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Use of water uptake and capillary suction time measures for evaluation of the anti-diarrhoeic properties of fibrous clays

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Abstract

This study explores the use of water sorption/retention measures as alternative methodologies to the official methylene blue adsorption test for the evaluation of the anti-diarrhoeic properties of some fibrous clay. Three fibrous phyllosilicates—palygorskite from Ciudad Real (PCR), and sepiolite from Vicalvaro (SV) and Yunclillos (SY)—have been studied. Two commercial anti-diarrhoeal products—Pharmasorb Colloidal© (PHC) and Pharmasorb Regular© (PHR)—each mainly consisting of palygorskite, were also included in the study. The 75–125-μm sieve fraction was selected and methylene blue adsorption (MBA) capacity and water uptake characteristics—total amount of water retained (Q_{max}) and water uptake velocities (I_w)—measured. Finally, the water retention capacity, with dispersions of 10% w/v, was assessed by means of capillary suction measures (CST). MBA capacity was similar for all the samples, with PHC showing the highest capacity to adsorb the dye. PHC was also the sample which retained the most water ($Q_{max} > 2.5$ mg/mg), followed by PCR and PHR ($Q_{max} \approx 1.5$ mg/mg) and finally SV and SY ($Q_{max} < 1$ mg/mg). Regarding the velocity for water entry, water uptake was almost total after 10 s for sepiolite samples, 100 s for PHR and 600 s for PCR and PHC. Finally, water retention time of the PHC dispersion (> 160 s) was almost twice those of the rest of studied materials. A linear correlation was found between the amount of palygorskite in PCR, PHC and PHR and their water uptake capacities. This was not possible for the sepiolite samples. An inverse correlation was found between velocity of water suction (I_w) and capacity of methylene blue adsorption. Water uptake and water retention measures are proposed as complementary to the methylene blue adsorption assay in the evaluation as anti-diarrhoeics of the studied materials.

Keywords: Palygorskite; Sepiolite; Anti-diarrhoeic; MBA; Water uptake; CST

1. Introduction

Palygorskite and sepiolite are both fibrous phyllosilicates belonging to the same mineral group (Bailey, 1980). Their ideal formulae are $Si_8O_{20}(Mg,Al,Fe)_5(OH)_2(OH_2)_4 \cdot 4H_2O$ for palygorskite and $Si_{12}O_{30}Mg_8(OH)_4(OH_2)_4 \cdot 8H_2O$ for sepiolite. Palygorskite has a BET surface area of approximately 120–180 and sepiolite 300 m^2/g. Both minerals present interesting rheological (resulting from the anisotropy of the particles) and adsorbent (due to their large surface area) properties. This clearly dif-

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ferentiates these minerals from other phyllosilicates and accounts for their economic importance (Alvarez, 1984; Galán et al., 1985). In particular, they are usefully applied in the symptomatic treatment of diarrhoea, on the basis of their capacity to adsorb and retain water (DuPont et al., 1990). In Europe, there are at present, four products (Gastropulgit©, Actapulgite©, Mucipulgite© and Diocalm©) commercialised in a total of seven countries that include fibrous phyllosilicates as pharmaceutical agents under different commercial names. All of these are intended for symptomatic treatment of gastrointestinal disorders (Garlot et al., 1992). Outside the European Community, we can find, for example, six products (Enterofuran©, Fultrapec©, Nefurox©, etc.) in the Mexican market, and another six (Donnagal©, Kaopectate©, Diasorb©, etc.) in the USA (Braun, 1994). In all of these, palygorskite is present together with other agents with which it shares the pharmacological effects of the preparation.

The official method for the evaluation of the non-specific anti-diarrhoeic capacity of an adsorbent comprises a measure of its capability for the adsorption of methylene blue (MBA test, United States Pharmacopoeial Convention, 1995). The major limitations of this test are associated with the chemical particularities of the dye. Methylene blue is an organic base combined with an acid, the dimensions being 130–135 × 20–25 Å (Hang and Brindley, 1970). At low concentrations, the molecules in solution are unassociated but when they reach concentrations over 5–10 mol/l, associations of two or more molecules result. Moreover, the molecule is an organic base that appears as a blue water solution. However, the presence of a stronger base in the solution may reduce the dye, resulting in a colourless solution. Additional sources of confusion are the complex nature of the adsorbents. According to Sanson et al. (1968), 90% of the total exchange capacity of phyllosilicates is a consequence of isomorphic substitutions between Al^{3+} and Si^{4+} on the tetrahedral layers. The resultant charge deficits are compensated by exchangeable ions (mainly Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) present in the interlayer. The remainder making up 100% results from OH^{-} ions on the crystal surface and also from organic impurities present in the sample. On the other hand, free $R–Si–O^{-}$ groups are present on the crystal surfaces of phyllosilicates, and these need to be balanced with positive ions. The previous considerations show that there are serious difficulties which prevent reproducible values of adsorption capacities being obtained by using the MBA test, and consequently, it is mostly used as an indicative test rather than as a definitive method.

