Influence of combined natural deep eutectic solvent and polyacrylamide on the flocculation and rheological behaviors of bentonite dispersion

Dana I. M. Al-Risheq [a], Shifa M.R. Shaikh [a], Mustafa S Nasser [a,b,*], Fares Almomani [a], Ibnelwaleed A. Hussein [a,b], Mohammad K. Hassan [c]

[a] Gas Processing Centre, College of Engineering, Qatar University, Doha, Qatar
[b] Department of Chemical Engineering, College of Engineering, Qatar University, Doha, Qatar
[c] Center for Advanced Materials, Qatar University, Doha, Qatar

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ABSTRACT

The influence of hybrid coagulation/ flocculation systems on the degree of flocculation and rheological behavior of highly stable bentonite suspension has been investigated throughout this study. Natural deep eutectic solvent (NADES) synthesized from choline chloride (ChCl) and lactic acid (LA) was utilized as the coagulant in the hybrid system at a fixed dosage of $1.78 \times 10^{-2} M$. Two cationic polyacrylamides (CPAM) and two anionic poly-acrylamides (APAM) with varying charge density (CD) were the studied flocculants in the hybrid system. The flocculation efficiency of the anionic and cationic hybrid systems (i.e., NADES/ FO 4350 SH, NADES/ FO 4800 SH, NADES/ AN 923 SH, and NADES/ AN 956 SH, respectively) was evaluated based on specified criteria, including the zeta potential, turbidity, floc size, and rheology of the treated suspension. Compared to a single system, the utilization of a hybrid system significantly influenced the treatment efficiency of APAMs and CPAMs. At an optimum APAM dosage of $10\,mgL^{-1}$ and $15\,mgL^{-1}$ for NADES/ AN 923 SH and NADES/ AN 923 SH, respectively, the systems showed an exceptional improvement with a turbidity removal > 99%, zeta potential in the range of $-10\,mV < \zeta < 0\,mV$, and floc size > 60 μm. On the other hand, NADES with CPAMs (i.e., NADES/ FO 4350 SH and NADES/ FO 4800 SH) demonstrated a setback in their treatment efficiency due to the charge reversal exhibited by the hybrid systems hence, re-stabilization of the suspension. The conducted rheological analysis revealed that the studied hybrid systems could enhance the properties of produced sediment. The formation of larger, more compacted flocs resulted in nono-Newtonian shear-thinning sediment with a shear re-sistivity and elastic modulus more than ten times higher compared to the single systems. The tested hybrid systems with low CD CPAM and APAM (i.e., NADES/ FO 4350 SH and NADES/ AN 923 SH) achieved higher viscosity, elastic modulus, and shear resistivity than systems with high CD PAMs. Furthermore, APAM hybrid systems exhibited superior performance compared to CPAM hybrid systems. Consequently, the NADES/ AN 923 SH hybrid system was the most efficient for treating bentonite suspension resulting in viscosity of 223,340 mPa.s, an elastic modulus of 32,487 mPa, and yield stress of 694 mPa at the optimum coagulant/ flocculant dosage.

1. Introduction

Enormous quantities of wastewaters are periodically discharged from the mining industry from mineral processing operations, pulp and paper industry, and sludge treatment operations. These wastewaters contain a wide range of contaminants such as dissolved and suspended heavy metals [1], organic components (i.e., cellulosic fibers) [2], and clay minerals [3]. The presence of high quantities of clay minerals in industrial wastewater effluents is predominant. For instance, large

amounts of clay minerals are released in effluents while washing mineral ores with water during mineral processing operations [4]. Likewise, clay minerals also end up in wastewater effluents from the paper industry, chiefly used as fillers to enhance paper quality during production [2]. The clay minerals are insoluble particles that generate persistent colloidal suspensions in large quantities of water. These wastewaters require energy-intensive techniques to destabilize the suspensions, settle the clay minerals, and recover the clarified water. Clay minerals that are most commonly encountered in such wastewaters include kaolinite,

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bentonite, and other montmorillonites [2,5,6].

