



Mechanisms for efficient clay dispersing effect with tannins and sodium hydroxide

Yi Du^a, Coralie Brumaud^{a,*}, Frank Winnefeld^b, Yin-Hung Lai^c, Guillaume Habert^a

^a Institute of Construction and Infrastructure Management, Chair of Sustainable Construction, Swiss Federal Institute of Technology (ETH Zurich, Stefano-Franscini-Platz 5, Zürich 8093, Switzerland

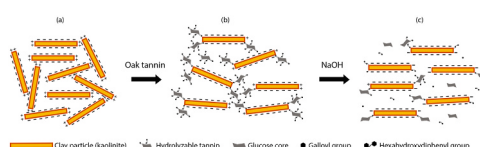
^b Laboratory for Concrete/Construction Chemistry, Empa, Swiss Federal Laboratories for Material Science and Technology, Überlandstrasse 129, Dübendorf 8600, Switzerland

^c Laboratory of Organic Chemistry, Swiss Federal Institute of Technology (ETH Zürich), Vladimir-Prelog-Weg 3, Zürich 8093, Switzerland

HIGHLIGHTS

- Oak tannin is an efficient and natural dispersant for clay materials.
- In combination with sodium hydroxide, the deflocculation action of tannin is amplified.
- Oak tannin and NaOH disperse clay particles via combined steric repulsion forces and electrostatic repulsive forces.
- Oak tannin coupled with NaOH is a promising superplasticizer for earthen materials and an environmentally friendly alternative to industrial product.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Clay material
Tannin
Deflocculation
Interaction
Surface charge
Rheology

ABSTRACT

Substituting the industrial additives in building materials with natural ones can reduce the embodied carbon in the construction sector. In this paper, the dispersing effect of oak tannin as natural dispersant on clay materials is studied in combination with sodium hydroxide. Through rheological measurements, adsorption tests, and zeta potential measurements, the deflocculation mechanism of tannin under varied NaOH environments has been highlighted. The results show that the dispersing ability of tannin can be increased greatly with the incorporation of NaOH. By adding NaOH in the system, the kaolinite deflocculation mechanism of tannin is changed from steric hindrance to combined steric hindrance and electrostatic repulsion forces. This shift stems from two aspects: the transformation of the tannin chemical structure and the modification of kaolinite by NaOH. The results indicate that tannin coupled with NaOH can be a promising superplasticizer for earthen materials, with the potential of producing poured earth based on this combination.

1. Introduction

The large utilization of concrete in the construction field is linked with significant environmental impacts, mainly related to resource

consumption and greenhouse gas emission during cement production [1]. Due to this concern and to achieve the goals of EU strategy for a climate-resilient society by 2050, building materials with lower environmental impact need to be pushed forward. Clay materials, which

* Corresponding author.

E-mail address: brumaud@ibi.baug.ethz.ch (C. Brumaud).

<https://doi.org/10.1016/j.colsurfa.2021.127589>

Received 25 June 2021; Received in revised form 14 September 2021; Accepted 16 September 2021

Available online 21 September 2021

0927-7757/© 2021 The Authors.

Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

consist of aggregates of different sizes (gravels, sands, slits, and clay), have been used since time immemorial and have been proved to be the lowest environmental impact construction materials because of their local availability, lower cost, and infinite recycling possibilities [2]. Recent years have witnessed a strong development of clay materials, and contemporary architecture made out of clay materials has emerged around the World [3,4]. There are many ways in which simple, unprocessed clay materials have been used in earthen construction, such as adobe and rammed earth [3]. Among these, a castable poured earth similar to concrete, where the colloidal state of clays has been tuned to propose a clay suspension that would evolve in time from a highly dispersed state (deflocculated) to a coagulated one with the help of dispersants and coagulants, have been put forward and are gaining more and more attention [5–8]. With this technique, the construction process can be speeded up greatly which saves cost and labor. In this process, dispersants play an important role and different chemicals have been explored in various papers. In principle, chemicals that can increase the thickness of clay's electrical double layer or steric hindrance between the clay particles can take over this role. Sodium hexametaphosphate Na-HMP [9–13], sodium polyacrylate PAAS [11], carboxymethylated xylan CMX [14,15], and sodium silicate with different silica moduli [12,16,17] have been found are effective dispersants for clay materials because of their ability to control edge and face charges of clay minerals and by modifying clay interactions from 'house of cards' structure to organized order. With the help of a dispersant, the yield stress and viscosity of pastes can be reduced, as well as water content. The microstructure of clay particles after hardening will be denser, thus the mechanical strength of clay materials can be improved [9,11].

However, the choice of dispersants for clay materials is still limited, and are mostly industrial products [18]. To minimize the environmental burden of clay materials, researchers have sought natural additives to substitute the industrialized plasticizers. Tannin, as a bio-additive, can be found in many plants and has been reported to act as a dispersant for clay materials [19,20]. As the polyphenolic secondary metabolites of higher plants, tannins can play various biological roles, like anti-infection, protection against insects, or herbivorous. They are found mainly in the barks, leaves, stems, seeds, and roots of plants [21]. Tannins are classified based on their resistance or not, to hydrolysis in aqueous solution or the enzyme tannases. They can be grouped into condensed tannins and hydrolyzable tannins, and the latter can be further divided into gallotannins, ellagitannins, and complex tannins, depending on which units (polyol-, catechin-, and triterpenoid) galloyl moieties or their derivatives are bounded to [22]. Tannins have enormous structural variations, with molar masses between 300 and 3000 g/mol, and can precipitate metal ions, alkaloids, and proteins, which leads to wide applications in various fields, like tanning, dyeing, ink, wines, and pharmaceuticals [23].

Tannins can interact with clay particles via different bonds, and each interaction brings different benefits to the corresponding clay materials. Due to the slightly acidic and negatively charged properties, the phenolate anion of tannins can adsorb on the edge or face of colloidal particles via ionic bonds, and thus can distribute the orientation of grains and reduce the yield stress and viscosity of paste through electrostatic repulsion forces and large ionic sizes [19,20,24,25]. Besides, the hydrogen bonds between the hydroxyl radicals of the tannins and clay particles can provide other binding forces between clay platelets besides the solely capillary forces [26]. Moreover, the covalent bonds between tannins during the polymerization process, which is the oxidation of polyphenols to quinones and their subsequent condensation, can help to improve the strength and water resistance of clay materials [27,28]. However, the studies about using tannin in clay construction are limited, and its usage is just based on empirical knowledge. Moreover, its deflocculation efficiency is inconstant as its molecular structure varies depending on its source. To expand their application as a dispersant for clay materials, the methods which can improve the efficiency should be put forward and a good understanding of interactions

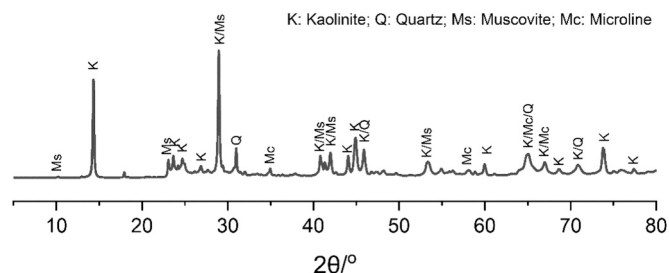


Fig. 1. XRD pattern of FP80 clay.

between clay and tannin should be obtained for better utilization.

In this paper, the dispersing effect of oak tannin (OT) with and without sodium hydroxide (NaOH) addition was studied by rheological experiments. Yield stress and viscosity of clay paste with different amounts of OT and different NaOH/OT mass ratios were characterized. Zeta potentials of kaolinite and tannin adsorption were also explored to gain a solid understanding of the role of each additive. Furthermore, the UV-Vis spectra and mass spectra of oak tannin solution under different pH were also obtained and an illustration of the mechanism of deflocculation was proposed based on the results.

2. Materials and experimental procedures

2.1. Materials

2.1.1. Clay

A pure clay referred to as FP80, sourced from Dorfner (Germany) with a specific density of 2.62 g/cm³ determined by helium pycnometer (AccuPyc II 1340 Micromeritics) was used in this study. The specific surface area SSA_{BET} measured by nitrogen adsorption (Micromeritics Tristar II 3020) was 9.10 m²/g. The average particle size of 8.7 μm was measured using a laser particle size analyzer (Partica LA-950, Horiba, Munich, Germany) in Na-polyphosphate dispersing solution with ultrasonic treatment.

