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Fabrication of bentonite nanosheets from natural bentonite using ultrasonic-assisted liquid phase exfoliation method and its application for adsorptive removal of Methylene Blue from water

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ABSTRACT

Clays (especially bentonite) are widely used as barriers in landfills to prevent contamination of subsoil and groundwater by leachate containing heavy metals or toxic organics. However, the future application of bentonite nanomaterials is still limited due to complicated and expensive preparation process requiring several steps, toxic chemical agents, or additional surfactants. In this study, a green approach was proposed to produce bentonite nanoplatelets by an ultrasound-assisted liquid-phase exfoliation method using natural clay minerals containing bentonite as a precursor. The materials were then characterized by SEM, BET, AFM and XRD. The produced material was used to remove methylene blue (MB) from aqueous solution by batch adsorption. Results showed that the bentonite nanoplatelets gave high adsorption ability with Langmuir maximum adsorption capacity of 312.50 mg/g, which could be a good adsorbent for removing dyes and other toxic organics in wastewater.

Introduction

Bentonite, a kind of adsorbent clay, has attracted much research attention due to its wide application in body heath [1], metal ions removal [2,3], electrochemical sensors [4], improving soil and aquaculture conditions [6], treatment of radioactive waste [7], as adsorbent for water and wastewater treatment [5]. As expandable montmorillonite, bentonite contains 2:1 type of mineral with one Al^{3+} octahedral sheet as its unit layer structure [5]. Interlayer water presents between these layers and tends to form hydrate with cation composition, which makes montmorillonite easy to swell and form micron-sized particles with high internal and external surface area [5],[8]. In contrast to inorganic nanomaterials, specific nano-structured bentonite syntheses seem

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surprisingly sparse. To date, most investigations on bentonite have been carried out only in the solid-state and studies of their properties were limited to investigations at the macroscopic scale. The potential use of bentonite would seem to be very extensive as nanometer-scaled materials often exhibit the new interesting size-dependent physical and chemical properties that cannot be observed in their bulk analogous. Thus, several modification methods have been developed and applied to improve bentonite's physicochemical properties, including thermal activation, treatment by inorganic acid and alkali, and amendment by metal oxide or organic compounds (e.g. surfactants) [5, 9]. Their practical application is limited because of the required expensive equipment's, strong acids/bases and surfactants to obtain high-quality nano bentonite, therefore, a cost-effective, scalable, and reproducible method for producing bentonite nanomaterial is still a big challenge.

In this study, a facile method was presented for exfoliation of clay mineral containing bentonite into bentonite nanoplatelets using ultrasound-assisted liquid-phase exfoliation. The adsorption activity of the obtained materials was then evaluated as adsorbents for the removal of methylene blue (MB) in water.

Experimental

Clay mineral containing bentonite (taken form Binh Thuan, Vietnam, denoted as B0) was ground, added with 500 mL of 5% NaOH (supplied from Sigma-Aldrich) solution at B0/NaOH ratio of 50:1 (w/w) in a beaker, and stirred at 400 rpm for 15 min. This beaker was then placed in an ultrasonic bath for 60 min (Ultrasons H-D, Selecta 40 kHz, 400W). The collected supernatant was then washed and filtrated with water several times until a neutral pH value was reached. The material was finally dried at 80°C for 48 h (denoted as UB) and kept in a desiccator.

The morphology of the materials was determined by scanning electron microscopy (SEM, Hitachi SU8000) and transmission electron microscopy (TEM, TECNAI G2 20 operated at voltage of 200 kV). Crystalline structure of the materials was examined by using X-ray diffraction (XRD, Bruker D2 Phaser). Atomic force microscopy (AFM) images of materials was obtained using a Digital Instruments Nanoscope III Atomic Force Microscope using silicone tip in tapping mode at 130 kHz.