Bentonite is a ubiquitous inorganic clay characterized by a mixture of crystalline smectite clay minerals like montmorillonite (dominant mineral), saponite, nontronite, beidellite, and hectorite [7]. It occurs naturally in soils resulting from hydrothermal synthesis or weathering of volcanic ash [8]. Bentonite's chemical structure comprises a central octahedral alumina (Al_2O_3) sheet packed between two tetrahedral silica (SiO_2) sheets. The octahedral Al^{3+} ions are susceptible to isomorphic substitution with lower valent metal ions like Fe^{2+} and Mg^{2+}. Likewise, the tetrahedral Si^{4+} ions may also undergo substitution by the lower valent Al^{3+} ions. Consequently, the structure is rendered with a net negative charge that is electrically balanced by the presence of exchangeable cations of alkali and alkali-earth metals like Na^+ and Ca^{2+}, alongside water molecules from the surrounding environment [9]. Therefore, the presence of a negatively charged surface and the abundance of exchangeable cations impart outstanding adsorption and ion exchange capacity [7].

The abundance and distinctive physical and chemical properties of bentonite make it commercially significant. The clay exhibits high absorption capacity for water and is consequently utilized as active absorbents in drilling fluids, dyes, paints, adhesives, paper-making, cosmetics, pharmaceuticals, and wastewater treatment [10-16] in large quantities, exceeding 10 million tons per year [10]. Bentonite is also currently utilized in synthesizing innovative nanomaterials and fine chemicals [17]. The absorption and ion exchange properties of bentonite clays are also exploited in applications of landfill engineering [18], containment of highly radioactive wastes [19], and environmental remediation applications such as soil treatment [20]. The specific bentonite clay applications are primarily determined by the dominant mineral constituents and the quality and quantity of exchangeable cations present.

The presence of clay minerals like kaolinite, bentonite, and other smectites in various wastewater effluent streams from the industry poses a significant challenge in treating these wastewaters due to the formation of highly stable colloidal clay suspensions. Further, the treatment of these suspensions generates vast quantities of sludge containing up to 97% water content alongside the settled fine particles of clay. Therefore, effective handling and dewatering of this sludge can be tremendously challenging before discharge into water bodies [3,21]. Discharging the colloidal wastewater effluent streams directly into surrounding water bodies without efficient treatment can raise major environmental concerns regarding the health of aquatic species. For instance, high concentrations of colloidal particles in water and the resulting high turbidities have been stated to severely impact several aquatic species' feeding habits. A considerable decrease in fish species and their numbers have also been reported [2,22]. Extensive ongoing research has been devoted to optimizing wastewater treatment and sludge dewatering processes to ensure effective treatment and handling, low associated costs, and minimum ecological footprint.

A wide range of techniques based on different working principles has been examined in existing literature for treating stable colloidal wastewaters. Traditional techniques applied in the industry include coagulation/ flocculation, membrane filtration, and sedimentation coupled with gravity thickening [23,24]. Other conventional methods for treating colloidal wastewaters include adsorption, flotation, electrolysis, ion exchange, precipitation, and solvent extraction. Evolving technologies such as thermal-mechanical dewatering, crossflow membranes, electro-osmosis, and electrocoagulation are also gaining ground recently, aimed at encountering the particle surface charges, particle size, or both [25]. However, coagulation/ flocculation processes continue to be the most commonly employed industrial treatment methods for stable colloidal industrial wastewaters owing to their high separation efficiencies, cost, energy effectiveness, simplicity, and adaptability [13,23,26].

The coagulation/ flocculation process is a chemical separation technique that destabilizes highly stable clay wastewaters. Coagulation primarily constitutes the first step involving introducing chemical

agents that alter surface interactions between clay particles, essentially destabilizing the suspension to induce a solid-liquid separation. Flocculation is the subsequent process that further enhances the gradual aggregation of the separated colloidal clay particles to form larger aggregates (or flocs) that rapidly settle, eventually clarifying the water. The principal mechanisms that govern the flocculation performance of various flocculants include adsorption, surface charge neutralization, electrostatic patch mechanisms, bridging interactions, and sweep flocculation. Combining adsorption and surface charge neutralization alongside bridging facilitate the formation of large, compact, and shear resistant flocs [3,21].