The main mineralogical components, determined by X-ray diffraction powder technique (Fig. 1) and quantitatively analyzed by using Rietveld method, are kaolinite (87 ± 5 wt%), quartz (4.0 ± 0.3 wt%), muscovite (3.6 ± 0.6 wt%) and microcline (3.6 ± 0.5 wt%). Its chemical composition, obtained through X-ray fluorescence spectrometry (XRF) is given in Table 1.

2.1.2. Tannin

A commercial oak tannin (referred to here as OT), extracted from lightly thermally treated French oak (*Quercus robur* and *Quercus petraea*), in powder form (Agrovin, France) was used in this study. Its physicochemical properties, data provided by the supplier, are summarized in Table 2. Fourier-transform infrared spectroscopy (FTIR) and Ultraviolet-visible spectroscopy (UV-Vis) showed that the main component of this product is hydrolyzable tannins (Fig. 2). It is well established that the FTIR spectra of varied types of tannins show different peaks in the 'fingerprint region', ranging between 1500 and 950 cm⁻¹ [29]. Hydrolyzable tannins present C-O lactones stretching at 1325–1317 cm⁻¹ while condensed tannins display C-O pyran ring stretching at 1288–1282 cm⁻¹ [29,30]. In this study, oak tannins are characterized by bands at 1317 cm⁻¹, which is a typical peak of hydrolyzable tannins. More specifically, the peak at 1086 cm⁻¹ can be ascribed to gallotannins. For the UV-Vis spectrum, the oak tannin solution shows maximum absorbance at 219 nm and a shoulder at 276 nm, corresponding to the characteristic λ_{max} around 212 nm of gallotannins and the adsorption shoulder around 277 nm of ellagitannins [31].

2.1.3. Chemical additive and water

Sodium hydroxide pellets (ACS reagent, > 97.0%) sourced from

Table 1

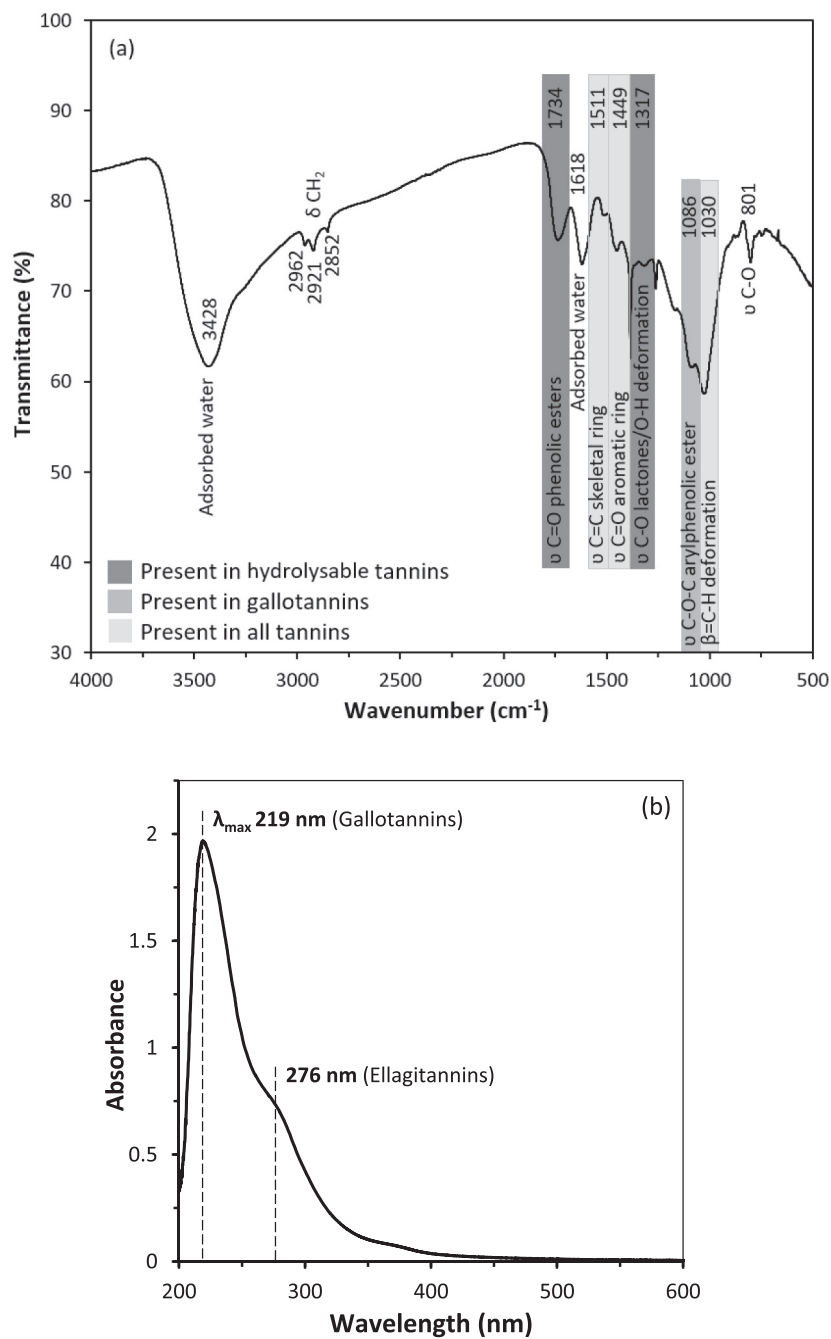
Chemical composition of the clay studied by X-Ray fluorescence analysis. Values are given in mass %. LOI = Loss of Ignition.

Physical properties			Chemical composition								
Density, g/cm ³	SSA _{BET} , m ² /g	Average size, μ m	Al ₂ O ₃	SiO ₂	K ₂ O	Na ₂ O	Fe ₂ O ₃	MgO	TiO ₂	Others	LOI
2.62	9.10	8.7	35.98	48.02	1.29	0.01	0.45	0.15	0.33	0.58	12.41

Table 2

Physicochemical properties of tannin used in this study.

Tannins (%)	Moisture (%)	Ash (%)	Insoluble fraction (%)	Arsenic (ppm)	Iron (ppm)	Lead (ppm)	Mercury (ppm)	pH
> 70	< 10	< 4	< 2	< 3	< 50	< 5	< 1	3.5–4.1

**Fig. 2.** (a). FTIR spectrum and (b). UV-Vis spectrum of oak tannin.

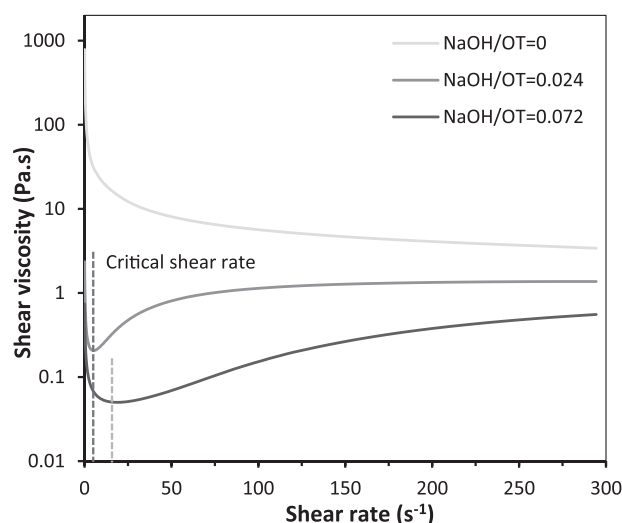


Fig. 3. Rheological behavior of studied clay pastes prepared with 1 wt% OT and their corresponding critical shear rate.

SigmaAldrich were used in this study. Water at ambient temperature was used for the preparation of samples for rheology measurements and zeta potential tests while ultra-pure water (Millipore SA) was used for the other experiments to eliminate the effect of potential dissolved ions.

2.2. Experimental procedures

2.2.1. Sample preparation

Considering that oak tannin might consist of various components with a chemical formula that cannot be precisely determined, the dosage of additives was expressed by the mass ratio of NaOH to oak tannin and not by molar ratio. Varying dosages of tannin (by mass of clay) and sodium hydroxide (by mass of tannin) were added into the water before mixing with kaolinite clay. The water to clay ratio (W/C) was kept constant at 0.69 for rheological measurements, corresponding to a solid volume fraction ϕ of 35.4 vol% (critical solid volume fraction of the kaolinite studied here where the rheological properties diverge), at 2 for adsorption measurements, and at 4 for Zeta potential measurements. The amount of NaOH was defined to reach the targeted pH value of solutions, from 4 to 11 (cf. Fig. 4). For rheological and adsorption measurements, clay powder and solutions were mixed with a mechanical stirrer equipped with a cross-blade impeller (Heidolph Instruments, Switzerland) at 700 rpm and 365 rpm, depending on the considered W/C ratio, for 3 min while the suspension for Zeta potential tests was mixed with stirrer cell of Zetaprobe analyzer. All the samples were prepared at room temperature (20 °C).

