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STUDY OF CITRIC ACID DISPERSANT IN THE SETTLING BEHAVIOUR OF SLATE POWDER SUSPENSIONS

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Abstract

The behaviour of aqueous suspensions of slate stabilized with citric acid was investigated using sedimentation and rheological techniques. In order to determine the more effective dispersing agent concentration and the maximum loading of solids, a series of 12 suspensions were prepared with citric acid content between 0.5 and 2.5% w/v and solid percentages of 40, 55 and 70%. Light scattering techniques were used to obtain sedimentation data and particle size distribution; flow curves were obtained with a rheometer. The results indicated that the interaction between particle surfaces could either induce flocculation, at higher citric acid concentrations, or enhance the stabilization, at low dispersant concentration and pH values around 6. The highest sediment bed density was obtained for suspensions with 40% slate powder and 1.0% citric acid. This behavior was explained on the basis of the carboxyl groups of citric acid promoting higher dispersion of the particles resulting in lower settling rate, better stability and enhanced compact sediment bed.

Key words: slate powder, sedimentation techniques, suspensions

Introduction

Brazil is the 2nd largest producer and exporter of slate, with Minas Gerais State accounting for about 90% of this production and almost all Brazilian exports. The production of slates in Minas Gerais totals approximately 500 000 tons/year, unfolding 18 million square meters of slabs, tiles, countertops, roofs and other products. (Feinar, 2006).

The system of extracting blocks of rock for the production of plates generates a significant amount of waste in the form of a sludge composed mainly of water, lubricants and crushed rock. This waste with no defined destination accumulates in yards, reservoirs and streams, affecting the environment. Generally, the waste amount is 25% of the production closed to 1.5×10^5 tons of tailings (Abirochas, 2012).

The waste generated by the extraction of slate as well as its processing can bring a series of impacts on the environment. Some industries use these rocks, after cutting and polishing them, for the production of ornamental rocks, which are, in turn, used in the construction industry.

The production of alternative materials having the waste generated in the manufacturing industries of rocks as constituents can reduce or even eliminate pollution in the extraction areas, apart from promoting new opportunities for jobs and income essential to the progress and development of the country.

The powder derived from the extraction of slate rock can be used in the manufacture of ceramic pieces by slip casting. The process, although quite old and simple, is currently used to make sanitary ware, sinks and crafts with a great variety of forms (Matias et. al., 2006). Slip casting process route involves the use of thin powders (usually <1 μm) so that interfacial forces have considerable impact on the properties of the suspensions.

The interparticle forces involved in suspensions are governed by colloidal processing in order to obtain dense particle-packing and uniform microstructures (Moreno, et. al., 2009; Sigmund, et. al., 2000; Lange, 1989, Palhares, et. al., 2006).

Colloidal processing offers the potential to reliably produce ceramic films and bulk forms through careful control of initial suspension “structure” and its development during fabrication. This approach involves five basic steps: (1) powder synthesis, (2) suspension preparation, (3) consolidation into the desired component shape, (4) removal of the solvent phase and (5) densification to produce the final microstructure required for optimal performance. Unintentional heterogeneities (or defects) introduced in any stage of the fabrication process persist or become exacerbated during densification. Hence, there is a continuous drive towards improved understanding of colloidal stability and assembly to achieve the desired spatial distribution of phases (including porosity) in as-consolidated bodies (Lewis, 2000).

The sedimentation processes of colloidal particle suspensions has been widely studied and used in many practical applications in ceramic processing (Lee et. al., 2008; Argillier et. al., 2002; Moreno et. al., 2009). The roles of particle-particle and particle-fluid interaction forces in the sedimentation process are of particular interest because of their function in determining the dispersion stability (Wasan, et. al., 2008) mainly in slip casting process, where the suspensions have high solids concentration.

Slip casting process requires stable suspensions, the characteristics of which are usually of crucial importance. The stability must be controlled in order to yield a final product with the best properties as well as to improve the economics of the process and to optimize energy requirements.

In the present work, aqueous suspensions of ceramic slate rock with citric acid were prepared in order to evaluate the behaviour of the systems by sedimentation and rheological techniques. Solid content and citric acid concentration also affect the suspensions properties and thus it was varied to verify the changes in the behavior of suspensions produced and to find the more effective dispersing concentration for maximizing the solid loading of suspension.

2. Materials and Methods

2.1. Materials

The slate powder used was generated by the process of stone calibration of the company Micapel Slate located in the town of Pompeu in the state of Minas Gerais (Figure 1). It was pre-treated prior to characterization aimed at removing impurities such as waste and contamination. The steps of this treatment were: preparing a suspension of the powder in water, wet sieving in a # 400 sieve; decanting for 24 hours; water removal and oven drying (temperature 100 ° C for 24 hours).

Figure 1: Localization of slate production areas (Chiodi, 2003)

The density of particles were measured using a Micromeritics AccuPyc 1330 (Micrometrics Instrument Corporation, US) and the BET method was used to determine the surface areas using the Quantachrome Instruments NOVA 2200 Multi-station Any-gas Sorption Analyser Standard Model v10.03.

Phase analysis by X-ray diffraction was obtained on Philips PW1710 (graphite monochromator and CuK=1.54Å radiation). The X-ray data were collected and analyzed by using the program package powder diffraction file APX63.

The suspension was prepared by mixing the slate powder and water (Milli-Q water, 18,2 MΩ.cm) followed by magnetic stirring for 24 hours in order to homogenize the suspension. A total of 12 suspensions were prepared with four different citric acid (Sigma-Aldrich Ltd.) concentrations: 0.5%; 1.0%; 1.5% and 2.5% w/v and three different solid percentages, 40%; 55% and 70% w/v.