Following the coagulation/ flocculation process, the generated sludge of flocs is pumped via pipeline towards the dewatering and sludge treatment unit in a continuous flow system. The strength of flocs becomes a critical factor here since loose aggregates in the sludge will break down during pumping, and the clay particles will be re-suspended into the water, adversely affecting the overall flocculation performance. This phenomenon highlights the importance of analyzing the rheological properties of the aggregates formed as a result of the coagulation/ flocculation process and the water treatment performance, and the size of the generated flocs. Extensive research is required to enhance the rigidity of the generated flocs to optimize wastewater treatment techniques in the industry [25,27].

Since the coagulation/ flocculation method involves adding chemical agents, recent research endeavors attempt to explore coagulants and flocculants that are increasingly more efficient, readily available, cost-effective, and environment-friendly [23,28,29]. The use of traditional coagulants like inorganic salts has been increasingly discouraged due to several limitations associated with their use in wastewater treatment, such as the generation and handling of large quantities of toxic sludge, high sensitivity of the salt performance to characteristics of the suspension, and the development of aggregates displaying low shear resistance [30]. Polymeric flocculants or polyelectrolytes are commonplace in treating industrial wastewaters owing to their high treatment efficiencies, low costs, versatility, and relatively low toxicity. Synthetic polyelectrolytes are frequently employed for flocculating highly stable clay suspensions as they can be widely adapted to a range of colloidal wastewaters and offer high flocculation efficiencies. However, these polyelectrolytes are typically non-biodegradable, thereby raising ecological concerns and the need to discover more environment-friendly alternatives. Natural polymers have also been successfully applied to treat several clay systems. Despite being biodegradable alternatives, the polymers are expensive, and their flocculation performances are reportedly lower than the synthetic polyelectrolytes [3,23].

One suitable and environmentally friendly coagulating agents class includes deep eutectic solvents (DES). This new generation of solvents emerged to prominence in research studies to overcome the drawbacks of expensive and relatively toxic ionic liquids recently utilized in the pretreatment of biomass [31]. DESs are generally synthesized by mixing two or three safe chemical components that can mutually associate to form a eutectic mixture. These components are characteristically renewable, inexpensive, non-toxic, and biodegradable. The set of components interacts via hydrogen bonds, including hydrogen bond donors and hydrogen bond acceptors. The characteristic melting point of a DES is lower than that of the original chemical components. DESs are also typically marked by a significant depression of freezing point and often occur as liquids at room temperatures. DES harbors another class of solvents termed natural deep eutectic solvents (NADES) that mainly constitute natural primary metabolites sugars, sugar alcohols, amines, amino acids, and organic acids [32,33]. These green solvents present wide-ranging advantages as they are generally non-toxic, biodegradable, cost-effective, and easy to synthesize. As a result, the application of NADES in the research areas of food, cosmetics, pharmaceuticals, and biomass processing is gaining significant interest [34].

The application of NADES as coagulating agents in treating colloidal clay suspensions was not reported in the literature prior to our published

studies [35-37]. In our previous studies, choline chloride (ChCl) based NADES were successfully applied as coagulants for effectively destabilizing persistent bentonite suspensions. NADES was synthesized from ChCl and lactic acid (LA), acting as the hydrogen bond acceptor and donor, respectively, in the ratio of 1:1 [37]. The impact of the individual components of the NADES on the coagulation of bentonite suspensions was also evaluated against that of the synthesized NADES. The efficiency of ChCl, LA, a binary mixture of ChCl-LA, and the synthesized ChCl based NADES as coagulating agents was investigated through a series of experimental analyses, including turbidity, zeta potential, floc size distribution, settling behavior (settling rate, sediment volume), and viscosity measurements. NADES was reported to offer the best coagulation performance resulting in an almost 100% removal in turbidity, considerable reduction in the negative zeta potential, and the production of large flocs.

Other ChCl-based NADES were synthesized and tested for their coagulation performance following the success of ChCl:LA based NADES. ChCl based NADES with three different hydrogen bond donors (malic acid (MA), lactic acid (LA), and citric acid (CA)) were synthesized in the ratio 1:1 and tested as coagulants on stable bentonite suspensions [36]. No significant differences were observed in the performance, except that the synthesis of ChCl:LA NADES was the easiest. This NADES also exhibited a relatively higher coagulation efficiency at low doses. Response surface methodology (RSM) and central composite design (CCD) were implemented to create an experimental design with two control variables, namely, the coagulant dose and the suspension solid content, in terms of turbidity, zeta potential, pH, and floc size analyses. Experimental and computational data together were used to optimize the operation conditions. Finally, the rheological characterization of bentonite suspensions coagulated with ChCl:LA NADES was conducted and contrasted against the suspensions coagulated with the binary mixture of ChCl-LA [35]. NADES treated suspensions were noted to form larger and more shear-resistant flocs. NADES was observed to provide the highest degree of destabilization alongside improved rheological properties of the treated suspensions (indicated by high initial viscosity and yield stress).

