Colloid Polym Sci 276:842–846 (1998)

SHORT COMMUNICATION

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An electron-microscopic study of Na-attapulgite particles

Received: 30 March 1998
Accepted: 27 April 1998

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Abstract A scheme for the separation, purification and preparation of submicron, homoionic, Na-attapulgite from a natural mineral deposit is presented together with representative analysis of the particle size distribution. Transmission electron microscopic examination indicated that particles were predominantly $<1\mu$m long and "lath-like" with aspect ratios (length:width:thickness) 100:3:1 which provide for a variety of modes of particle/particle interaction.

The scheme involves physical and mild chemical treatment of the natural material and appears to preserve the physico-chemical integrity of the attapulgite particles and provides material within a narrow size range.

Key words Attapulgite dispersions – lath-like particles

Introduction

Attapulgite has been classified as a clay mineral of fibrous morphology. It has relatively low abundance in comparison with clays of platy habit, such as kaolinite montmorillonite and illite [1], but has many applications in industrial processes and products. These exploit unusual behavior arising from the physico-chemical and structural properties of the particles [2, 3]. Particle morphology and size are also of interest in relation to cytotoxicity of such fibrous materials [4]. Fundamental information concerning the behavior of suspensions of such particles is frustrated by complexity arising from both asymmetry of their morphology and polydispersity (in terms of particle length, width and thickness). A reduction in the latter renders the effects of the former more amenable to specific investigation.

Monodisperse rod-like particles can be obtained by synthesis in the laboratory and or by selection and separation of material from natural deposits. Unfortunately samples from most deposits macroscopically identified as attapulgite (or palygorskite) are not of a high mineralogical purity [5, 6]. The preparation and properties (density and specific surface area) of relatively pure attapulgite have been previously described together with limited information about particle size and shape [7]. This paper presents representative statistics of fibre length for use in assessing polydisperity of prepared Na-attapulgite and presents evidence of mineralogical purity.

Experimental

All chemicals were of analytical reagent grade. Water, treated by reverse osmosis (single stage), a combination of mixed bed ion-exchange and adsorption over activated carbon and microfiltration (Elgastat Spectrum R) to give a conductivity of $<10\,\mu$ Siemens and with a pH of 5.7 ± 0.1 was used throughout.

Mineral Source

A sample of palygorskite, also known as Fuller's Earth, was obtained from deposits in NW Florida (Floridin, Co.,