2.2.2. Rheological measurements

The rheology measurements of clay pastes were performed using a Malvern Kinexus Lab+ (Malvern Instruments, Switzerland) stress-controlled rheometer equipped with vane geometry [32]. The vane geometry consisted of a four-bladed paddle with a diameter of 25 mm, the outer cup diameter was 25 mm, and its depth was 61 mm. Serrated parallel plates of diameter 40 mm were used for clay pastes displaying high yield stress, allowing the elimination of the wall slip effect [33]. The diameter of the upper plate was 40 mm and the gap between plates was 1 mm. During the measurement, the setup was kept at a constant temperature of 23 ± 0.1 °C with a thermostatic bath. Five minutes after the first contact of the constituents, the cup was filled and covered with a trap cover to limit evaporation and drying, and the sequence was started. An increasing shear rate ramp from 0.1 s^{-1} to 300 s^{-1} (with a logarithmic distribution of shear rates) was applied for 300 s followed by a decreasing shear rate ramp from 300 s^{-1} to 0.1 s^{-1} for 300 s. Only the

decreasing ramps were analyzed for the value of the yield stress, extrapolated at low shear rates through a linear regression according to the Herschel-Bulkley model with $\tau = \tau_0 + \eta_{HB}\dot{\gamma}^n$, where τ is the shear stress, τ_0 is the yield stress, $\dot{\gamma}$ is the shear stress, η_{HB} is the consistency index and n is the flow index [33]. Shear viscosity was obtained from the curve of shear viscosity over the shear rate at the point of 100 s^{-1} , and the critical shear rate, the turning point between shear thinning and shear thickening regions, was recorded (Fig. 3).

2.2.3. Zeta potential measurements

The ζ -potential, which is the electrokinetic potential in colloidal systems and, thus, the key indicator of the stability of dispersions, of the concentrated suspensions of kaolinite clay with tannin and sodium hydroxide, was measured with a ZetaProbe (Colloidal Dynamics, Hofheim, Germany), which is based on the electro-acoustic method. A high-frequency alternating electric field is applied and causes charged particles to oscillate. The motion of the particles generates a sound wave, which is recorded and delivers the dynamic mobility of the suspended particles. The software calculates the ζ -potential from the dynamic mobility [34,35]. The ζ -potential experiments were conducted on suspensions of solid volume fractions of approximately 20 wt% in deionized water with a tannin dosage with respect to the clay content. The tannin solution and kaolinite were pre-mixed for 5 min at 375 rpm before being titrated with 0.5 mol/L NaOH solution to achieve the required NaOH/OT ratio. Titration series with 600 s equilibration time between data points were realized to ensure the stability of the medium at each data point acquisition. The sedimentation issues and resulting measurement artifacts are avoided by blade stirring at 375 rpm. The single-point measurement performed enables to follow the ζ -potential overtime at constant dosage in the mineral soil. The reported value was recorded once no variation is observed in the surface charge. Meanwhile, the zeta potential of kaolinite suspension with the same amount of NaOH but without OT was also measured to compare the effect of sodium hydroxide and tannin. To eliminate the effect generated by the electrolyte ions in the suspensions, the electroacoustic signal from the background electrolyte was also measured and subtracted from the total signal. Background measurements were carried out for each kaolinite suspension and zeta potential was automatically corrected by the software.

2.2.4. Adsorption measurements

A Total Organic Carbon (TOC) analyzer (Shimadzu, Switzerland) to measure the potential adsorption of oak tannin at the surface of kaolinite particles was used in this work. The analysis technique involves a two-stage process commonly referred to as TC-IC. It allows for the measurement of both the amount of Inorganic Carbon (IC) by acidification of the sample and the amount of Total Carbon (TC) in the sample. TOC is calculated by subtraction of the IC value from the TC of the sample. Since the components of oak tannin are unknown, a tannin solution with a concentration of 4350 ppm was used as a reference to calculate the tannin concentration of solutions after filtration. The TOC analyzer was first calibrated with a kaolinite paste to take into account the amount of organic carbon already present in kaolinite clay. Furthermore, an analysis of the amount of organic carbon in reference solutions of OT was carried out to calibrate the TOC analyzer. To facilitate the extraction of the interstitial solution, diluted clay paste was prepared (W/C = 2). After mixing, the clay pastes prepared at different NaOH/OT ratios, were transferred into a funnel with filter paper to extract the interstitial solution, which was further filtered by the syringe membrane filter with a pore size of $0.45 \mu\text{m}$ and then tested with the TOC analyzer. By subtracting the TOC value measured on the extracted interstitial fluid from the reference TOC value (TOC value in reference OT solution), the amount of OT adsorbed on clay particles was computed. Only the NaOH/OT ratios below 0.072 were tested considering the intrinsic characteristic of kaolinite particles (negatively charged) and the chemical instability of tannin in a high pH environment. Langmuir [36] and

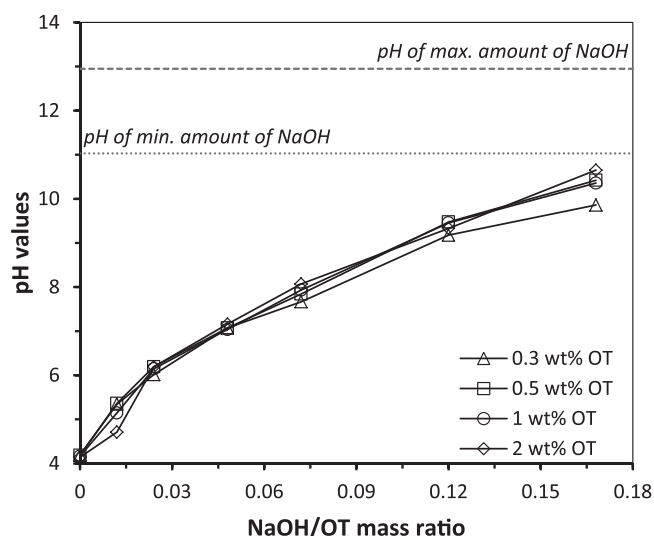


Fig. 4. pH values of tannin solutions as a function of NaOH/OT mass ratio.

Freundlich adsorption model [37] were chosen to fit the adsorption isotherms.

2.2.5. Solution characterization

The pH values of solutions were measured with a Multi-parameter meter MU6100 L (VWR, Switzerland), with an accuracy of 0.01 pH. All the measurements were conducted at room temperature and repeated three times for accuracy. To understand the reactions between tannin and NaOH, UV-Visible spectrophotometer UV-1800 (Shimadzu, Japan) and electrospray ionization LTQ-Orbitrap mass spectrometer (Thermo Fisher Scientific, Germany) was used to analyze the potential changes of tannin molecule after the addition of NaOH. The absorbance of light in the range of 200–700 nm of solutions with a low concentration of 43.5 ppm of tannin and different NaOH/OT ratios was measured. For the mass spectra measurements, OT solutions with 50 μM were prepared in 10 mM ammonium acetate buffer at pH 5 and pH 9, respectively. Nitrogen (10 arb. unit) was used as a nebulizing sheath gas. Electrospray of solutions was performed in the positive ion mode with a spray voltage of 3.5 kV and a flow rate of 5 $\mu\text{L min}^{-1}$. Data acquisition and subsequent analyses were conducted using XCalibur software (Thermo Fisher Scientific, Germany).

3. Experimental results

3.1. pH values of tannin solutions

In Fig. 4, the pH values of the solutions containing different amount of OT are plotted as a function of the NaOH to OT ratio. As expected, the pH of the solutions increases with the addition of NaOH. Furthermore, for a given NaOH/OT ratio, although the amount of tannin introduced varies in the preparation, the measured values are similar. Without the presence of NaOH, the solutions are slightly acidic displaying a pH around 4.2: by adding 1.2 wt% of NaOH the pH increases to around 5. A NaOH/OT ratio of 0.048 is needed to reach the neutral value of the pH (around 7–7.2). When the NaOH/OT ratio reaches 0.168, the pH of the solutions are in the range of 9.8–10.6: considering that the pKa of tannic acid is around 8.5 [38,39], it can be suggested that at a lower ratio, NaOH proportionally reacts with tannins and that phenates are formed linearly with the amount of NaOH introduced in the mix.