2.2. Slate suspensions characterization

The sedimentation experiments were carried out in a Turbiscan (Formulaction, Ramonville, France). In this device, the suspension is placed in a glass vial and multiple light scattering in both transmission and backscattered mode is measured. The intensity of light scattered across the cell length is measured as a function of time, in order to establish the sedimentation profile of the particles under gravity. For each volume fraction the sample was ran for 15 min and data were collected every 30 s. Data treatment was carried out with the software (Turbiscan Software 1.3) which gives the evolution of kinetics in terms of size and concentration variations.

A Lumisizer (L.U.M., GmbH, Berlim) was employed to complement the data sedimentation especially those related to smaller particles in suspension. The Lumisizer (figure 2) measures the intensity of transmitted light as a function of both time and position over the entire sample length. Up to 12 different samples can be simultaneously analyzed at centrifugal force. Our experiments had the following parameters: volume ~400μL, extracted using a syringe from suspension and transferred into a polyamide (PA) cell, 500 profiles were collected at intervals of 2h for suspensions at 500 rpm. Data is displayed as a function of the radial position, i.e. the distance from the center of rotation. The shape and progression of the transmission profiles provide information on the kinetics of the separation process and allows particle characterization as well as evaluation of particle-particle interactions (LERCHE, D; SOBISCH, T., 2008). Again, the software (Lumisizer Software) provides the data treatment about sedimentation rate and sediment bed obtained.

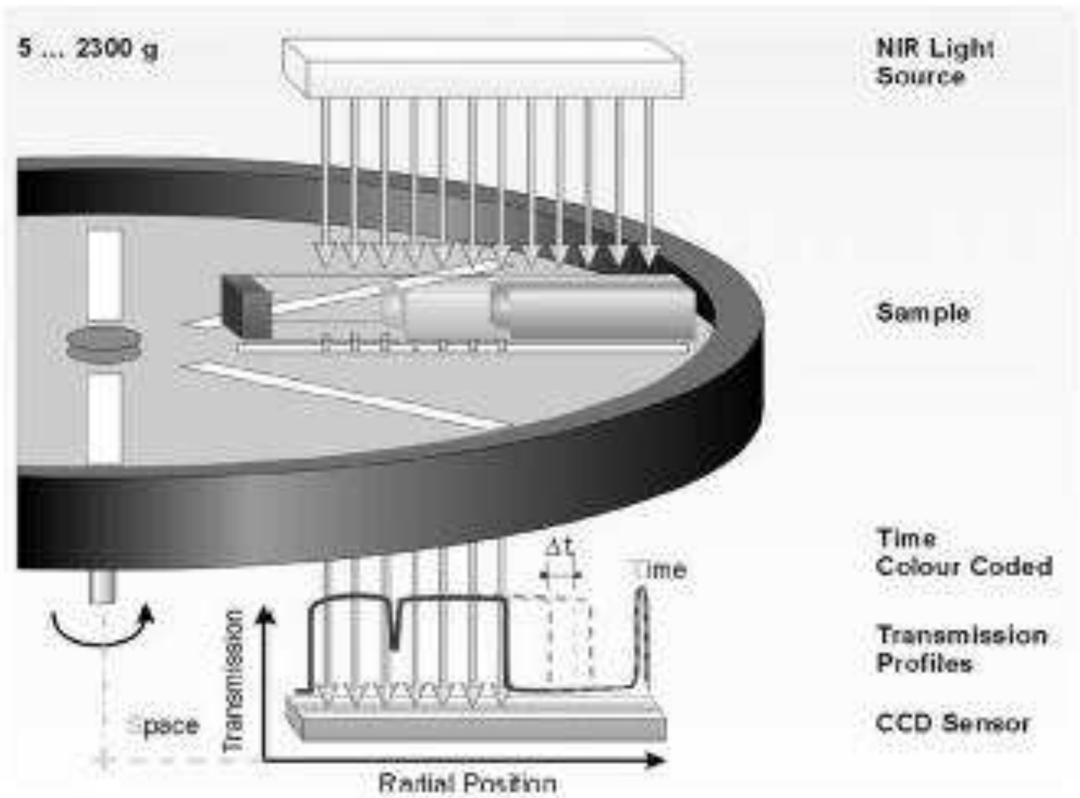


Figure 2: Measurement scheme of the multisample analytical centrifuge. Parallel NIR-Light incides through the sample cells and the distribution of local transmission is recorded at intervals over the entire sample length (LERCHE, D; SOBISCH, T., 2008).

A Bohlin C-VOR Rheometer was employed to obtain rheological flow curves. Either a cup and bob system or a vane system was used (see figure 3), depending on the suspension viscosity. A cup (solid) and bob system is suitable for low viscosity suspensions, whereas the vane tool is suitable for high viscosity systems with high solids content. A vane V25 tool was used with a C35 cup which requires ~40 mL of material. The temperature was maintained at 25°C for all experiments.

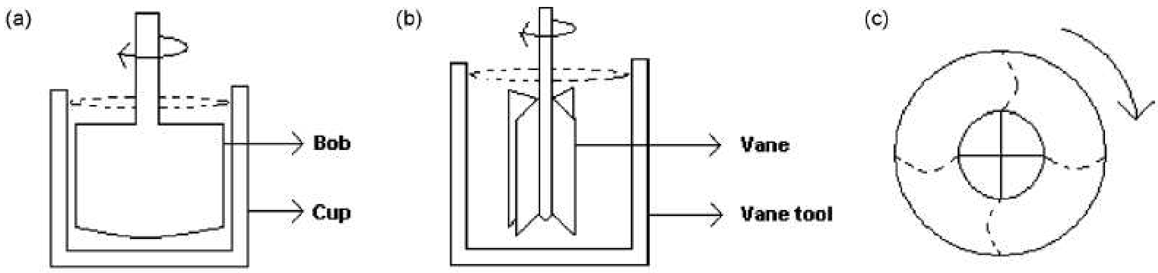


Figure 3: A schematic diagram of the different geometries employed (a) the cup with a diameter of 30 mm and bob with a diameter of 25 mm (b) the vane tool with a diameter of 25 mm and a cup with a diameter of 37mm (c) a cross section of the vane tool (PAUL, N. et. al., 2013).