The experiments for adsorption of MB were conducted at room temperature (~25 ± 2 °C) by stirring 0.05 g of UB in a volume V = 50 mL of MB solution with initial concentration C_o from 22.69 to 340.73 mg/L for 60 min. The initial pH of aqueous solution was chosen at 6.0 ± 0.3 by adding NaOH (1 M) and HNO_3 (1 M). The mixture was then centrifuged at 4000 rpm for 15 min and the supernatant was then taken for determination of equilibrium MB concentration C_e using a UV-Vis spectrophotometer (Hitachi UH5300) at wavelength of 664 nm. The adsorption capacity q (mg/g) and Langmuir coefficients (b and q_{max}) were calculated ~~as~~ by the following equations.

$$q = \frac{(C_o - C_e)V}{0.05} \qquad (1)$$

$$\frac{C_e}{q} = \frac{C_e}{q_{max}} + \frac{1}{b.q_{max}} \qquad (2)$$

Results and discussion

The SEM and TEM images of B0 and UB are displayed in Figure 1. Clearly, the B0 shows the bulk bentonite under the same conditions without sonication (Figure 1a). The morphology of B0 is a thick aggregate of layers and contains large particles with large pores inside. After treatment by NaOH under ultrasonication, there is an obvious morphology change of bentonite material from bulk form to nanoplatelets. Thanks to the cavitation effect, the layers of bentonite are intercalated by Na^+ ions and then exfoliated into thin nanoplates with size ranging from approximately 0.1 to 0.5 µm (Figure 1b). To confirm the effect of sonication on the change of morphology, the TEM measurement was taken out. As can be seen from Figure 1c and 1d, UB reveals a reasonably thin layer of bentonite (more transparent zones) and B0 with a mixture of multi-layers bentonite (black areas). The EDX of B0 and UB is shown in Figure 2, confirming bentonite components. The large dimension of bentonite nanoplatelets of UB was further confirmed by a typical AFM image (Figure 3). Figure 3 shows some typical platelets with a width of about 2 µm and thickness of about 50-60 nm, suggesting that the bulk bentonite was transformed to nano-platelets bentonite. Taking into consideration the advantage aspects such as simple setup and convenient operation, UB can be superior to previous methods.

The structure of as-prepared samples was observed from the XRD patterns (Figure 4). It is clearly seen that B0 had a sharp peak with high intensity at 2θ of 26.7° of quartz (α-SiO_2), and other small peaks at 2θ of 12.3, 19.8 and 35.1° of montmorillonite, indicating that silica is the major component of B0. The 2θ of 24.6° is assigned to kaolinite. However, the silica peak was dramatically reduced after exfoliation, as observed for UB, proving that the ultrasonication can simultaneously exfoliate and enrich the montmorillonite composition of bentonite.