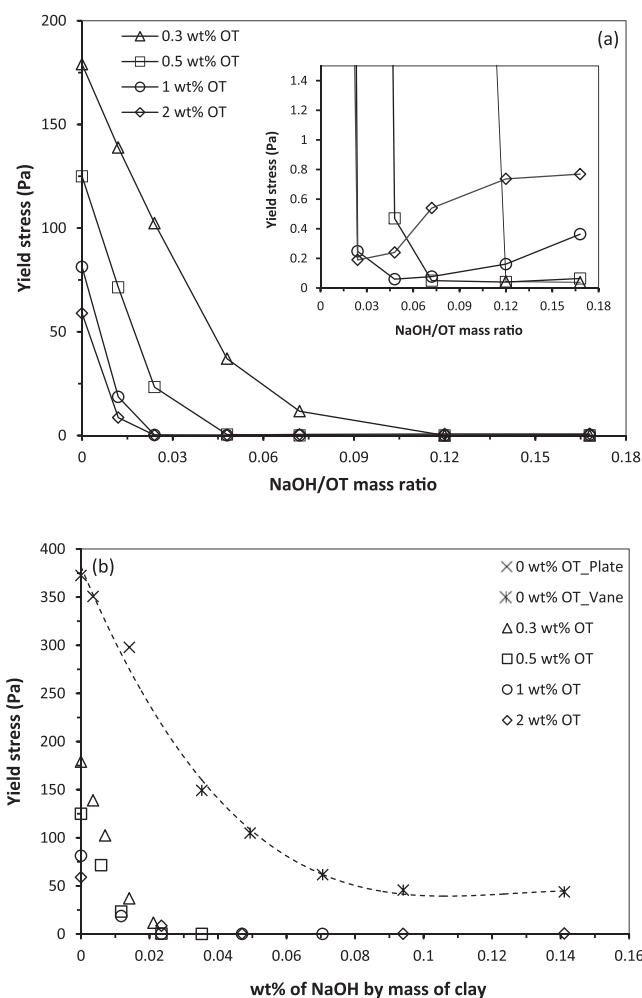


Fig. 5. The yield stress of clay pastes as a function of (a) NaOH/OT mass ratio and (b) amount of NaOH added in the mix.

3.2. Influence of tannin and sodium hydroxide on the rheological behavior of clay paste

3.2.1. Yield stress

In Fig. 5(a), the yield stress of kaolinite clay paste prepared with different amounts of tannin is plotted as a function of the NaOH/OT mass ratio. The addition of tannin modifies the yield stress of the mixture and improves the fluidity of the material. Adding 2 wt% of tannin decreases the yield stress of the mix by a factor of 3. Nevertheless, the dispersant action of tannin alone is not as efficient as required to obtain a fluid material. However, when a small amount of NaOH is incorporated into the mix, the yield stress of the clay pastes decreases drastically. As an example, when NaOH is added to the mix at a NaOH/OT mass ratio of 0.024, the yield stress of the paste containing 0.3 wt% OT decreases from 176 Pa to 102.4 Pa, which represents a reduction of 42.8%. Further increase in NaOH brings a less slow decrease rate of yield stress. Assuming that the yield stress of the constitutive paste for a flowable concrete should be of the order of 10 Pa, for different dosages of OT (i.e. 0.3, 0.5, 1, 2 wt%), 12 wt%, 4.8 wt%, 2.4 wt% and 1.2 wt% of NaOH by mass of tannins seem to be sufficient to reach that point. Surprisingly, the yield stress of pastes with 1 wt% and 2 wt% tannins at NaOH/OT mass ratio above 0.048 starts increasing slightly, but still less than 1 Pa (the inserted figure of Fig. 5(a)). This trend has been reported in the literature [12] when NaHMP is used as a dispersant. According to the authors, this phenomenon may be induced by the higher electrolyte concentration leading to a thinner double layer and a stronger

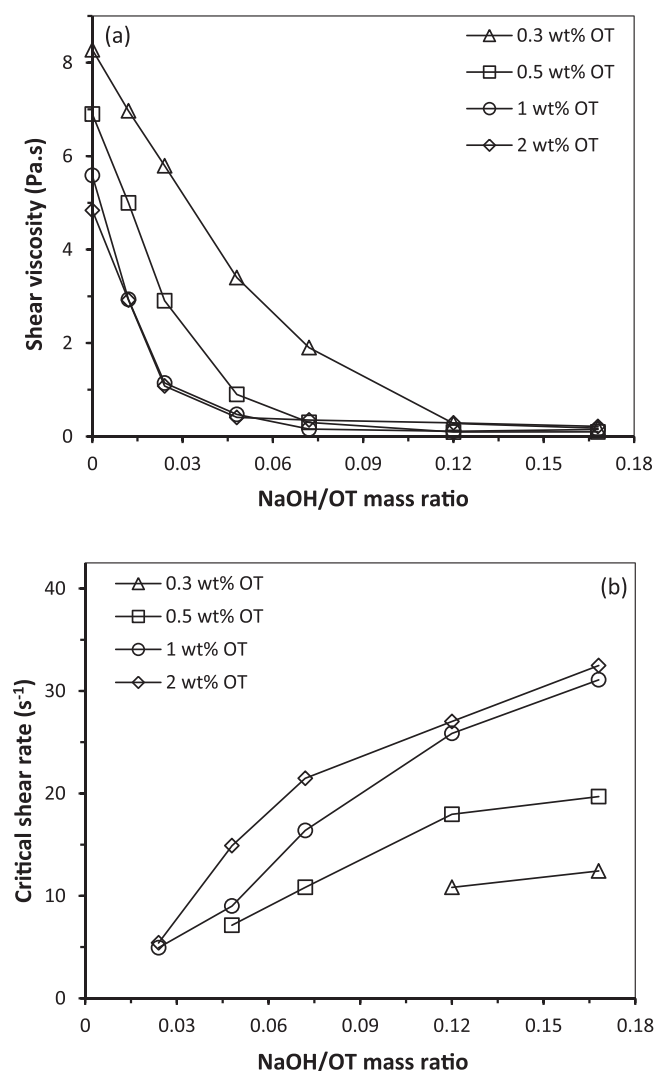


Fig. 6. (a). Shear viscosity of pastes at a shear rate of 100 s^{-1} and (b) Critical shear rate of shear thickening pastes as a function of NaOH/OT mass ratio.

interaction between clay particles. Meanwhile, to compare the effect of solely using NaOH, the yield stress of pastes with different amounts of NaOH was measured and the results are presented in Fig. 5(b), as well as four mixes with NaOH/OT mass ratio below 0.072. The results show that the yield stress value of clay paste prepared with oak tannin in combination with NaOH is lower than the yield stress of the clay paste prepared with pure NaOH, even just with a low dosage of tannin.

3.2.2. Shear viscosity and critical shear rate

In Fig. 6(a), the shear viscosity of clay pastes prepared with different NaOH/OT mass ratios is plotted. The evolution of the shear viscosity of pastes as a function of NaOH/OT mass ratio shows a similar trend as the yield stress (cf. Section 3.2.1). With the addition of NaOH in clay paste containing OT, the shear viscosity decreases gradually, from 5 to 8 Pa.s to around 0.3 Pa.s. The turning point between shear thinning and shear thickening regimes is defined as the critical shear rate. The critical shear rates of the clay pastes are gathered in Fig. 6(b). It is remarkable to note that the clay pastes whose shear viscosity is lower than 1 Pa.s displayed shear-thickening behaviors. This observation is in agreement with the literature [40,41] where the prerequisite of a shear thickening phenomenon is a fully deflocculated suspension. Indeed, when a small force is applied to a fully deflocculated paste, the particles transit from an immobile state to a mobile state and form small aggregates to minimize the collision between particles. The movements of particles are thus

facilitated and, consequently, the viscosity decreases. However, when the force increase continuously, small groups of particles start forming hydroclusters, resulting in an increase in the viscosity, and shear thickening is observed. Thus the critical shear rate is the shear rate at which the shear forces pushing the particles together are equivalent to the repulsive particle interactions, and the repulsive forces are getting higher with the increase of NaOH. The mechanisms at the origin of the increase in repulsive forces will be discussed in the following sections.