A Malvern Mastersizer 2000 (Malvern Instruments Ltd., UK) was used to obtain particle size distribution of the slate suspensions. For each sample tested, a few drops of suspensions were added to a water-filled, stirred measuring cell until the correct obscuration value needed for accurate data was obtained. Each sample was analyzed over 10s and the result was taken as the average after 10 measurements.

3. Results

3.2. Characterization of the slate suspensions

The powder main constituents are quartz, clinochlore, muscovite, albite, hematite and orthoclase. The size distribution data shows a monomodal distribution with particle size between 1 and 10 microns. The powder density and surface area were respectively: 2.76g/cm^3 and 8.25m^2/g.

The suspensions are opaque due to the high solids percentage, therefore the transmission is close to zero. For this reason only the evolution of backscattering data was analyzed. Figure 4 shows typical curves of the backscattering measurements as a function of time obtained for the sample with 70%w/v slate powder and 1.5%w/v of citric acid.

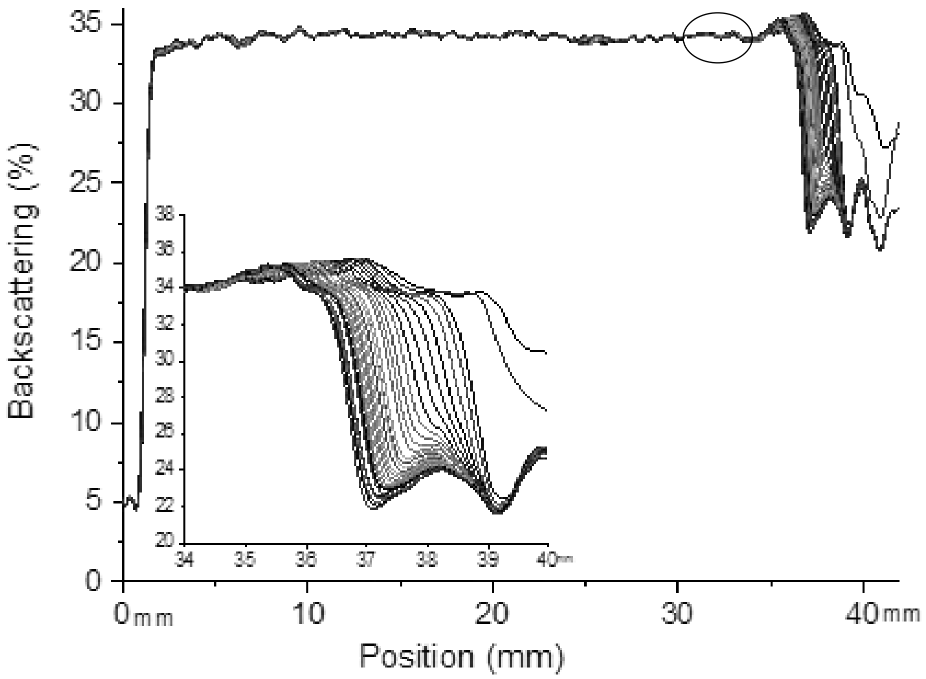


Figure 4: Evolution of backscattered light of a slate suspension registered along the sample for 15 min, each profile collected every 30 s.

From the scattering analyses, two specific zones can be clearly identified: one at the bottom and another at the top of the cell. Backscattering at the bottom shows only a slight variation while at the top it decreases with time due to the clarification of the suspensions as settling takes place. This is the most representative zone in the sedimentation process. From the scattering data is possible to plot the sediment height in the cell as a function of time and a typical plot is shown in Figure 5, obtained from the data of suspension with 70%w/v with different acid citric concentrations.

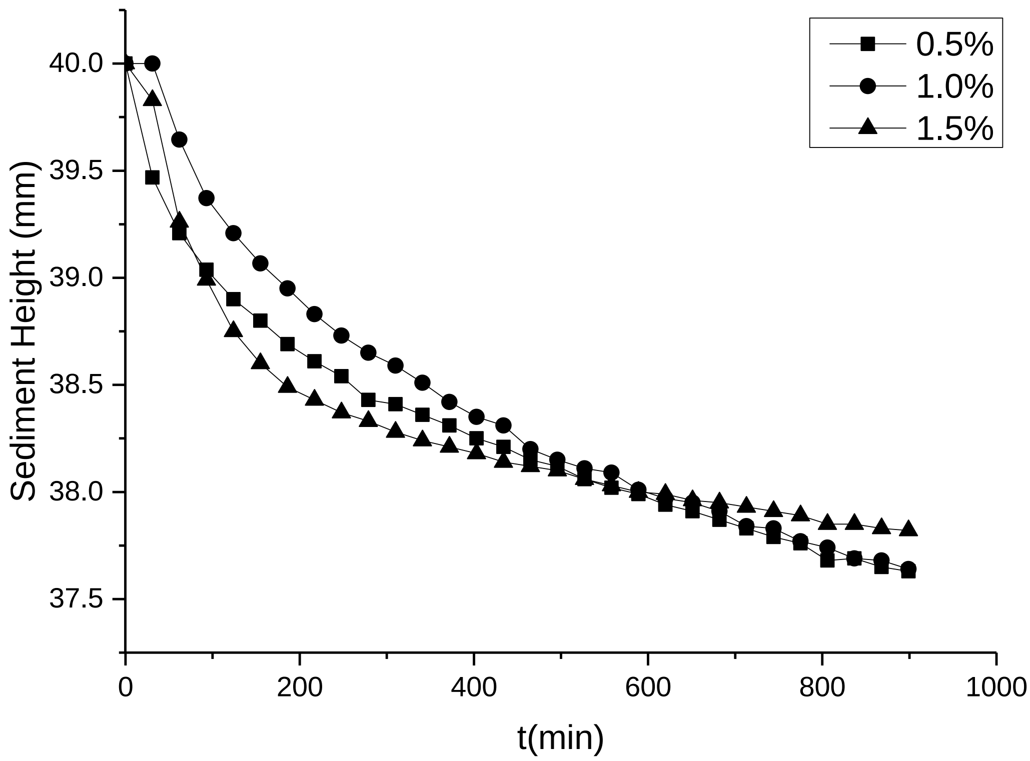


Figure 5: Settling data for slate suspensions with 70%w/v.