Therefore, for the first time, the impact of a hybrid coagulation/ flocculation process was assessed in this study to treat highly stable bentonite suspensions. The ChCl:LA NADES was implemented as the coagulating agent, followed by commercial high molecular weight polyacrylamides (PAM) as flocculating agents. This study aims to examine and optimize the electrokinetic and rheological behavior of bentonite suspensions in the presence of the ChCl:LA NADES coagulant and PAM flocculant. The ChCl:LA NADES coagulant was synthesized using a 1:1 M ratio of ChCl and LA as the hydrogen bond acceptor and donor, respectively. Experimental parameters of turbidity, Zeta potential, floc size distribution, and capillary suction time were employed to assess the electrokinetics behavior of the suspensions. The rheological behavior of the treated bentonite suspensions was then linked to the above results through initial viscosity, yield stress, and the viscoelastic moduli measurements.

2. Materials and methods

2.1. Materials

The utilized chemicals in the following study were purchased from Sigma Aldrich (St. Louis, Missouri, United States), including choline chloride with 98% purity (CAS Number 67–48-1), lactic acid with 85% purity (CAS Number 50–21-5), and bentonite (CAS Number 1302–78-9). SNF Floerger, France supplied all polyacrylamide flocculants. The characteristics of each flocculant (i.e., molecular weight, charge type, and density) are summarized in Table 1.

Table 1
Characteristics of the utilized Polyacrylamide flocculants.

Polyacrylamide	Charge type	Molecular weight (g/mol)	Charge density (%)
FO 4800 SH	Cationic	$10-15$ million	80
FO 4350 SH	Cationic	$10-15$ million	25
AN 956 SH	Anionic	>15 million	50
AN 932 SH	Anionic	>15 million	20

2.2. Methods

2.2.1. Coagulant/ flocculant preparation

This paper studies the influence of a hybrid coagulation/ flocculation process using NADES/ PAMs on the electrokinetics and rheological behavior of bentonite suspensions. Choline chloride (ChCl) and lactic acid (LA) were used as the hydrogen bond acceptor and donor (HBA and HBD), respectively with a 1:1 M ration to synthesize ChCl:LA NADES. To prevent any water content in the synthesized NADES, ChCl was stored in a desiccator with silica gel due to its hygroscopicity. The required amount of each component (i.e., ChCl and LA) was measured carefully using an analytical balance and placed in a glass bottle with a magnetic stirrer. The two components were mixed at a constant speed of 200 RPM and heated at a temperature of 80 °C continuously using a IIKA-COMBIMAG RET magnetic stirrer/ hot plate. The completion of the synthesis process was indicated by the dissolution of all solids and the formation of a clear viscous liquid. The synthesized ChCl:LA was stored in an airtight container at room temperature. A complete characteristic analysis (i.e., Fourier transform infrared analysis (FT-IR) thermal stability and density profile) was conducted on the synthesized NADES in our previous studies to confirm the formation of NADES through hydrogen bonding [36,37]. Polyacrylamides (PAMs) stock solutions with a $1gL^{-1}$ concentration was prepared by mixing 1 g of the desired PAM (i.e., FO 4350 SH. FO 4800 SH, AN 923 SH, or AN 956 SH) in 1 L of deionized water. A continuous mixing at a moderate speed was performed using a magnetic stirrer and stirring plate until the solid particles were dissolved completely and a homogeneous solution was detected.