3.3. Surface charge characterization

The zeta potential of kaolinite clay suspension with different dosages of tannins as a function of NaOH/OT mass ratio is plotted in Fig. 7. When no additives are added to the clay paste, the kaolinite particles exhibit a negative charge, which is attributed to the existence of permanent negative charged basal planes where the Si^{4+} and Al^{3+} in the crystal lattice are substituted by lower valence cations [42]. With the addition of tannins alone, the potential slightly increases and then decreases, with a peak at 0.3 wt%. When NaOH is introduced, the zeta potential of all the suspensions increases linearly which is an already known phenomenon [43,44]. The order of zeta potential is always kept the same with a higher dosage showing a higher negative charge. The mechanisms at the origin of the increase in negative charges will be discussed in the following sections.

3.4. Adsorption of tannin

The adsorption of tannin at the surface of kaolinite particles in presence of NaOH is shown in Fig. 8. All the adsorption isotherms display the 'L' shape, showing a fast adsorption rate at the beginning followed by a gradual slowdown, except when NaOH/OT ratio is equal at 0.072. As presented in Fig. S1 a. and b. in Supplementary Materials, the Freundlich model shows a better fit to the adsorption data than the Langmuir model except for the clay pastes prepared at a NaOH/OT ratio of 0.072. This result indicates that the affinity of adsorption sites is not equal: the stronger binding sites are occupied first by tannins until the binding energy decreases exponentially with the increase in occupation sites [45]. By comparing the adsorption of tannin at the surface of clay particles under different pH environments, an evident decrease of adsorption with the increase of NaOH can be observed for the pastes containing a higher dosage of tannin while it is slightly different for the clay pastes prepared with a lower amount of tannin. An increase in pH generally leads to a reduction of the amount of adsorbed compounds since the adsorption sites (here $-\text{AlOH}_2^+$ for kaolinite particles) decrease [46]. However, it is more complex in the case of tannin given that its molecular properties, i.e. structure and ionization, are changing with the pH. As a weak acid, tannin can be ionized and dissociated by the base. Ionization of molecules can enhance their adsorption affinity and thus increase the total adsorbed content [47] while on the contrary, dissociation can reduce the adsorption rate. By observing the adsorption of tannin at low dosage, where the sites' effect can be neglected, a small addition of NaOH slightly increases the adsorption rate whereas the adsorption starts decreasing at a high pH environment. This finding seems to validate the argument previously described (i.e. the reaction between tannin and NaOH is controlling the adsorption kinetics).

4. Discussion

The yield stress of colloidal systems is related to the nature and strength of inter-particle forces. According to the literature [11], dispersants can increase the inter-particle forces via electrostatic or steric repulsive forces, either alone or in combination with each other, leading to a deflocculation of the colloidal particles. For the kaolinite pastes prepared with tannin and NaOH simultaneously, the decrease in yield stress and the increase in critical shear rate can be interpreted in the same manner as the increase in inter-particles repulsive forces, which is

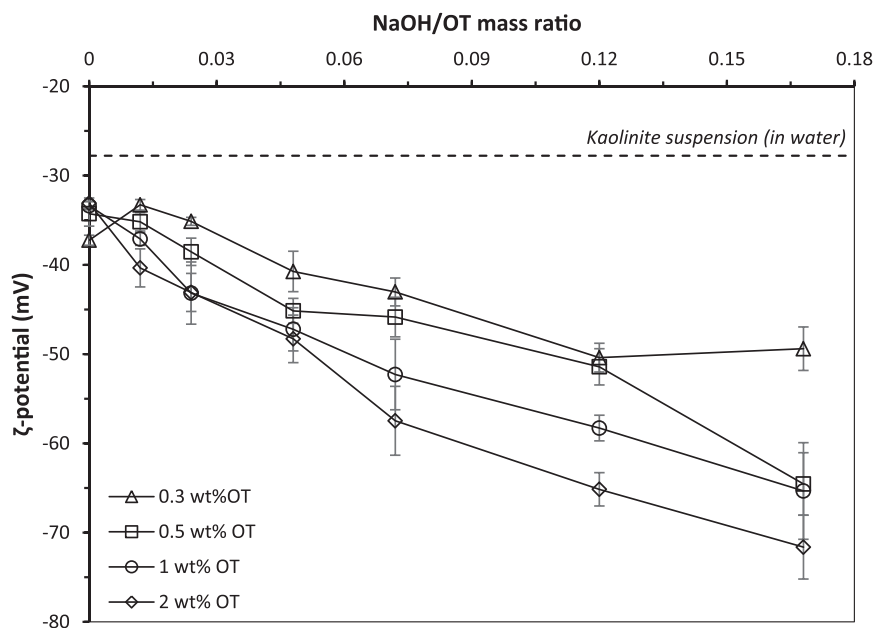


Fig. 7. Zeta potential of kaolinite as a function of NaOH/OT mass ratio.

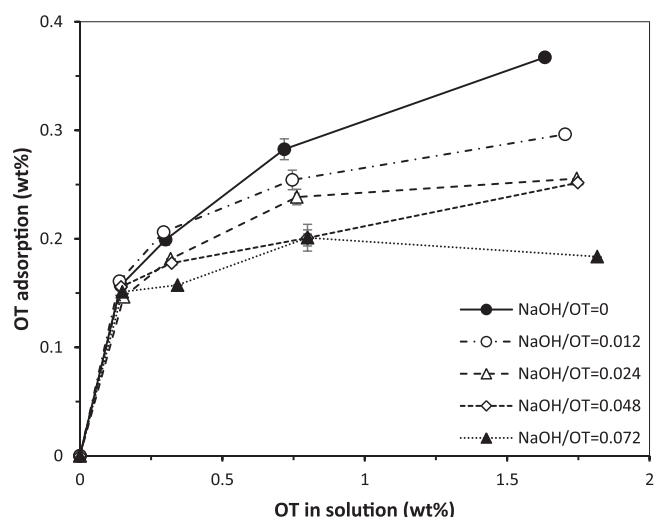


Fig. 8. Adsorption isotherms of oak tannin under different NaOH/OT environments.

attributed to the higher charge density or higher polymer grafted density of particles. The detailed interaction forces can be identified with yield stress-DLVO theory [48]. Considering Van der Waals and electrostatic forces between particles, the relationship between yield stress and zeta potential can be expressed as (Eq. 1)

$$\tau_0 = \frac{3\phi^2}{2\pi a} \left(\frac{A_0}{48\pi d_0^2} - B\zeta^2 \right), \quad B = \frac{K\kappa}{4\pi} (1 - \tanh k d_0) \quad (1)$$

Where τ_0 is the yield stress, ϕ the solid volume fraction, a the radius of particles, A_0 the van der Waals constant, d_0 the interparticle distance, ζ the zeta potential of suspension, K the permittivity of free space and the area of interaction is assumed to be given by πa^2 , and κ the Debye parameter.

As stated in [12,49], a linear correlation between the yield stress and the squared zeta potential, at a given solid volume fraction, suggests the presence of electro-static repulsion forces between particles while it is more complex when non-DLVO forces, e.g. steric, hydrophobic

interactions forces, are involved in the system.

4.1. Deflocculation mechanism of NaOH

The yield stress of kaolinite pastes with different amounts of OT and NaOH as a function of the corresponding squared zeta potential is presented in Fig. 9(a). NaOH is used as a reference as its effects on the reduction of the yield stress and the change in kaolinite surface charge is exclusively due to a change in pH. Indeed, under alkaline environments, amphoteric groups $-AOH$ (A can be Si or Al) of kaolinite particles, which are pH-dependent, can release the H ion and form negative charge sites $-AO^-$ [42]. Since the basal planes of kaolinite particles possess permanent negative charge, the negative edge and face combination can break the small aggregate with a “house-of-cards” structure and disperse the particles via electrostatic forces [50], resulting in a linear decrease between τ_0 and ζ^2 .