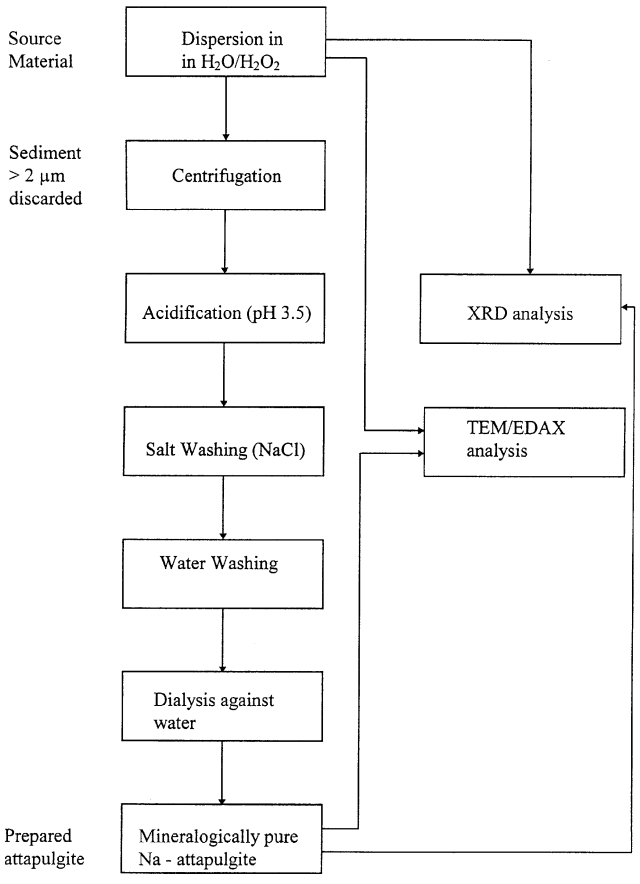


Fig. 1 Outline preparative scheme for preparation of Na-attapulgite

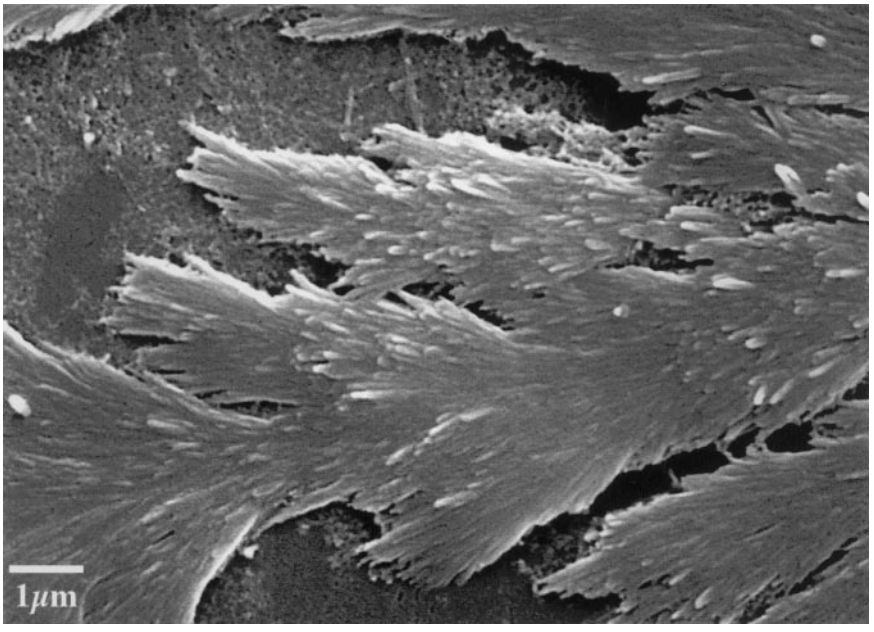
Florida, USA). The material was an off-white, fine, granular powder. The suppliers literature suggests that attapulgite is the predominant constituent with quartz and dolomite as the major impurities. Attalpulgite was separated and prepared as previously described [7] using a procedure (summarized in Fig. 1).

Preparation of specimens for transmission electron microscopy

Samples of particles from both source and prepared material were dispersed in aqueous alkali at pH ~ 10 in the presence of sodium hexametaphosphate (in order to inhibit particle aggregation), ultrasonicated for ~30 min and either deposited directly on to carbon-coated gold EM grids or drawn on to capillary pore membrane filters (0.2 μm). Selected membrane specimens were then shadowed with gold/palladium 40 : 60 (alloy) at an angle of either 15 or 30° prior to being carbon coated. The membrane was then dissolved in chloroform and the carbon film floated on to a gold EM grid.

Particle size and shape were examined using a transmission electron microscope (TEM), (Philips EM400T) fitted with an energy dispersive X-ray detector (Kevex) and EDAX data analyser. Estimates of particle thickness were made from shadowed specimens. Particles were identified by analysis of emitted X-rays, characteristic of their metallic constituents.

Plate 1 Scanning electron micrograph of attapulgite (source material)



Colloid & Polymer Science, Vol. 276, No. 9 (1998)

Powder X-ray diffractometry

Powder specimens of material were prepared for analysis by allowing aliquots of suspension (0.3 w/v%) to settle under vacuum on to silver membrane filters (0.2 μm, capillary pore, Osmonics Inc) and allowed to dry at 25 °C. Diffraction patterns were obtained from the filters using a powder diffractometer (Philips PW 1729 X-ray generator and PW 1710 control system) operating at 35 kV, 40 mA with Cu Kα radiation.

Results

Specimens of source material were found, by TEM/EDAX, to contain apparently isometric particles containing either Ca or Si as major components. Attapulgite particles were recognized by their rod-like silhouettes and from corresponding spectra bearing signals for Si, Al and Mg as major components. X-ray count rates from such particles were generally below those of isometric particles and reflect the thinness of the former. Specimens of the prepared attapulgite did not contain any particles bearing Ca X-ray signatures and those bearing Si signatures were seldom encountered [ibid].

The separated and prepared attapulgite was found to constitute $\approx$20 wt% of the raw material. The remainder comprised large particles and aggregates (Plate 1) which were not readily disrupted. As fibrous materials may suffer mechanical entanglement, adjustment of the chemical environment is unlikely to facilitate liberation and recovery of significant quantities of material from such entanglements.