In our opinion, a complete characterization of the water uptake and retention abilities of these materials represents the key to a rational evaluation of their anti-diarrhoeic properties. The first objective of this work was to evaluate the intrinsic anti-diarrhoeic capacities of sepiolite and palygorskite samples. On the basis that the mechanism of their action is mainly based on their abilities to first sorb and then retain water efficiently, measures of their water adsorption/retention abilities have been made. The main purpose of the work was to search the possible correlations between water uptake and retention values and methylene blue adsorption results.

2. Material and methods

Two sepiolites, from Vicálvaro, Madrid (SV), and Yunclillos, Toledo (SY), one palygorskite from Ciudad Real (PCR) and two pharmaceutical products consisted mainly of palygorskite—Pharmasorb© regular (PHR) and colloidal (PHC); Engelhard, Attapulgus, GA, USA—were studied. The 75–125 μm fractions were sieved and stored at 40% relative humidity and room temperature for at least 48 h before any study was performed. Methylene blue extra pure grade was purchased from Sigma Aldrich, St. Louis, MO, USA.

2.1. Water and methylene blue adsorption

MBA measures were undertaken according to the United States Pharmacopoeial Convention (1995), 10 ml of a silicate/water dispersion (10% w/v) were agitated for 15 min at 1000 rpm, with 80 ml of methylene blue/water solution (0.1% w/v), the product was centrifuged and 5 ml of the resultant solution was diluted with 495 ml of water. The absorbance at 625 nm of the diluted solution was measured by means of an UV-visible spectrometer Perkin–Elmer Lambda 2, Perkin Elmer, Ueberlin-

Table 1
Results of the MBA test expressed as UV absorbance of the resultant solution vs. absorbance of the 0.15 μg/ml solution

Sample	Relative absorbance at 625 nm (±sd)
PCR	5.87±0.25
PHC	0.98±0.09
PHR	3.58±0.14
SV	2.14±0.18
SY	4.12±0.34

gen, Germany, and compared to that of a 0.15 μg/ml solution. Water uptake was measured on 300 mg of powder sample following Caramella et al. (1988); the values were plotted vs. time and the corresponding profiles were adjusted by means of a non-linear model equation (i.e. RRSBW equation, known also as Weibull equation as used by Langenbucher, 1972) in order to obtain the total amount of water adsorbed (Q_{max}) and the water uptake velocity (I_w).

2.2. Water retention

Reproducible results of water retention capacities may only be obtained if the clay has been previously