4.2. Deflocculation mechanism of oak tannin

Regarding the pastes prepared with OT only, no linear relationship can be estimated since the zeta potential does not decrease with increasing dosage of OT as shown in Fig. 9(b), where the results of zeta potential of kaolinite particles with OT alone and OT combined with NaOH were plotted as a function of the adsorbed amount of tannins. Tannins hold negative charges with a density of around 6–8 when dissolved into the water [20], thus the absolute value of zeta potential of pastes with tannin is higher than pure kaolinite and even higher than kaolinite with NaOH under the same pH as long as the tannin is adsorbed on the kaolinite edge. However, the zeta potential does not decrease with the increased adsorption of tannins. This unusual increasing trend is related to the molecular size of tannin as it can determine the charge distribution associated with particles and the measuring positions [51, 52]. The large charged molecules can shift the measuring plane from a Stern layer in the inner region to a slipping plane in the diffuse region. In this region, the concentration of ions is lower, leading to lower zeta potential. As seen in Fig. 4 (cf. Section 3.1), the pH values of tannin solutions are independent of the concentration when no NaOH is used, as the kaolinite particles retain almost the same charge density. With a lower addition of tannin, the negatively charged tannin will increase the ions concentration in inner regions and decrease the zeta potential of

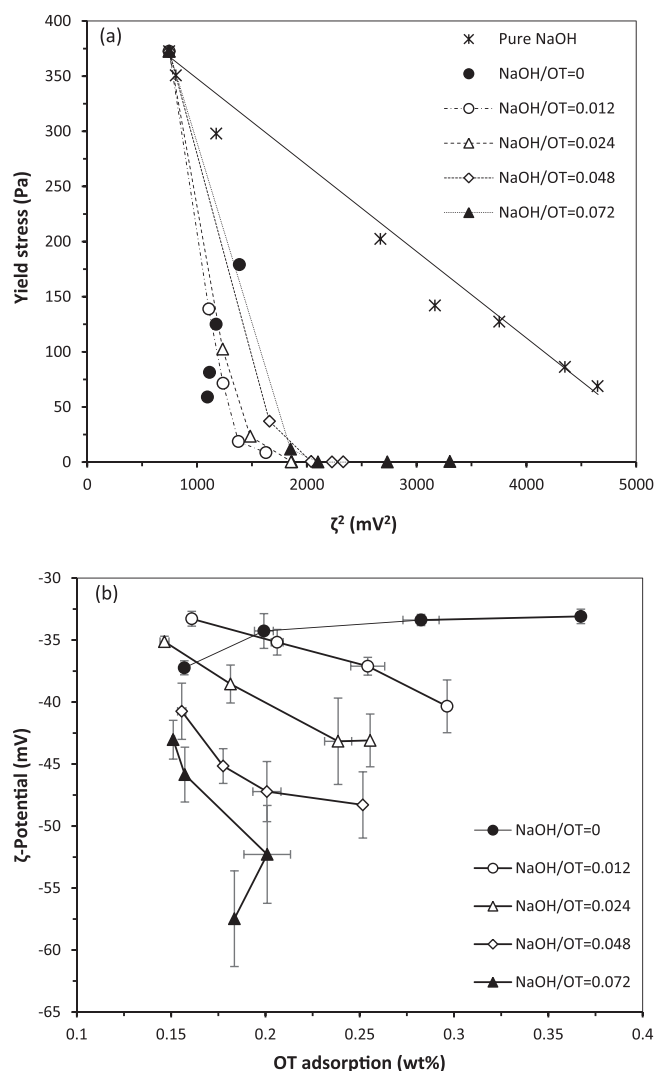


Fig. 9. (a) Yield stress of kaolinite pastes with different mixes as a function of squared zeta potential (b) zeta potential of kaolinite particles as a function of the amount of tannin adsorbed at the surface of the clay particle.

kaolinite. Due to the high molecular weight of tannin, the further increased adsorbed tannin layer will push the measuring layer from a Stern plane to a slipping layer thus increases linearly the zeta potential. The higher grafted molecules layer can push away kaolinite particles from each other and disperse the kaolinite particles. Considering the negatively charged characteristic of tannin, it can be suggested that OT disperses kaolinite clay particles via combined electrostatic and steric repulsion forces, with a dominant effect of the latter.

4.3. Deflocculation mechanism of oak tannin in combination with NaOH

Concerning the clay pastes prepared with tannin and NaOH simultaneously, no linear relationship between τ_0 and ζ^2 exist. As shown in Fig. 9(b), a decreasing evolution instead of an increasing trend between zeta potential and tannin adsorption was observed for the mixes of NaOH/OT = 0.012, 0.024, and 0.048, suggesting that the electrolyte sizes are not an important factor to change the zeta potential as OT alone does. For a given NaOH/OT ratio, the pH of tannin solutions with different concentrations of OT is similar (cf. Fig. 4), suggesting the configurations of tannin and kaolinite, i.e. the molecular structure and charge density are the same. The more tannin has been adsorbed, the more negatively charged the kaolinite particles are. With the addition of NaOH, tannin loses its macromolecule structure characteristic.

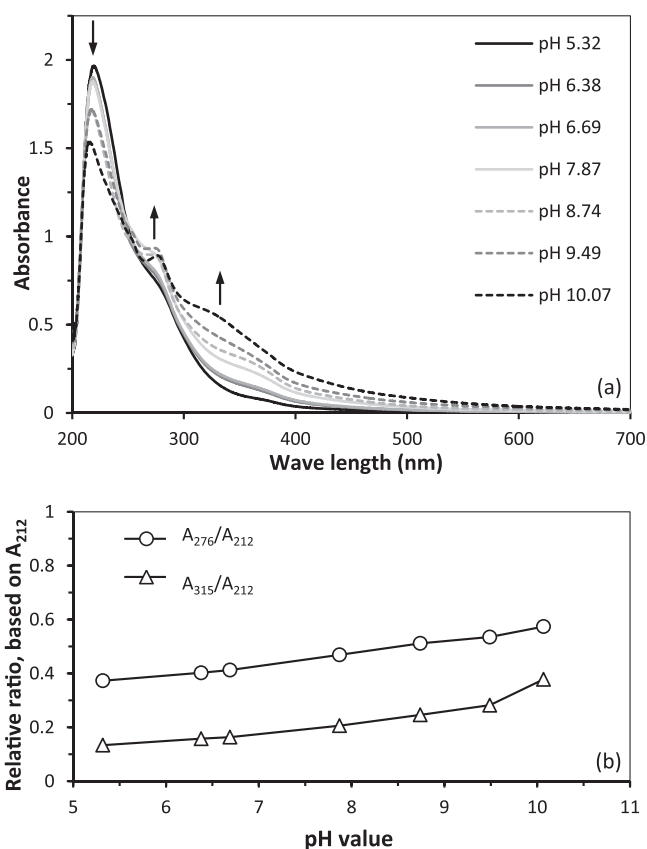


Fig. 10. (a). UV-Vis spectra of oak tannin solution and (b) ratio of phenolate to neutral form absorbance for oak tannin at different pH.

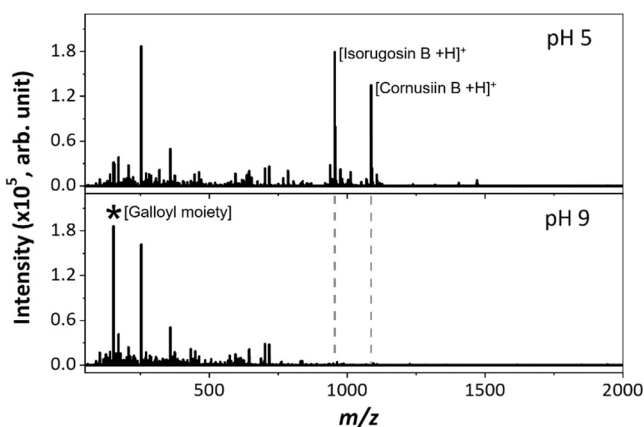


Fig. 11. Mass spectra of oak tannin solution under different pH values in the positive ion mode.

By focusing on the zeta potential of kaolinite particles at a given amount of adsorbed tannin, although the desorption of tannin from kaolinite particles occurred because of the decrease of the positively charged sites $-AOH_2^+$, it can be seen that the zeta potential becomes more negative when the NaOH/OT ratio increases. The increasing pH of tannin solutions might be one explanation, but the rising charge density of tannin seems to also play a role, as the tannin is unstable in an alkaline environment. As a result, the electrostatic forces are getting more prominent in between kaolinite particles. In presence of NaOH, tannin still deflocculates kaolinite particles via combined forces, but the weakened steric forces and growing electrostatic forces make the correlation between τ_0 and ζ^2 moving towards NaOH.