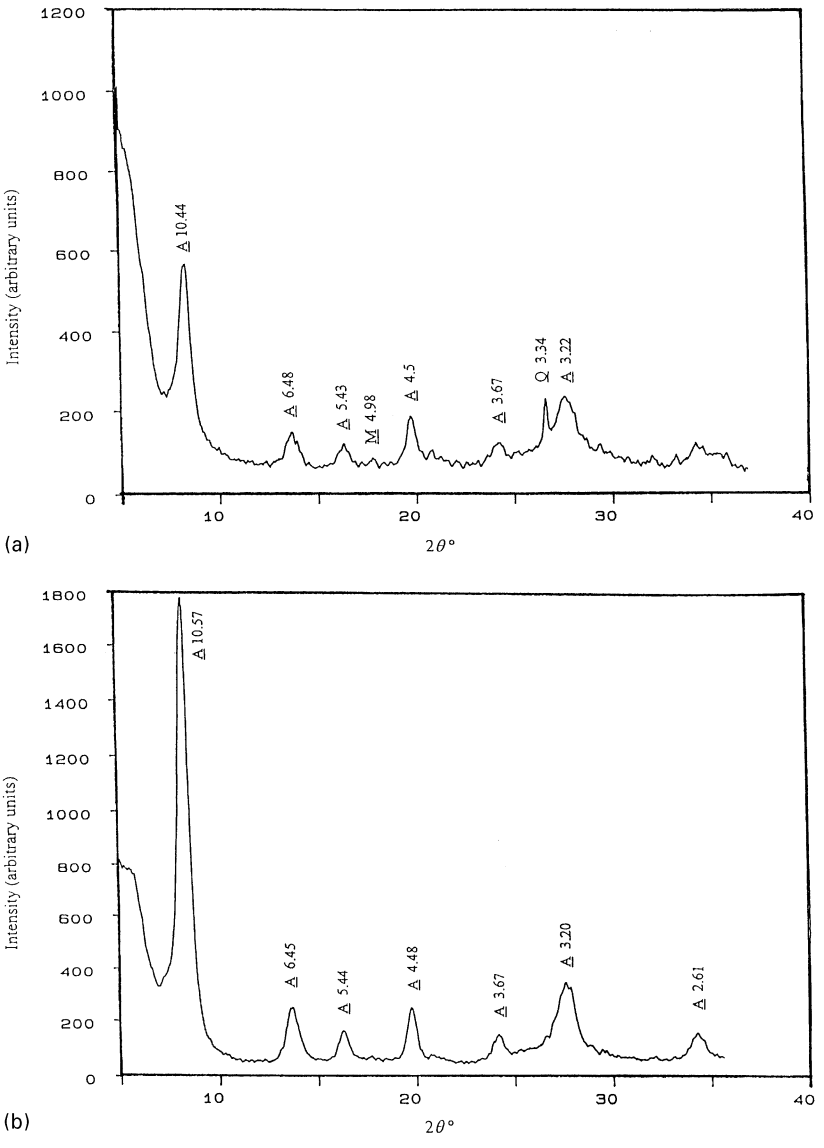


Fig. 2 Powder X-ray diffraction patterns of attapulgite; (a) source material and (b) prepared material. (Peak identification: A attapulgite; M Mica and Q quartz)

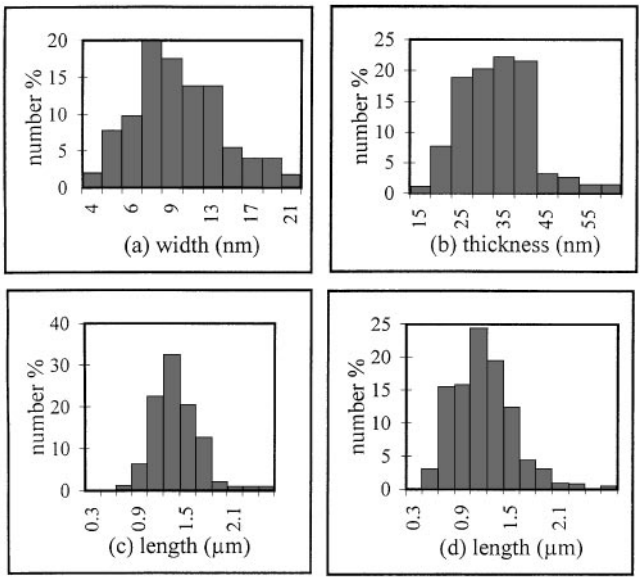


Fig. 3 Size distributions of attapulgite particles (a) width, (b) thickness (c) length (shadowed specimens, 150 particles) and (d) length (unshadowed specimens, 712 particles)

Table 1 Summary of statistics of samples of particle length

Average [μm]	Standard deviation [μm]	Number of particles
1.220	0.775	16
1.102	0.348	34
0.972	0.230	42
0.959	0.419	53
0.958	0.383	63
0.949	0.350	71
0.948	0.376	66
0.94	0.378	61
0.931	0.350	92
0.927	0.287	37
0.926	0.394	33
0.921	0.341	53
0.921	0.188	19
0.905	0.281	40
0.955	0.366	680

The X-ray diffraction pattern of the source material indicates the presence of quartz, calcium minerals, mica and attapulgite, (Fig. 2a) whereas that of the prepared material indicates only the presence of attapulgite (Fig. 2b). The maximum level of impurities is, therefore, at the detection limit of the technique.

