0.1	0.2	0.3	0.4	0.8	1.0	1.2	1.6	2.0
KLN	0.002	0.004	0.01	0.02	0.05	0.1	0.2	0.3		

3. Results and discussion

3.1. BNMA sorption isotherms

In order to study the adsorption equilibrium of BNMA, Langmuir and Freundlich isotherm model were applied to simulate the equilibrium characteristics of the adsorption. The linearized form of Langmuir and Freundlich adsorption isotherms are as follows.

The Langmuir model [30]:

$$\frac{1}{q_e} = \frac{1}{q_{\max} K_L C_e} + \frac{1}{q_{\max}}$$

The Freundlich model [31]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where q_e ($mmol \cdot g^{-1}$) and q_{max} ($mmol \cdot g^{-1}$) are the amount of BNMA adsorbed at equilibrium time and the maximum quantity of BNMA per unit clay to form a complete monolayer on the surface, respectively. C_e ($mmol \cdot L^{-1}$) is the equilibrium solute concentration. K_L ($L \cdot mmol^{-1}$) is Langmuir affinity, which represents enthalpy of sorption and related to temperature. K_F and n are the Freundlich constants related to the sorption capacity and sorption intensity, respectively. The correlation coefficient (R^2) calculated from Langmuir and Freundlich isotherm models are list in Table 2 and the sorption isotherms were shown in Fig. 1.

It is obviously clear that the relative parameters R^2 (0.9995 and 0.996) for the Langmuir model was higher than that (0.898, 0.956) of the Freundlich for both MMT and KLN. These results indicated that it is more likely for BNMA to form monolayers while adsorbed onto MMT and KLN, and that the processes of adsorption were homogeneous. However, while adsorbed onto REC, the adsorption isotherm fits the Freundlich model better, indicating multilayer sorption of BNMA onto the surface of REC.

Meanwhile, it can be seen from Table 2 that the maximum adsorption amounts of the three clays are in the following order: KLN < REC < MMT. It shows a good agreement with the order of their CEC. It is possible that the adsorption process mainly depends on the exchange of the cations of the three clays. KLN has a low CEC of the order of 3–15 meq/100 g (0.12 meq/g in our case) and therefore it is not expected to be an ion-exchanger of high order. The small number of exchange sites is located on the surface of kaolinite and it has no interlayer exchange sites [32]. Thus, the theoretical maximum adsorption amount of KLN was only 0.0196 $mmol \cdot g^{-1}$. Due to the swelling property of MMT and REC, they demonstrated higher adsorptive capacities than KLN [33]. Between MMT and REC, MMT had a much higher

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