For a given solid percentage, the citric acid concentration showed little influence on both backscattering and sedimentation rate, so that only a slight variation in the sediment height was observed over extended times. At the beginning there is a continuous decrease of backscattering light. In the final part of the curves the slope and the sedimentation rate decrease. At the cell top particles appear to sediment with constant rate up the formation of sediment front; afterwards this sediment front move slowly by compression due to the network formed between particles.

Figure 4 shows a region where a slow increase in the backscattering can be observed, suggesting an accumulation of particles and possible heterogeneities in the system. A similar behaviour was reported by Moreno et. al., (2009) who investigated the destabilization process of alumina and silica suspensions. These authors justified the heterogeneities on the basis of a higher solids concentration and the presence of agglomerates.

The graph showed the sediment seemed to process in a linear model with time indicating “hindered settling”, which means the constraint on an individual particle from moving freely with Stokes velocity. The hindrance basically arises from the collective interaction of the particles with the fluid phase and between the particles themselves (Ramkrishna et. al., 2000).

Figure 6 shows the sediment height to suspensions with 55% slate and 1.0% citric acid concentration. As the solids concentration increase the sedimentation rate decrease, as expected.

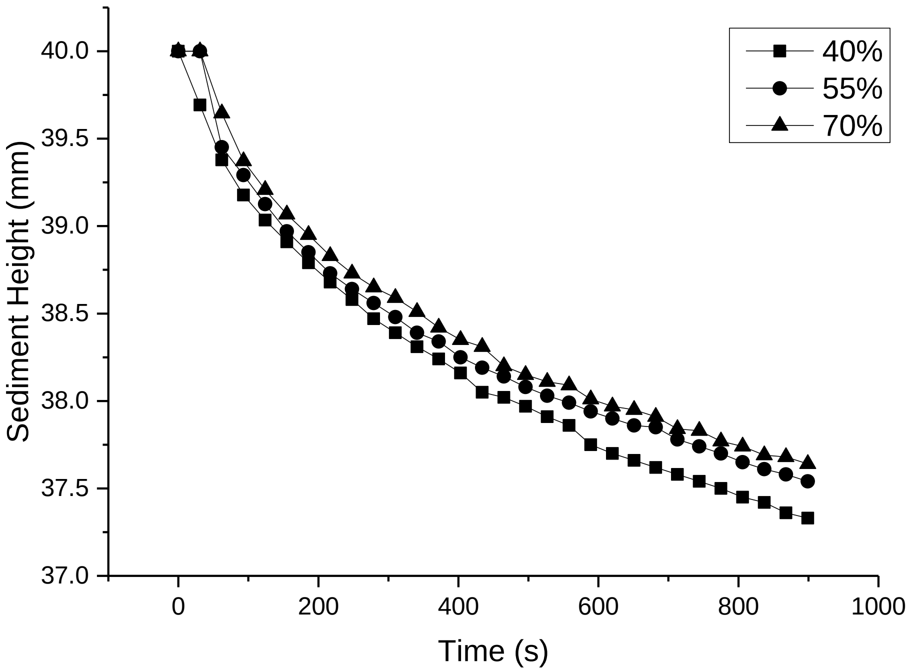


Figure 6: Settling data for slate suspension with 55% slate and 1% citric acid concentration.

Lumisizer offers an alternative method to follow the settling rate by using a centrifugal force. The sedimentation rate of particles and the sediment bed density can be estimated from the increased transmission of the settling front border with the supernatant (Paul et. al, 2013), as shown in Figure 7 for dispersions with citric acid in percentages from 0.5% to 2.5%. In this figure position 115 corresponds to the middle of the sample cell and the bottom is at 130 mm. The first profile was recorded at about 15 s when transmission was 1% and the last, after 2h of centrifugation with about 70% transmission. All suspensions show a similar behaviour with the transmission increasing very early upon centrifugation.