The distribution of particle dimensions made from shadowed specimens of prepared attapulgite (Fig. 3a–c) indicates that the length distribution (Fig. 3a) is relatively narrow, but the width and thickness distributions appear to be broader (Fig. 3b–c resp.). There is some uncertainty as to whether or not particle orientation within the specimen is consistent such that the largest projected area of particles is presented for observation. The significant difference between the distributions of thickness (estimated from the dimensions of shadows and width suggest that particles were predominantly oriented in this fashion, but the breadths of these distributions are probably enhanced as a result of some mutual confusion of these dimensions.

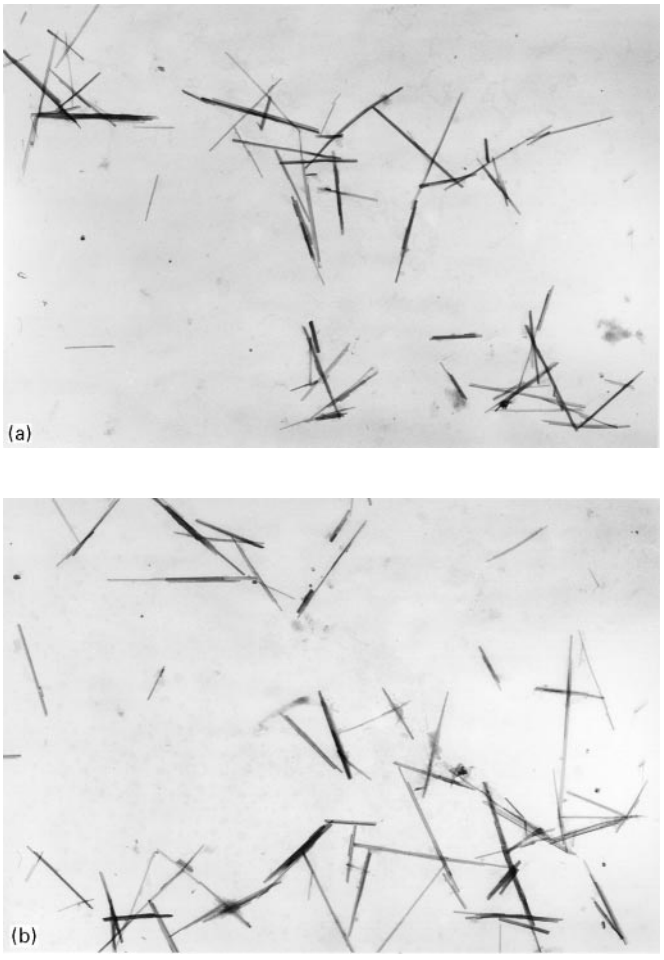


Plate 2 (a–b) Transmission electron micrographs of prepared attapulgite particles

Estimates of average particle length made from shadowed specimens of the treated material (Fig. 3c) were found to be in relatively in good agreement with those of unshadowed specimens (Fig. 3c). High values of average particle length, arose from the presence of 1 or 2 particles in excess of 2 μm.

The pooled average length and standard deviation of 680 particles were found to be $0.955 \pm 0.366\,\mu$m (Table 1) giving a coefficient of variation of 38%. A student t-test between groups with the longest ($1.22\,\mu$m) and shortest ($0.905\,\mu$m) number average lengths suggests no significant difference between them at the 90% level.

Particles of average length ($\approx 0.95\,\mu$m) occurred with a high frequency and fragments of $0.22\,\mu$m were present at 2% on a number basis, but few particles $>2\,\mu$m (long) were observed.

Although some particles may contain several parallel unit cells, they appear to be resilient and stable particle structures. Typical transmission electron micrographs of prepared attapulgite fibres are shown in Plate 2 (a and b).

In summary the scheme described here provides a source of relatively uniform attapulgite particles with an aspect ratio 100 : 30 : 1 which is essentially (physically and chemically) free of the minerals associated with its sedimentary deposits.

Acknowledgements Transmission electron microscopy services and assistance were kindly provided by Prof FD Pooley and Mr M Griffiths, Univeristy of Wales College of Cardiff.

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