2.2.2. Coagulation/ flocculation test

The coagulation/ flocculation process was mimicked through jar test experiments using A PHIPPS & BIRD jar tester programmable model (PB-900). The device consists of six compartments with rectangular-shaped paddles. Fig. 1a, 1b, and 1c demonstrate the jar test procedure for single NADES, single PAM, and hybrid NADES/ PAM systems, respectively. For single systems, a two stages program was applied to perform the coagulation/ flocculation test. First, the coagulant or flocculant was added to the suspension, followed by a rapid mixing at 180 RPM for 1 min then a slow mixing at 50 RPM for 20 min. These two stages are essential as the former ensures the uniform distribution of the utilized chemical agent within the suspension while the latter encourages the formation of larger flocs. In the hybrid NADES/ PAM system, the NADES concentration was fixed the optimum concentration of $1.78 \times 10^{-2}M$ obtained from our pervious study [37], while the PAM concentration was varied. As illustrated by Fig. 1c, the coagulation/ flocculation test for the hybrid NADES/ PAM system consists of three stages. Two rapid mixing stages upon the addition of NADES and PAM, respectively, followed by a single slow mixing.

2.2.3. Turbidity and zeta potential

Bentonite suspension with $1.5gL^{-1}$ concentration was prepared to perform the electrokinetics analysis. For every 1 L of deionized water, 1.5 g of bentonite clay was mixed in with a Fisher Scientific homogenizer for 5 min at a constant speed to prepare the suspension. At the end of the jar test experiments, a settling time of two minutes was given for the treated suspension to separate the solid flocs from the water. Afterward, samples of the resultant supernatant were taken from a fixed
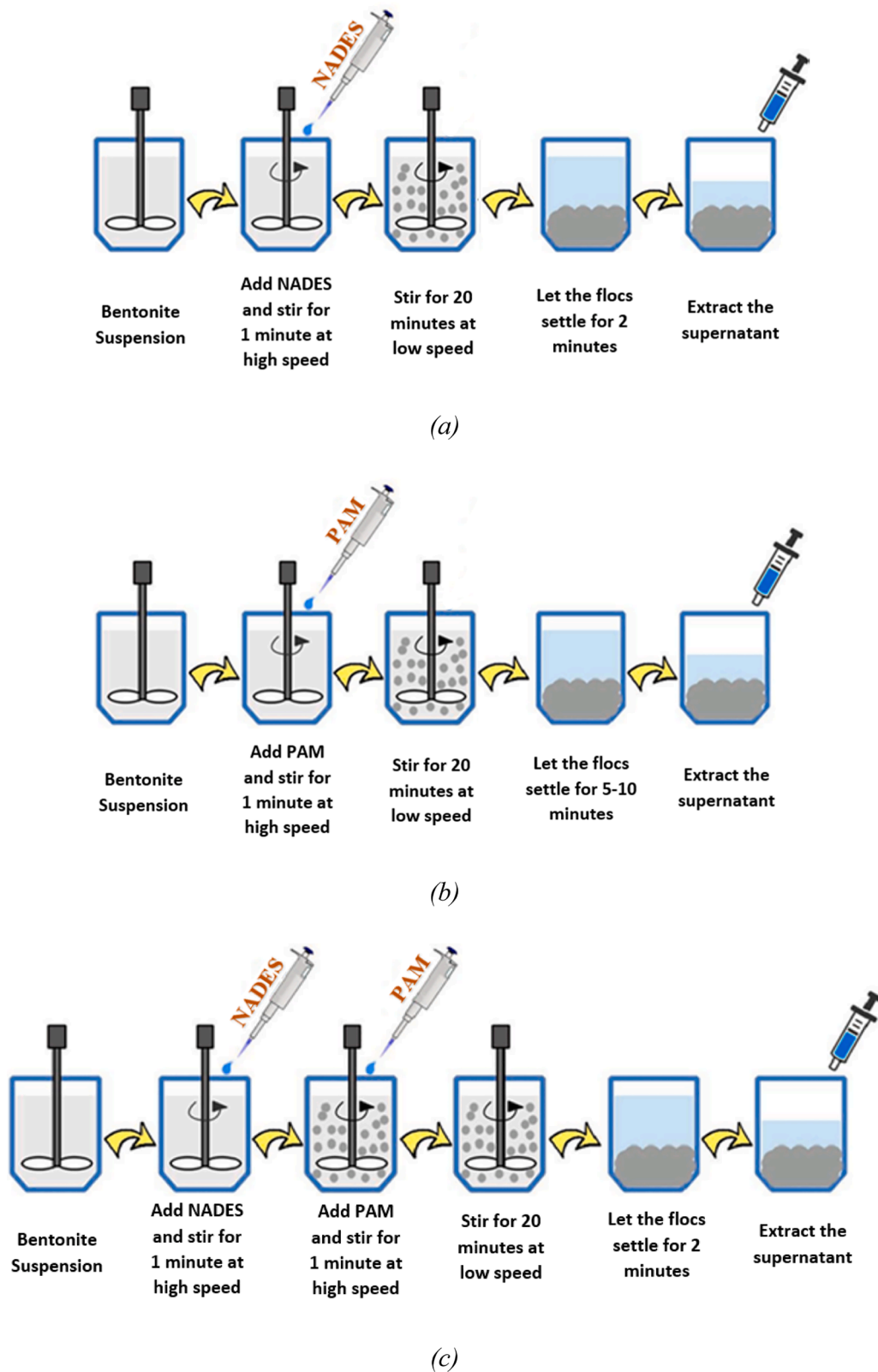
(a)