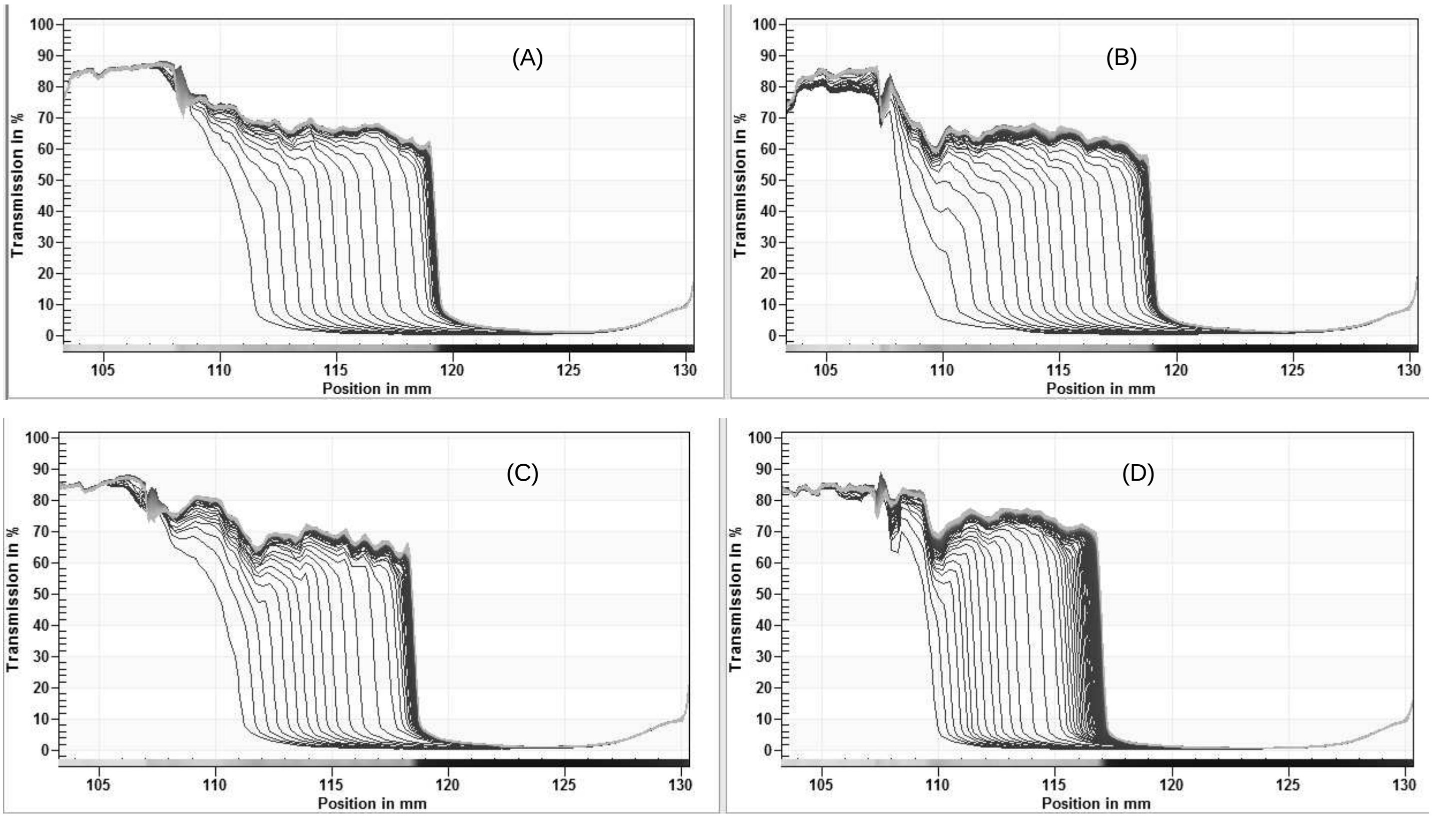
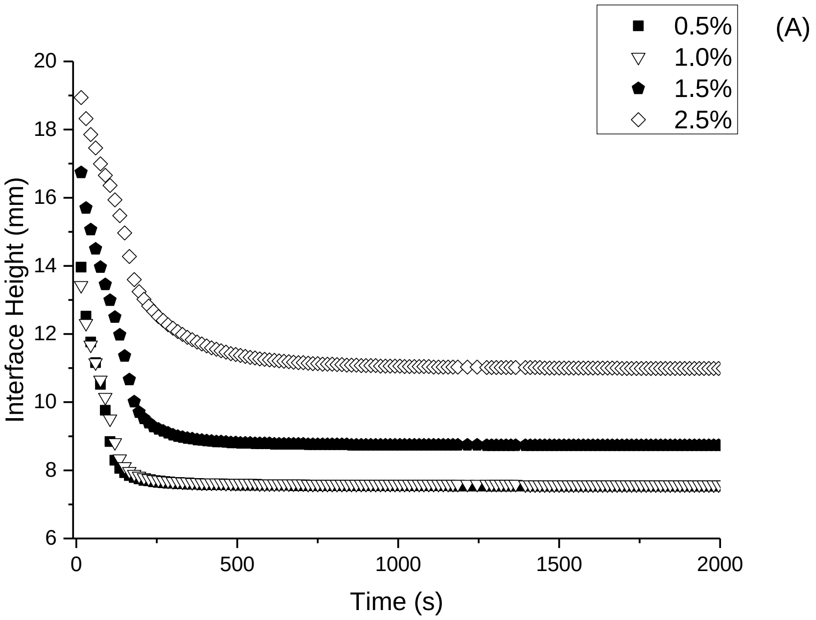
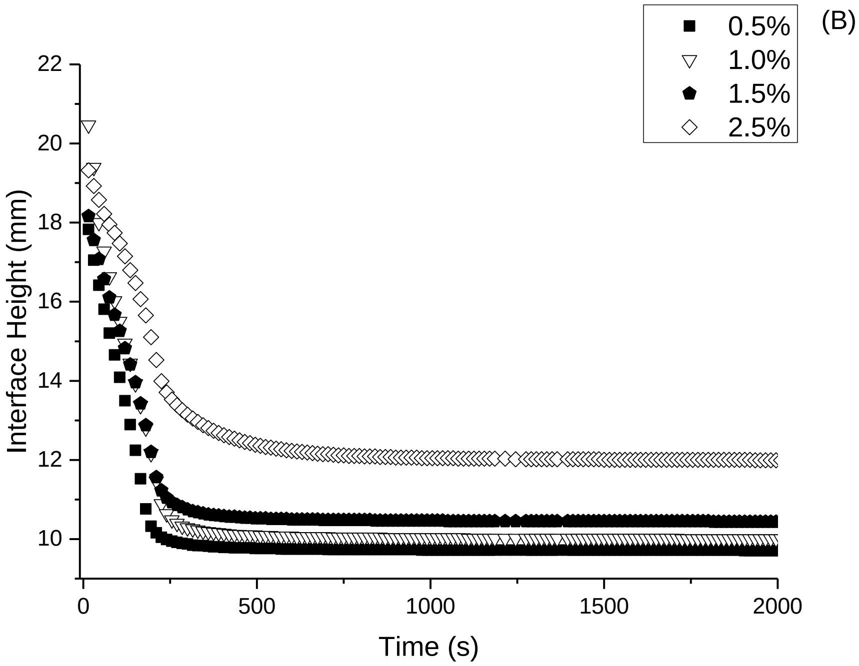


Figure 7: Recorded evolution to slate powder suspensions (55% w/v) with citric acid. In (A) 0.5%; (B) 1.0%; (C) 1.5%w/v and (D) 2.5%w/v

For a better comparison between the effects of different citric acid percentages, the change of the interface position between the particle and the dispersion as a function of time is shown in Figure 8. The sedimentation rate can be calculated, taking the linear region of these plots into account and the corresponding values for each suspension are listed on Table 1.