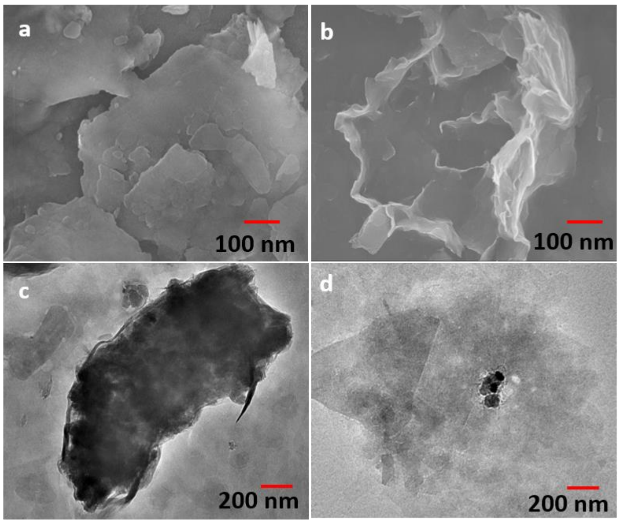
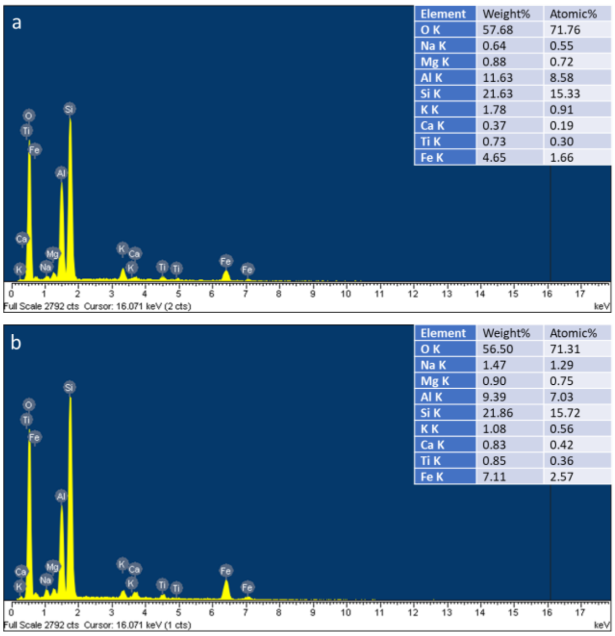


Figure 1: (a, b) SEM and (c, d) TEM images of B0 and UB, respectively



Element	Weight%	Atomic%
O K	57.68	71.76
Na K	0.64	0.55
Mg K	0.88	0.72
Al K	11.63	8.58
Si K	21.63	15.33
K K	1.78	0.91
Ca K	0.37	0.19
Ti K	0.73	0.30
Fe K	4.65	1.66

Element	Weight%	Atomic%
O K	56.50	71.31
Na K	1.47	1.29
Mg K	0.90	0.75
Al K	9.39	7.03
Si K	21.86	15.72
K K	1.08	0.56
Ca K	0.83	0.42
Ti K	0.85	0.36
Fe K	7.11	2.57

Figure 2: EDX of (a) B0 and (b) UB

A proposed mechanism for the formation of bentonite nanoplatelets from natural bentonite clay is illustrated in Figure 5. There are three steps during the activation using ultrasonication and alkali treatment: (1) The swelling and expansion of natural bentonite by absorbing water, thus favoring intercalation of cations; (2) The introduction of cation (e.g. Na$^+$) into the interlayers of swelled montmorillonite structure, thus weaken intermolecular forces between the layers; (3) The exfoliation of weakened interlayers by ultrasonication to form bentonite nanoplatelets and nanoparticles.