(b)

(c)

Fig. 1. Schematic illustration of the coagulation/ flocculation test for (a) NADES single system, (b) PAM single system, and (c) NADES/ PAM hybrid system.

position for analysis. The turbidity and zeta potential were measured using a Hach 2100 N turbidity meter and a Malven ZEN3600 Zetasizer ((Malvern Instruments, UK), respectively. All measurements were reproducible with an error of less than 5%.

2.2.4. Floc size distribution (FSD) and capillary suction time (CST)

After the coagulation/ flocculation test, the settled sediment was sampled to conduct the FDS and CST measurements. Bentonite suspension with a concentration of $3.5 gL^{-1}$ was utilized to perform the following tests. The primary purpose of conducting FSD and CST is to

analyze the influence of PAM concentration, charge type, MW, and CD on the floc size and CST of the hybrid NADES/ PAM system at a constant NADES concentration. The FSD analysis was carried out using a Mastersizer 2000 (Malvern Instruments, UK), while a Titron electronic type 319 multi-CST was employed to perform CST.

2.2.5. Rheological measurements

The main goal behind conducting a rheological analysis on the dense phase of the treated bentonite suspension is to evaluate its flowability and viscoelasticity. Bentonite suspension with $6gL^{-1}$ concentration was prepared, and the jar test was conducted following the procedure mentioned above. The selected coagulant/ flocculant dosage for the rheology test was the optimum dosage obtained from the first part. After completing the jar test and a settling time of 15 min, the water was removed entirely, and the sediments were left to stabilize for 24 h before conducting the test. The rheological measurements were carried out at a controlled temperature of 25 ± 0.1 °C using Anton Paar Rheometer Model MCR 302 with cup and bob measuring geometry. The samples of the flocculated suspension dense phase were carefully loaded into the measuring cup, and an equilibrium time of 5 min was given to stabilize. Three tests were performed for each system: shear stress, time-dependency, and frequency sweep. The shear stress was conducted over a shear rate ranging from 0.01 to 1000 s^{-1} to study the flow behavior of the dense phase. The viscosity data were successfully fitted on the Herschel Bulkley model using RheoPlus software. On the other hand, time dependency was tested under a constant shear rate of $1s^{-1}$ for 10 min. The elastic and viscous modulus were obtained from the frequency sweep test over a range from 0.1 to 600 rad/s and a constant strain of 0.3%