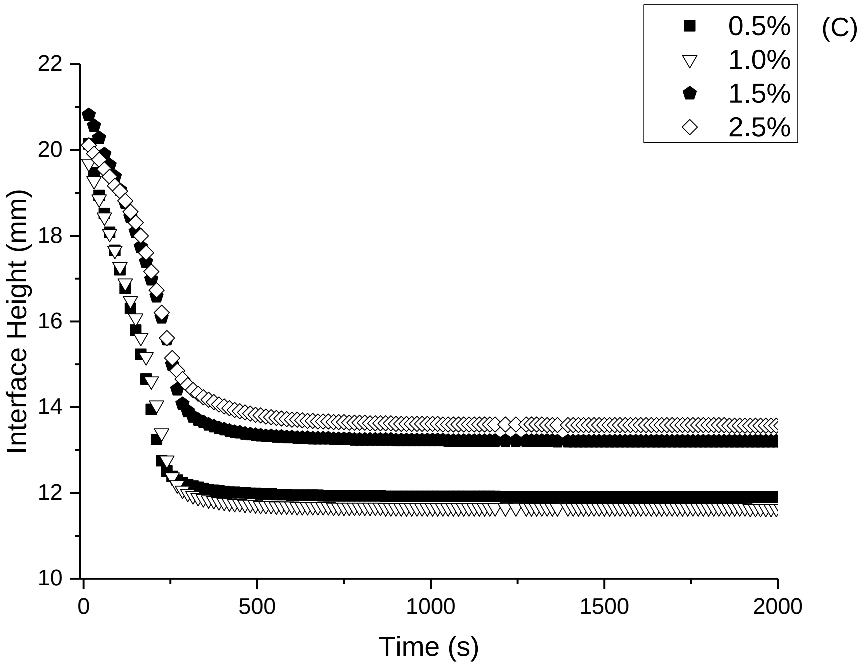


Figure 8: Sedimentation profiles for slate powder suspensions. In (A) 40% w/v; (B) 55%w/v and (C) 70%w/v.

Table 1: Approximate settling rates of the slate suspensions

Citric Acid (%w/v)	Slate suspension (%w/v) / rate (µm/s)		
	40%	55%	70%
0.5%	44.7	38.9	33.9
1.0%	38.6	40.2	28.8
1.5%	37.9	32.4	21.9
2.5%	30.0	23.8	17.5

The suspension with 40% solids and 0.5% citric acid showed the fastest settling rate and that with 70% solids and 2.5% citric acid, the slowest. For suspensions with the same solids percentage, the higher the citric acid concentration, the lower the settling rate. When suspensions with higher solids percentage are considered, the rate decreases for the same citric acid concentrations, although suspensions with 40% and 55% of solids have shown very similar settling rates. This behaviour can be accounted for by a hindered settling phenomenon, by which the collective particle interactions and the sedimenting particles themselves are influenced and slowed by neighboring particles (Kumar, et. al., 2000; Vesaratchanon, et. al., 2008).

Figure 9 is a plot of the sedimentation profiles for suspension with 2.5% citric acid and different solid percentages it reveals that the sediment height increases with solid percentage, as expected. The sediment bed density is lower with increasing citric acid concentrations because the bonding between the particles causes floc formation. The results indicate that these suspensions are more stable when the citric acid concentrations are low. This is supported by the low thickness of the sediments formed (Figure 9) and the average rates of particles migration to 70%w/v suspensions.

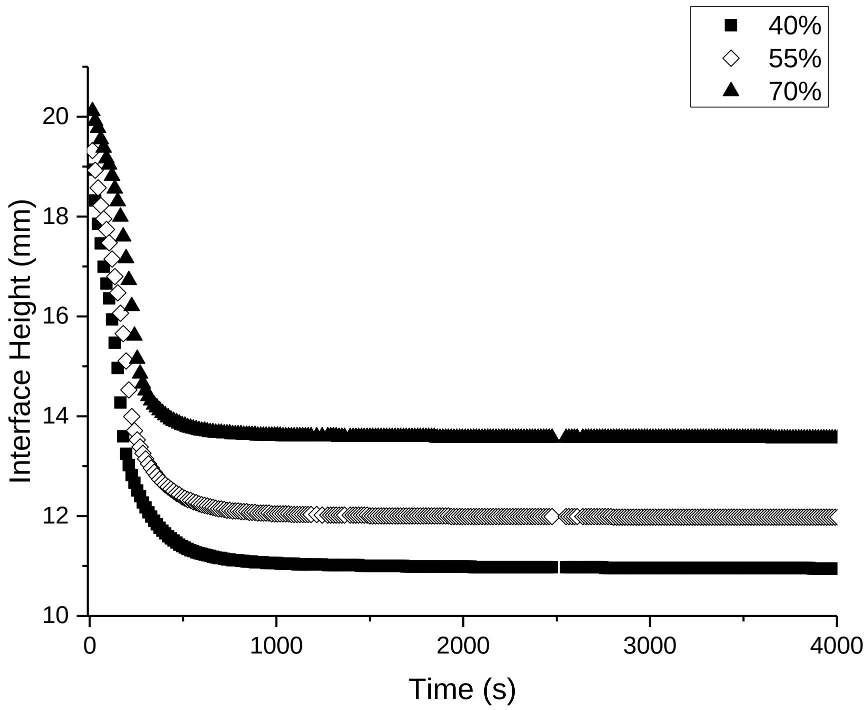


Figure 9: Sedimentation profiles for slate powder suspensions with 2.5% citric acid