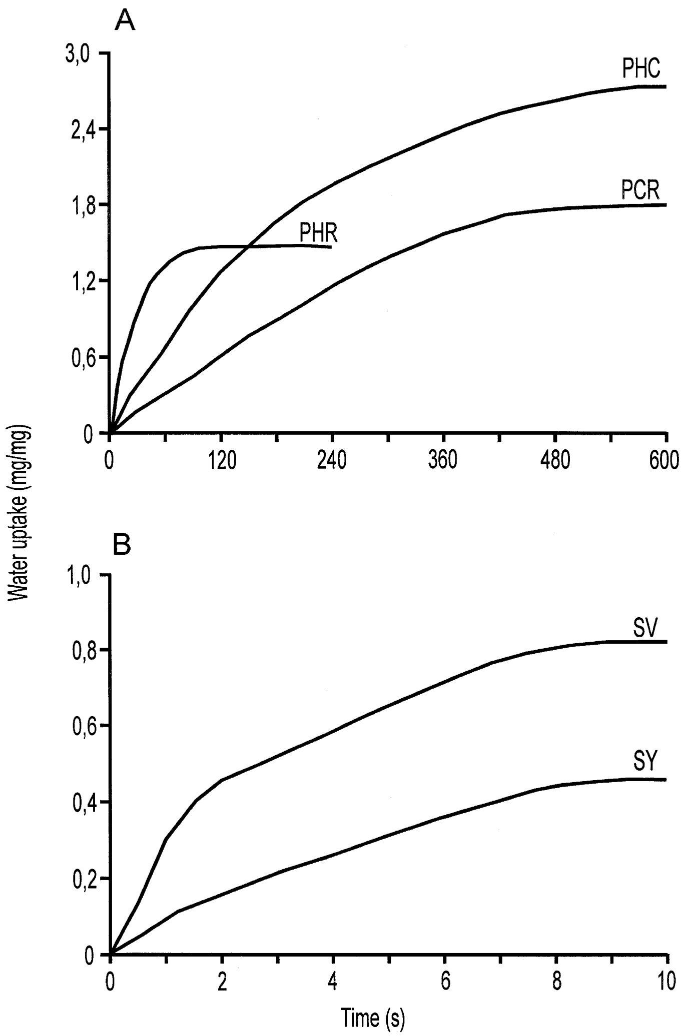

Fig. 1. Water uptake profiles of palygorskite (A) and sepiolite (B) powder samples.

dispersed homogenously. With this aim, dispersion of each sample (10% w/v) was made by using a Silverson® L4RT mixer (Silverson, England) working at 8000 rpm for 10 min. These were found to be the optimal conditions for obtaining a homogeneous structured system with these materials (Viseras et al., 1999). Capillary suction (CST) measures were undertaken on 3 ml of fresh dispersions according to Meeten and Smeulders (1995). A Perchem© CST instrument (Triton Electronics, Essex, England), with an 18-mm inner diameter holder and Wathman® Chromatography 17 Chr paper was used.

All the results are the average value of at least three replicates.

3. Results and discussions

3.1. Methylene blue adsorption

Table 1 presents the values of MBA capacity expressed as absorbance of the tested solution vs. absorbance of the 0.15 μg/ml solution. Absorbance is inversely related to MBA values. As observed, the capacity was higher for PHC than for the rest of samples. PHC was the only sample complying with the official requirement (absorbance of the filtered solution ≤ absorbance of the 0.15 μg/ml solution). PHC probably suffered some kind of thermal treatment (Viseras, 1997). This treatment may have had the effect of increasing its capacity of adsorption by reducing the amount of surface water. In fact, therapeutic use of fibrous clays was greatly increased when it was found that specific thermal activation of palygorskite could increase its capacity to adsorb toxins and pathogenic bacteria (DuPont et al., 1990).

Table 2
Maximum water uptake capacity (Q_{max}) and water uptake velocity (I_w) of the studied samples

Sample	Q_{max} (mg/mg)	I_w (mg/s)
PCR	1.8 ± 0.02	$2.38 \times 10^{-3} \pm 0.081 \times 10^{-3}$
PHC	2.8 ± 0.04	$3.16 \times 10^{-3} \pm 0.39 \times 10^{-3}$
PHR	1.5 ± 0.01	0.018 ± 0.008
SV	0.85 ± 0.01	0.059 ± 0.040
SY	0.48 ± 0.01	0.021 ± 0.026

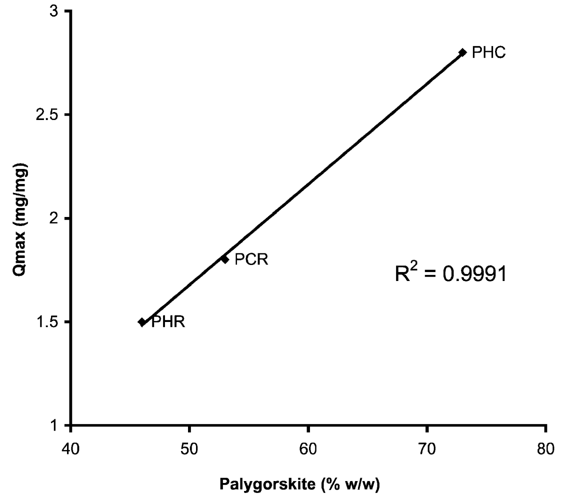

Fig. 2. Relationship between palygorskite amount (% w/w) and maximum water uptake capacities (mg/mg).