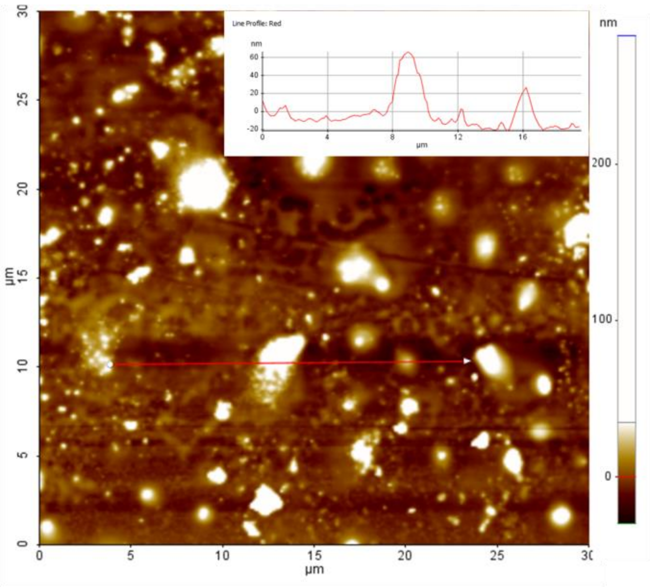


Figure 3: AFM image of UB

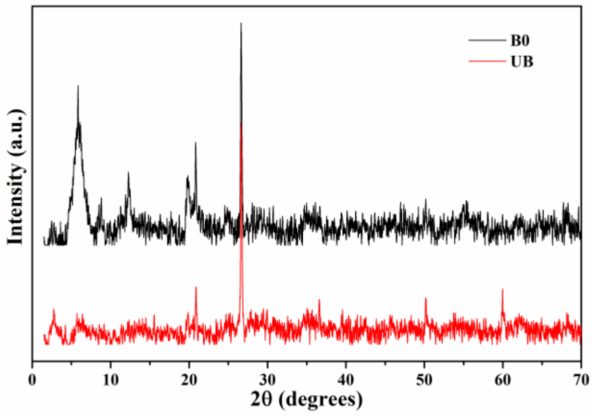


Figure 4: XRD of B0 and UB

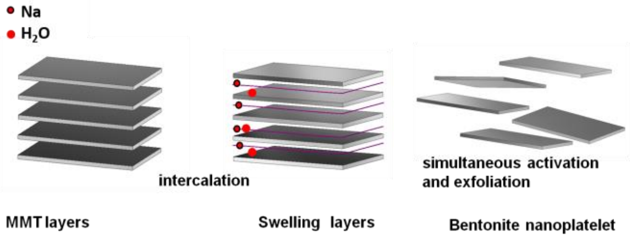


Figure 5: Mechanism for exfoliation of bentonite nanoplatelet by ultrasonication under alkali condition

As displayed in Figure 6, both isotherms can be identified as a combination of type I and type IV according to the IUPAC classification [10]. An initial increase at the relative pressure P/P° < 0.1 should be attributed to the micropore filling. The obvious hysteresis loop in the relative pressure range of 0.45-1.0 can be related to the capillary condensations of N_2 molecules in the mesopores. Moreover, the N_2 quantity adsorbed has a sharp increase when the P/P° is over 0.9, suggesting the presence of macropores. So, we can draw a conclusion that the UB and B0 own hierarchical pore structures, including micropores, mesopores and macropores, which is in good agreement with the SEM and TEM observations. According to the standard Brunanuer-Emmett-Teller (BET) method, the BET-specific surface area of UB and B0 were calculated to be 63.85 and 45.61 m^2/g, respectively. The pore size distribution curve is shown in the inset of Figure 6, both materials were centered at mesopores of about 4 nm and obtained a fairly porous structure with similar hysteresis. The higher BET-specific surface area of UB than that of B0 could be originated from swelling and exfoliating of bentonite layers and the extreme turbulent flows, as well as extensive mixing, attained from sonication. For the adsorption process, the mechanism of porous material is mostly attributed to pore filling, along with several other interactions (i.g., electrostatic attraction, surface precipitation, hydrogen bonding...) [11]. Obviously, the UB sample with the high surface area and hierarchical pore would provide more adsorption sites, which is greatly desirable for the high-efficiency of methylene blue removal.

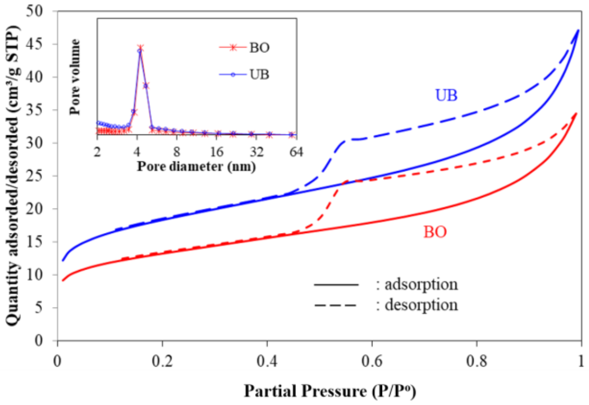


Figure 6: N_2 adsorption – desorption isotherms of BO and UB (inset is the pore size distribution)

Methylene blue removal

Although the adsorption and kinetic studies of organic dyes using bentonite-based materials have been investigated frequently before [12-15]. However, this work focuses only on a facile and green approach of bentonite nanoplatelets via a simple, low-cost and convenient method and its ability to remove methylene blue in aqueous solution. At a glance, the removal efficiency of the bentonite nanoplatelets for adsorption of MB was demonstrated at a neutral pH and evaluated via maximum adsorption capacity (q_{max}).