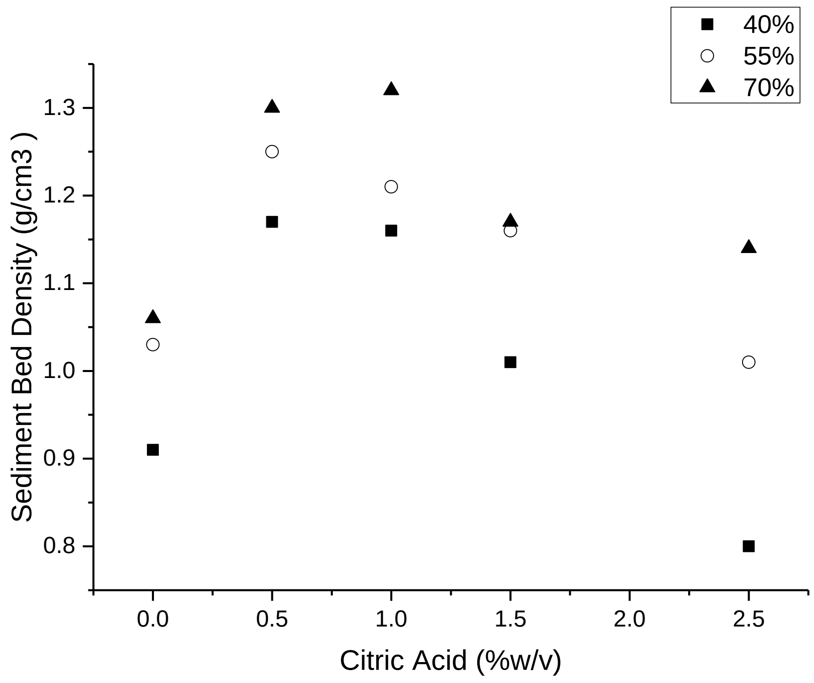


Figure 10: Sediment Bed Density for slate powder suspensions with 2.5% citric acid

The particle size distributions of suspensions with 40% solids are represented by essentially mono-modal curves (Figure 11). The curve representing pure slate is distinguished by a major peak at higher sizes with an adjacent shoulder associated with smaller material; the remaining curves show a relatively narrow distribution. When the citric acid percentages are high, the curves are shifted to left with the %volume peaking between 0.1 and 1, compared to pure slate. By comparing these results with Lumisizer data it can be said that the citric acid is acting as a dispersant, but as the solids concentration in suspensions increases (40%w/v to 70%w/v) the particles stick together as if forming a network. Even though these particles are smaller, they do not increase the bed density due to the network adhesion.

Each molecule of citric acid contains three functional carboxyl group which undergo sequential dissociation with increasing pH, increasing the ionization degree of the molecules, so that, at high pH values all of the three carboxyl groups are dissociated. At pH values near 6, probably three carboxyl groups per molecule are dissociated for all suspensions with 1.0% citric acid. According to Hidber et. al., (1996), the specific adsorption of a carboxylic acid does not necessarily lead to a change of the surface charge. These can be achieved only if an additional carboxylate group that is not coordinated to the surface is present in the molecule generating a negative surface charge to each molecule adsorbed. Guimarães (2008) found that, depending on characteristics such as surface charge and zeta potential, involved in the electrostatic interaction, the amount of carboxyl adsorbed necessary to promote stabilization of systems containing alumina decreases when pH increase. The same probably holds true for slate suspensions with 40%w/v and a concentration of 1.0% citric acid seems to be capable of promoting a better deflocculated system when compared to the others.

These results suggests that the saturation limit of adsorption was not reached for suspensions with 55 and 70% solids and the particles suspended cause destabilization and flocculation.