3.2. Water adsorption

Fig. 1(A) and (B) present the water uptake profiles of the palygorskite and sepiolite samples, respectively. The corresponding Q_{max} and I_w values, obtained following Caramella et al. (1988) are shown in Table 2. PHC retained the highest amount of water, followed by PCR and PHR. Regarding the velocity of incorporation, water uptake for PHR is almost total after 100 s, being several times slower for PCR and PHC. Sepiolite samples presented the lowest capacities for water adsorption and the highest water uptake velocities ($Q_{max} < 1$ mg/mg and $I_w > 0.02$). Mineral composition and textural characteristics should help to explain these differences. Clay particles normally form aggregates. In a previous study, we demonstrated that palygorskite aggregates are more closely compacted than those of sepiolite (Viseras and Lopez-Galindo, 2000). Moreover, sepiolite fibres present more surface defects than palygorskite and are generally more disordered. We postulate that the aggregates may work as a geometrical barrier to the passage of water and that water uptake occurs more quickly in the less-compacted and disordered sepiolite aggregates. The differences between the palygorskitic samples may be explained on the basis of their purities. In fact, there was a linear correlation between the percentage of palygorskite in each sample (Viseras et al., 1999) and the maximum water uptake capacities measured (Fig. 2).

4. Water retention

Table 3 presents the capillary suction times of the samples. PHR, SV and SY dispersions had similar capillary suction times (around 100 s). Suction times were appreciably lower (around 80 s) for the PCR sample and considerably higher (around 160 s) for the PHC dispersion. We have recently screened the differences in the rheological properties of dispersions prepared with these materials (Viseras et al., 1999), and have shown that fibrous clay dispersions behave as high-viscosity systems when prepared under the conditions used in this work. We proposed that the formation of a three-dimensional network of fibres is responsible for the high viscosities. On the other hand, laminar clays required a swelling period to form structured systems. Meeten and Lebreton (1993), working with laminar clay suspensions, suggested that flocculated suspensions filter at the surface of the CST paper, while non-flocculated suspensions invade the paper. Suction times should be higher in non-flocculated suspensions because they compacted better. However, this is not always the situation and aggregation of non-flocculated particles can reduce the time to filtrate. As a result of their high anisotropy, fibrous particles did not penetrate the paper and a good agreement between CST results and water retention abilities can be obtained. PCR included a substantially important amount of illite (> 20% w/w) as an impurity, reducing its ability to form a good fibrous network. The same would happen with PHR (with > 25% w/w of laminar silicates). Regarding the sepiolite samples, their mineral contents are both high enough to obviate the effect of impurities and the times measured are, in our opinion, representative of the intrinsic capacity of water retention by the mineral under the suction pressure applied. An inverse correlation was found between capillary suction times and the methylene blue adsorption capacities, as can be observed in Fig. 3.

Table 3
Capillary suction times (CST) of the water dispersions (10% w/v) prepared with the studied samples

Sample	CST (s)
PCR	79.0 ± 3.14
PHC	157.9 ± 5.2
PHR	103.4 ± 3.6
SV	125.3 ± 4.3
SY	105.5 ± 8.1

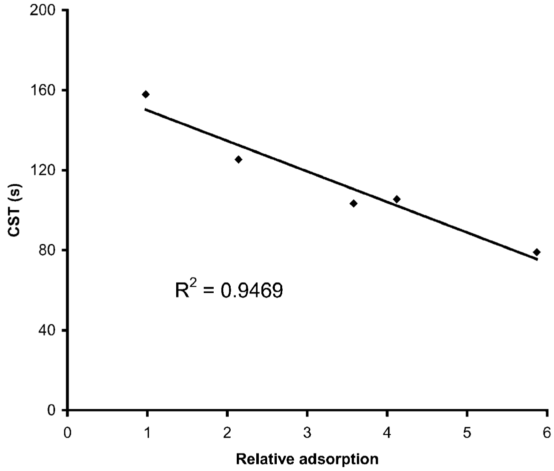

Fig. 3. Relationship between capillary suction time values and methylene blue adsorption capacities on sepiolite samples.

5. Conclusions

As shown in Fig. 3, water retention (CST) values correlated well with those obtained with the official test (MBA test) and may be considered as a complementary technique for the evaluation of the anti-diarrhoeic properties of a material.

Information obtained from water uptake capacity, water uptake velocity and water retention of the dispersions permits a quantitative evaluation of the effectiveness of the studied materials for the non-specific treatment of diarrhoea.

According to the results obtained, only PHC could be used as a non-specific anti-diarrhoeic. The other clays required some kind of sorption activation. In this study, we were interested in the valuation of the methodologies more than in the evaluation of the materials and consequently, we have preferred to use the materials as received. Work is now in progress to evaluate the effect of different treatments on the water sorption/retention properties of these materials.

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