Langmuir adsorption model was employed for describing the adsorption of MB using UB and B0 materials and the results are demonstrated in Figure 7. Results showed that UB had higher maximum adsorption capacity (312.50 mg/g) than that of B0 (277.78 mg/g) with high R^2 values of 0.9899 and 0.9954 and b coeficients of 0.31 and 0.55, respectively.

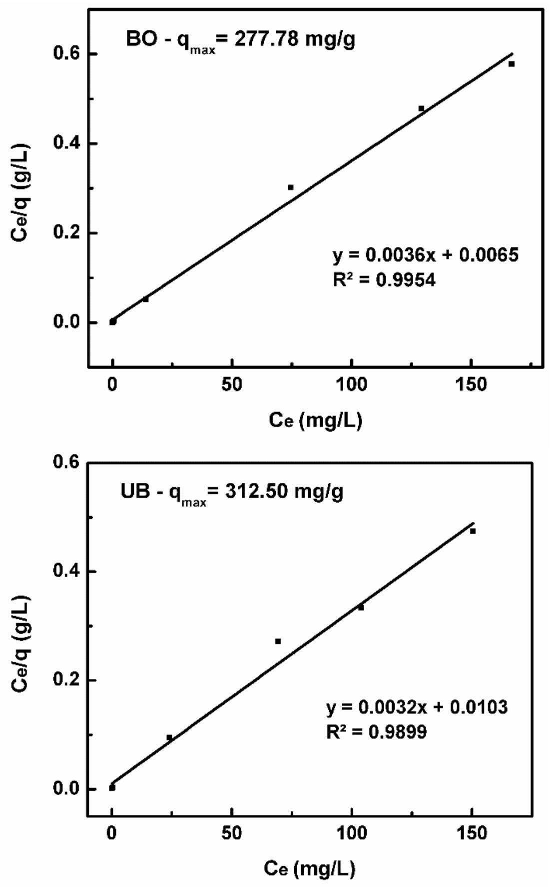


Figure 7: Langmuir adsorption model for BO and UB materials

This suggests that ultrasonication facilitates the adsorption ability of the bentonite material via increasing the surface area of the porous material. Compare to other studies, the maximum adsorption capacity of UB material (312.50 mg/g) is higher than that of bentonite-based adsorbents such as chitosan/bentonite (142.86 mg/g,[12]), bentonite modified by plasma (303 mg/g, [13]), bentonite/zeolite-NaP composite (36.23 mg/g, [14]), and organo-bentonite (194 mg/g, [15]). This made UB material as a very potential bentonite material for water and wastewater treatment.

Table 1: The comparison of UB and previously reported materials

Materials	Maximum adsorption capacity (mg/g)	Ref.
Chitosan/bentonite	142.86	[12]
Bentonite modified by plasma	303.0	[13]
Bentonite/zeolite-NaP composite	36.23	[14]
Organo-bentonite	194.0	[15]

Conclusion

Bentonite nanoplatelets were successfully produced using clay mineral containing bentonite via ultrasound-assisted liquid-phase exfoliation. Results from SEM, TEM, AFM, and XRD showed that bentonite nanoplatelet material had size of 0.1 – 0.5 µm, the thickness of 50 – 60 nm, and surface area of 63.85 m^2/g. For removal of MB in water, the material had a Langmuir maximum adsorption of 312.50 mg/g, which could find many applications in health, chemical and environmental engineering.

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