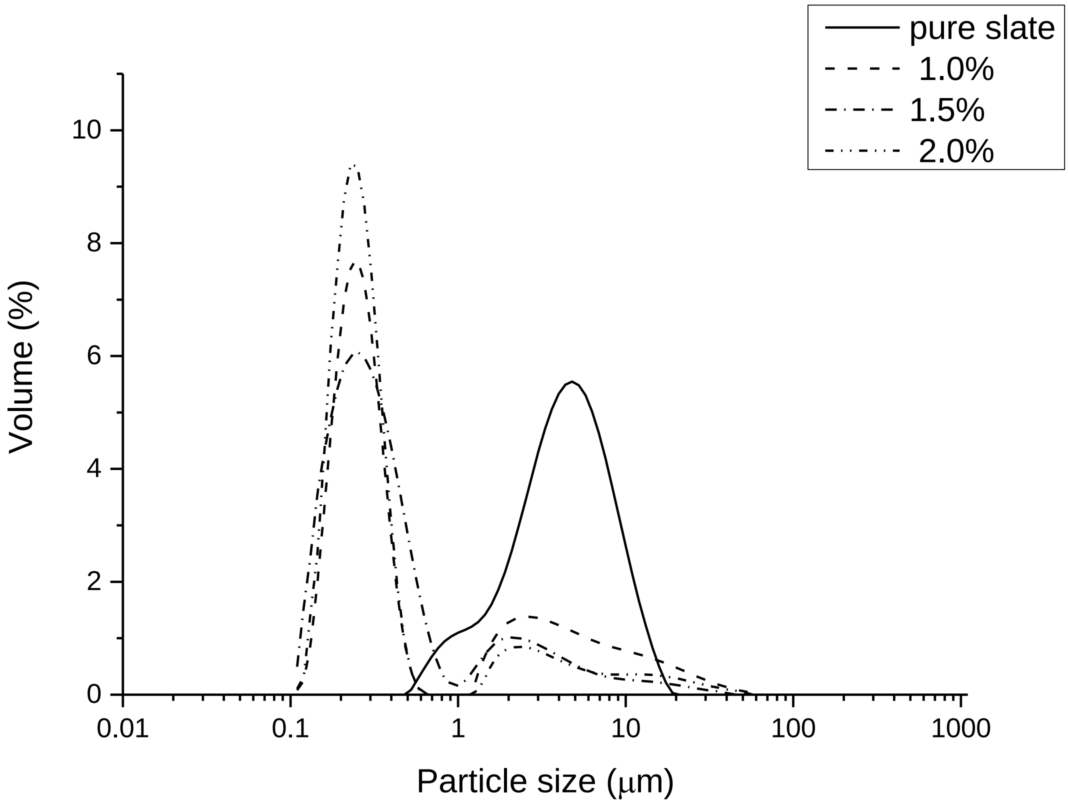
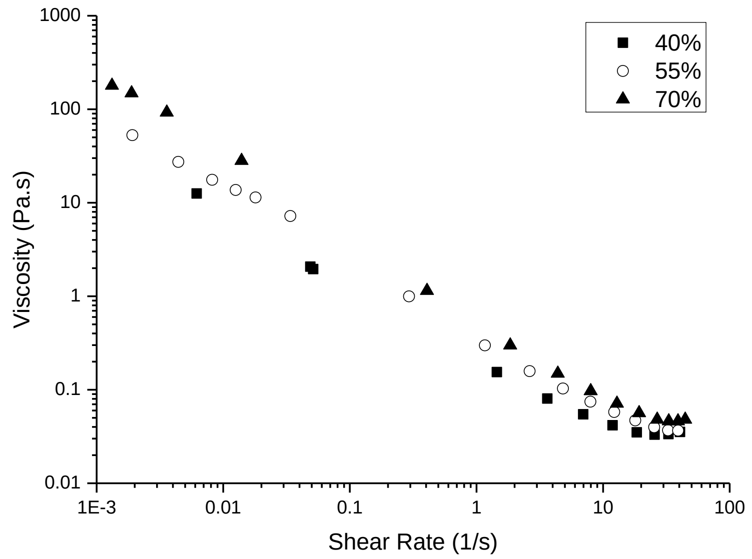


Figure 11: Particle size distribution of slate suspensions with 40% solids.

Standard flow curve data for samples are given as a function of volume fraction, in Figure 12. The suspensions are strongly shear thinning fluids with a large reduction in viscosity as a function of shear rate, so that increasing the solids fraction the viscosity also increases as shown in Figure 12-A.

(A)



(B)

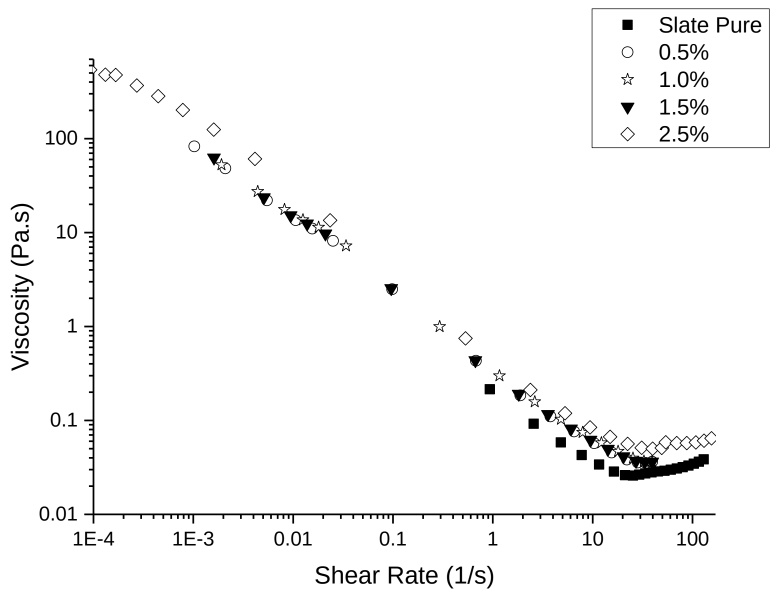


Figure 12: Viscosity as function of shear rate for slate suspensions (A) 1% of citric acid and (B) 55% of solids.

Shear thinning is a feature typical of agglomerated suspensions such as ceramics slurries, where, at low shear rates, the attractive interparticle forces overcame the hydrodynamic ones, leading to the formation of flocs. As the shear rate increases, the hydrodynamic forces exerted by the flow field become higher and higher, causing these flocs to be broken down into smaller and smaller flow units. The liquid entrapped within them is gradually released concomitantly decreasing the viscosity (Papo, et. al., 2002).

Figure 12-B shows the influence of dispersant concentration in the suspensions viscosity and it is always higher when compare to the pure slate suspension. Changing the citric acid percentage did not have a great influence on viscosity; however high level such as 2.5% are lightly to increase the adhesion force of the particles increasing the viscosity.

Conclusions

In this study we investigated the sedimentation and rheological characteristics of slate suspensions containing citric acid. Light scattering techniques were effective in analyzing the settling rate, aggregates and the sediment bed density.

We found that the citric acid concentration influenced the stability of all suspensions investigated. The interactions between particles surfaces could either induce flocculation, to higher citric acid concentrations, or enhance the stabilization at lower dispersant concentrations and pH values around 6.

The highest sediment bed density was obtained for suspensions with 40% slate powder and 1.0% citric acid. In this case the carboxyl groups of citric acid promotes higher dispersion of particles, that shows lower settling rate, enhancing the stability of suspension and therefore the compact sediment bed. Slate has a complex composition reflecting a range of structural charges, so that the citric acid did not prove to be a dispersant as effective in stabilizing this system as we would expect. Further work will focus on testing other polymers or dispersants, in order to produce more stable systems that could be used in slip casting process to produce ceramic pieces.

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