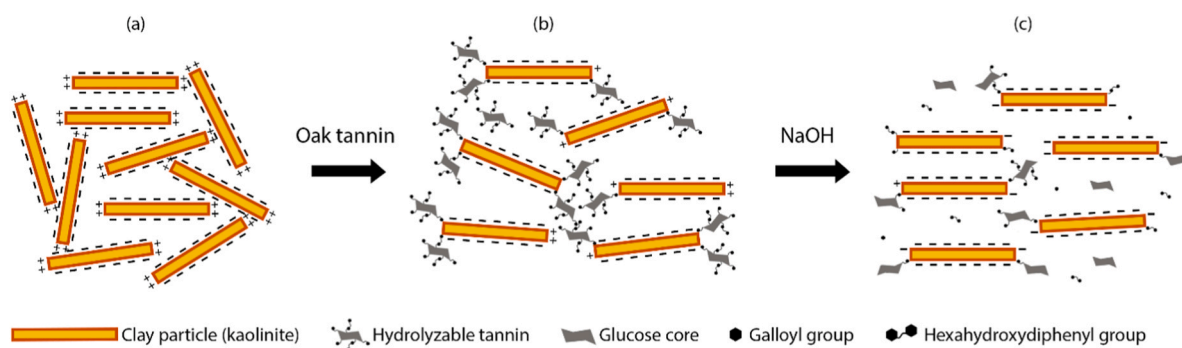


Fig. 12. Proposed kaolinite deflocculation mechanisms using oak tannin and NaOH, (a) non-dispersed kaolinite paste with water (b) dispersed kaolinite particles with oak tannin via steric forces (c) dispersed kaolinite particles with oak tannin and NaOH via combined steric repulsion forces and electrostatic repulsive forces.

The reactions between tannins and NaOH, which depend on the pH of the environment, were characterized by UV-Vis spectroscopy and Mass Spectrometry techniques, as shown in Figs. 10 and 11, respectively. The UV-Vis spectra of oak tannin solution under different pH environments (adjusted with NaOH) are presented in Fig. 10. At natural pH of 5.32, OT solution shows a maximum absorbance (λ_{\max}) at 219 nm and a shoulder at 276 nm. With an increase in pH, the λ_{\max} shifts to a lower value of 212 nm, and its corresponding absorbance decreases as well. However, the evolution of the shoulder at 276 nm over pH is slightly different: no changes are observed under pH 7.87 while a peak is transformed at the same position and a new shoulder at 315 nm appears when the pH is above 7.87. The tendency is consistent with the tannic acid [53,54], which shows similar shapes of UV curves at lower pH while a quite different shape at higher pH can be attributed to a lack of stability of tannins inducing a change in the molecular structure. By observing the decreasing peak at 219 nm and the rising shoulder around 315 nm, it can be suggested that the large structured components of tannins are deprotonated and cleaved into small molecules when the pH increases. The dissociation of tannin can be confirmed thanks to Fig. 11, where it can be observed that the distribution of masses of OT is downshifted to a lower mass range when the pH value was tuned from 5 to 9. The high-mass peaks found at pH 5, such as protonated isorugosin B at m/z 955 and protonated cornusiiin B at m/z 1087, disappeared at pH 9, whereas the intensity of protonated galloyl moiety at m/z 153 increased at pH 9 compared to pH 5. Indeed, the gallic acid or ellagic acid units forming tannin can be partially ionized in the hydroxyl para-carbonyl position because its conjugate base is better stabilized by resonance than hydroxyl meta-carbonyl position [55]. As a result, the tannin chemical structure is dissociated and the galloyl or hexahydroxydiphenyl (HHDP) groups are released, as well as the glucose core. Combining those spectra with the DLVO-yield stress relationship previously discussed, the reaction between tannin and sodium hydroxide can be concluded as follow: at a lower NaOH/OT ratio, the dissociation and the deprotonation of hydroxyl groups both exist but at a higher NaOH/OT ratio, the dissociation into ellagic acid or gallic acid dominates the reaction, since the pH of solutions is already higher than the pK_a of tannin. The difference of reactions between tannin and NaOH under different pH environments explain the different dispersing capacity presented in Fig. 9(a). The proposed deflocculation mechanism is illustrated in Fig. 12.

5. Conclusions

In this paper, the influence of oak tannin as a substitute for commercial dispersant on the deflocculation of kaolinite particles and its combination with NaOH was studied. In presence of oak tannin, the yield stress and shear viscosity of kaolinite clay pastes are reduced, and its effect is amplified by using NaOH. The higher dosage of tannin, the less amount NaOH is needed to fluidify the pastes. The reaction between

sodium hydroxide and tannin increases the amount of negative charges in the system, enhancing the dispersion of clay particles. The presence of NaOH within the system allows an increase in the charge density of tannin via ionization of phenolic hydroxyl groups and dissociation of ester bonds and phenolic groups. As a consequence, we highlighted that tannin alone and the couple OT-NaOH act as dispersant agents following different mechanisms of action: by using DLVO theory, we suggested that OT disperses via steric forces while OT-NaOH acts through combined electrostatic and steric repulsion forces. Although the steric forces will be weakened by the dissociation of tannin, the increasing electrostatic forces originating from the ionization of tannin will disperse the kaolinite particles and enhance the deflocculation action even when a small amount of NaOH is added. Finally, the use of tannin as an efficient superplasticizer for earth materials seems promising and lays the foundation for producing the poured earth in an environmentally friendly way. However, further work regarding the tannin sources and suitability for other clay minerals needs to be explored.

CRediT authorship contribution statement

Yi Du: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing. **Coralie Brumaud:** Conceptualization, Methodology, Supervision, Writing – original draft, Writing – review & editing. **Frank Winnefeld:** Resources, Reviewing. **Yin-Hung Lai:** Resources, Reviewing. **Guillaume Habert:** Conceptualization, Methodology, Supervision, Reviewing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors warmly thank Dr. Sara Mantellato for the help to conduct adsorption measurement. The first author also thanks the scholarship (No. 201806090282) supported by China Scholarship Council for pursuing his study.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.colsurfa.2021.127589](https://doi.org/10.1016/j.colsurfa.2021.127589).

References

- [1] G. Habert, S.A. Miller, V.M. John, J.L. Provis, A. Favier, A. Horvath, K.L. Scrivener, Environmental impacts and decarbonization strategies in the cement and concrete industries, *Nat. Rev. Earth Environ.* 1 (11) (2020) 559–573.

- [2] H.G. Hugo Houben, Earth construction: a comprehensive guide, Pract. Action (1994).
- [3] H. Van Damme, H. Houben, Earth concrete. stabilization revisited, Cem. Concr. Res. 114 (2018) 90–102.
- [4] M.R. Hall, R. Lindsay, M. Krayenhoff, Overview of modern earth building, Mod. Earth Build. (2012) 3–16.
- [5] G. Landrou, C. Brumaud, F. Winnefeld, R.J. Flatt, G. Habert, Lime as an anti-plasticizer for self-compacting clay concrete, Materials 9 (5) (2016) 330.
- [6] A. Pinel, Y. Jorand, C. Olagnon, A. Charlot, E. Fleury, Towards poured earth construction mimicking cement solidification: demonstration of feasibility via a biosourced polymer, Mater. Struct. 50 (5) (2017) 224.
- [7] G. Landrou, C. Brumaud, G. Habert, Influence of magnesium on deflocculated kaolinite suspension: mechanism and kinetic control, Colloids Surf. A: Physicochem. Eng. Asp. 544 (2018) 196–204.
- [8] D. Ardant, C. Brumaud, G. Habert, Influence of additives on poured earth strength development, Mater. Struct. 53 (5) (2020) 127.
- [9+] K. Rossington, U. Senapati, W. Carty, A Crit. Eval. Dispersants Clay-Based Syst. (1998).
- [10] A. Perrot, D. Rangeard, A. Leveigneur, Linking rheological and geotechnical properties of kaolinite materials for earthen construction, Mater. Struct. 49 (11) (2016) 4647–4655.
- [11] M. Moevus, Y. Jorand, C. Olagnon, S. Maximilien, R. Anger, L. Fontaine, L. Arnaud, Earthen construction: an increase of the mechanical strength by optimizing the dispersion of the binder phase, Mater. Struct. 49 (4) (2016) 1555–1568.
- [12] G. Landrou, C. Brumaud, M.L. Plötze, F. Winnefeld, G. Habert, A fresh look at dense clay paste: deflocculation and thixotropy mechanisms, Colloids Surf. A: Physicochem. Eng. Asp. 539 (2018) 252–260.
- [13] F. Andreola, E. Castellini, J.M.F. Ferreira, S. Olhero, M. Romagnoli, Effect of sodium hexametaphosphate and ageing on the rheological behaviour of kaolin dispersions, Appl. Clay Sci. 31 (1–2) (2006) 56–64.
- [14] M.K. Konduri, P. Fatehi, Dispersion of kaolin particles with carboxymethylated xylan, Appl. Clay Sci. 137 (2017) 183–191.
- [15] M.K. Konduri, P. Fatehi, Influence of pH and ionic strength on flocculation of clay suspensions with cationic xylan copolymer, Colloids Surf. A: Physicochem. Eng. Asp. 530 (2017) 20–32.
- [16] P. Izak, L. Oglaza, W. Mozgawa, J. Mastalska-Popławska, A. Stempkowska, Influence of the type of aqueous sodium silicate on the stabilization and rheology of kaolin clay suspensions, Spectrochim. Acta Part A: Mol. Biomol. Spectrosc. 196 (2018) 155–159.
- [17] A. Stempkowska, J. Mastalska-Popławska, P. Izak, L. Oglaza, M. Turkowska, Stabilization of kaolin clay slurry with sodium silicate of different silicate moduli, Appl. Clay Sci. 146 (2017) 147–151.
- [18] C.M. Ouellet-Plamondon, G. Habert, Self-compacted clay based concrete (SCCC): proof-of-concept, J. Clean. Prod. 117 (2016) 160–168.
- [19] K.S. Hafshejani, A. Moslemizadeh, K. Shahbazi, A novel bio-based deflocculant for bentonite drilling mud, Appl. Clay Sci. 127 (2016) 23–34.
- [20] J.R. Clausell, C.H. Signes, G.B. Solà, B.S. Lanzarote, Improvement in the rheological and mechanical properties of clay mortar after adding Ceratonia Siliqua L. extracts, Constr. Build. Mater. 237 (2020), 117747.
- [21] R.V. Barbehenn, C.P. Constabel, Tannins in plant-herbivore interactions, Phytochemistry 72 (13) (2011) 1551–1565.
- [22] K. Khanbabae, T. van Ree, Tannins: classification and definition, Nat. Prod. Rep. 18 (6) (2001) 641–649.
- [23] T.B.E. Sieniawska, Tannins, in: R.D. Simone Badal (Ed.), Pharmacognosy: Fundamentals, Applications and Strategies 2017.
- [24] H.R.E. Kaspar, A. Pizzi, Industrial plasticizing dispersion aids for cement based on polyflavonoid tannins, J. Appl. Polym. Sci. 59 (7) (1996) 1181–1190.
- [25] S.N. Nurul Aimi Ghazali, Yoshihiro Masuda, Wan Asma Ibrahim, Noor Fitrah Abu Bakar, Eco-friendly drilling fluid deflocculant for drilling high temperature well: A review, 37th International Conference on Ocean, Offshore and Arctic Engineering, Madrid, Spain, 2018.
- [26] D.R.S. Guihéneuf, A. Perrot, Addition of bio based reinforcement to improve workability, mechanical properties and water resistance of earth-based materials, 3rd International conference on bio-based building materials, Belfast, UK, 2019.
- [27] I. Keita, B. Sorgho, C. Dembele, M. Plea, L. Zerbo, B. Guel, R. Ouedraogo, M. Gomina, P. Blanchart, Ageing of clay and clay-tannin geomaterials for building, Constr. Build. Mater. 61 (2014) 114–119.
- [28] B. Sorgho, L. Zerbo, I. Keita, C. Dembele, M. Plea, V. Sol, M. Gomina, P. Blanchart, Strength and creep behavior of geomaterials for building with tannin addition, Mater. Struct. 47 (6) (2014) 937–946.
- [29] L. Laghi, G.P. Parpinello, D. Del Rio, L. Calani, A.U. Mattioli, A. Versari, Fingerprint of enological tannins by multiple techniques approach, Food Chem. 121 (3) (2010) 783–788.
- [30] L. Falcao, M.E.M. Araujo, Application of ATR-FTIR spectroscopy to the analysis of tannins in historic leathers: the case study of the upholstery from the 19th century Portuguese Royal Train, Vib. Spectrosc. 74 (2014) 98–103.
- [31] L. Falcao, M.E.M. Araujo, Vegetable tannins used in the manufacture of historic leathers, Molecules 23 (5) (2018).
- [32] N.Q. Dzuy, D.V. Boger, Yield stress measurement for concentrated suspensions, J. Rheol. 27 (4) (1983) 321–349.
- [33] P. Coussot, Rheometry of Pastes, Suspensions, and Granular Materials, John Wiley & Sons, Inc., 2005.
- [34] R.W. O'Brien, A. Jones, W.N. Rowlands, A new formula for the dynamic mobility in a concentrated colloid, Colloids Surf. A: Physicochem. Eng. Asp. 218 (1–3) (2003) 89–101.
- [35] A. Zingg, F. Winnefeld, L. Holzer, J. Pakusch, S. Becker, R. Figi, L. Gauckler, Interaction of polycarboxylate-based superplasticizers with cements containing different C3A amounts, Cem. Concr. Compos. 31 (3) (2009) 153–162.
- [36] I. Langmuir, The constitution and fundamental properties of solids and liquids, part I. solids, J. Am. Chem. Soc. 38 (11) (1916) 2221–2295.
- [37] H. Freundlich, About adsorption in solutions, J. Phys. Chem. 57 (1) (1907) 385–470.
- [38] H. Fan, J. Wang, Q. Zhang, Z. Jin, Tannic acid-based multifunctional hydrogels with facile adjustable adhesion and cohesion contributed by polyphenol supramolecular chemistry, ACS Omega 2 (10) (2017) 6668–6676.
- [39] M. Krogsgaard, V. Nue, H. Birkedal, Mussel-inspired materials: self-healing through coordination chemistry, Chem. -A Eur. J. 22 (3) (2016) 844–857.
- [40] N.J. Wagner, J.F. Brady, Shear thickening in colloidal dispersions, Phys. Today 62 (10) (2009) 27–32.
- [41] X. Cheng, J.H. McCoy, J.N. Israelachvili, I. Cohen, Imaging the microscopic structure of shear thinning and thickening colloidal suspensions, Science 333 (6047) (2011) 1276–1279.
- [42] F. Bergaya, G. Lagaly, Handbook of Clay Science, Newnes, 2013.
- [43] D.J.A. Williams, K.P. Williams, Electrophoresis and zeta potential of kaolinite, J. Colloid Interface Sci. 65 (1) (1978) 79–87.
- [44] V. Gupta, J.D. Miller, Surface force measurements at the basal planes of ordered kaolinite particles, J. Colloid Interface Sci. 344 (2) (2010) 362–371.
- [45] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, Chem. Eng. J. 156 (1) (2010) 2–10.
- [46] H. Chen, L.K. Koopal, J. Xiong, M. Avena, W. Tan, Mechanisms of soil humic acid adsorption onto montmorillonite and kaolinite, J. Colloid Interface Sci. 504 (2017) 457–467.
- [47] R. Calvet, Adsorption of organic chemicals in soils, Environ. Health Perspect. 83 (1989) 145–177.
- [48] R.J. Hunter, S. Nicol, The dependence of plastic flow behavior of clay suspensions on surface properties, J. Colloid Interface Sci. 28 (2) (1968) 250–259.
- [49] A. Yamaguchi, M. Kobayashi, Y. Adachi, Yield stress of mixed suspension of silica particles and lysozymes: the effect of zeta potential and adsorbed amount, Colloids Surf. A: Physicochem. Eng. Asp. 578 (2019), 123575.
- [50] V. Gupta, M.A. Hampton, J.R. Stokes, A.V. Nguyen, J.D. Miller, Particle interactions in kaolinite suspensions and corresponding aggregate structures, J. Colloid Interface Sci. 359 (1) (2011) 95–103.
- [51] E.M. Hotze, S.M. Louie, S.H. Lin, M.R. Wiesner, G.V. Lowry, Nanoparticle core properties affect attachment of macromolecule-coated nanoparticles to silica surfaces, Environ. Chem. 11 (3) (2014) 257–267.
- [52] G.V. Lowry, R.J. Hill, S. Harper, A.F. Rawle, C.O. Hendren, F. Klaessig, U. Nobbmann, P. Sayre, J. Rumble, Guidance to improve the scientific value of zeta-potential measurements in nanoEHS, Environ. Sci.: Nano 3 (5) (2016) 953–965.
- [53] M. Ocwieja, Z. Adamczyk, M. Morga, Adsorption of tannic acid on polyelectrolyte monolayers determined in situ by streaming potential measurements, J. Colloid Interface Sci. 438 (2015) 249–258.
- [54] T. Shutava, M. Prouty, D. Kommireddy, Y. Lvov, pH responsive decomposable layer-by-layer nanofilms and capsules on the basis of tannic acid, Macromolecules 38 (7) (2005) 2850–2858.
- [55] A.F.M. Santos, L.J.A. Macedo, M.H. Chaves, M. Espinoza-Castañeda, A. Merkoçi, Fd.C.A. Lima, W. Cantanhêde, Hybrid self-assembled materials constituted by ferromagnetic nanoparticles and tannic acid: a theoretical and experimental investigation, J. Braz. Chem. Soc. (2015).