3. Results and discussion

3.1. Degree of flocculation for single flocculant systems

3.1.1. Turbidity and zeta potential

The addition of a coagulant or a flocculant to a stable suspension leads to changes in its electrokinetics properties such as turbidity, zeta potential, floc size, and CST. The amount of coagulant/ flocculant added to the system determines the degree of variations in those properties. Ideally, upon increasing the applied dosage, a decrease in the suspension's stability occurs, indicating an enhancement in the treatment efficiency. The point at which the system exhibits the lowest turbidity and negative zeta potential associated with a minimal coagulant/ flocculant dosage is distinguished as the optimum dosage. Further increase in the dosage above the optimum value may cause a suspension re-stabilization due to the saturation of the clay particles with the charged coagulant/ flocculant. Therefore, it is mandatory to accurately determine the optimum dosage to achieve high treatment efficiency and avoid undesirable consequences. The optimum dosages for the treatment of bentonite suspensions with single systems using NADES, CPAM, or APAM were defined in our previous studies according to the obtained residual turbidity, zeta potential, and floc size results [21,37]. Fig. 2 illustrates the optimum dosage for each of the five single systems with the corresponding zeta potential and turbidity. As shown in Fig. 2, flocculants with a negative charge represented by AN 923 SH and AN 956 SH demonstrated an insignificant reduction in the turbidity as it decreased from 350 NTU in untreated bentonite suspension to 332 NTU and 339 NTU, respectively. The obtained results were expected as the repulsive forces between the negatively charged particles and chains were dominant as indicated by the zeta potential values (i.e., $\zeta < -25mV$). Consequently, flocculation via adsorption between the the aluminol (Al-OH) and silanol (Si-OH) groups on the bentonite surface and the amide group in the APAM chains was limited which maintained the stability of the suspension [2,38]. Hence, the treatment of bentonite suspension with APAMs was concluded to be inefficient.
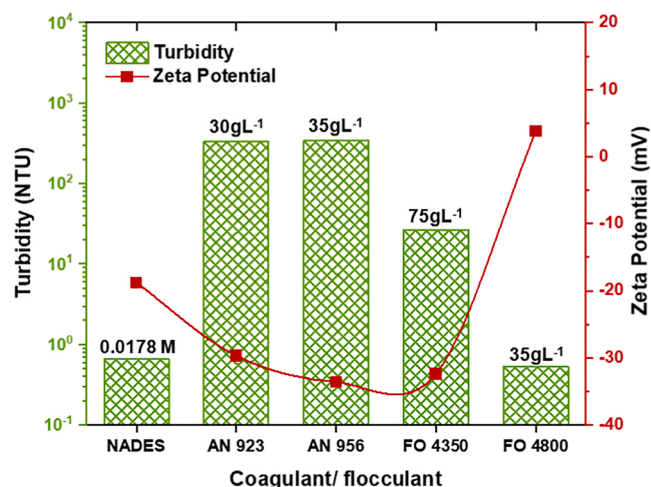

Fig. 2. Turbidity and zeta potential as a function of the optimum dosage for single systems.

CPAMs (FO 4350 SH and FO 4800 SH) and NADES, on the other hand, showed desirable outcomes when employed for the treatment of bentonite suspension. At the optimum dosage, the residual turbidity decreased by 92% with FO 4350 SH and more than 99% with FO 4800 SH and NADES. The significant reduction in turbidity is attributed to the reduction in the repulsive forces in the system. To further explain, both CPAMs and NADES carry a positive charge in their structure due to the presence of the quaternary ammonium cation (NR_4^+). Therefore, upon adding CPAMs or NADES, the repulsive forces between the bentonite particles diminish. In contrast, the attractive forces between the particles and the coagulant/ flocculant chains become more dominant. This behavior is confirmed through the zeta potential measurements displayed in Fig. 2. For FO 4350 SH, FO 4800 SH, and NADES, the zeta potential increased from $-40.4mV$ in unflocculated suspension to $-32mV$, $3.2mV$, and $-18.8mV$, respectively. The difference in the zeta potential values between the three chemicals can be explained through their destabilization mechanism and charge density. Flocculation with FO 4350 SH, FO 4800 SH occurs through adsorption, bridging, and charge neutralization. However, due to the difference in CD between the two flocculants (i.e., 25% for FO 4350 SH and 80% for FO 4800 SH), FO 4800 SH demonstrated higher flocculation efficiency. On the other hand, destabilization of bentonite suspension with low molecular weight NADES (i.e., $MW = 230g/mol$) with a positive charge occurs through the electrostatic patch (ESP) coagulation mechanism [39]. When ESP is exhibited, electrostatic patches (i.e., covered with the coagulant and uncovered patches) are formed on the surface of the bentonite particles. As a result, the patches with opposite charges will attract each other and aggregate forming larger particles that can settle under the influence of gravity. Accordingly, high turbidity removal percentage with a moderate decrease in the negative zeta potential is exhibited when NADES is utilized as a coagulant.

3.1.2. Floc size distribution (FSD) and CST

The changes in the electrokinetics properties of flocculated bentonite suspension in terms of turbidity and zeta potential are associated with variations in the median diameter of the presented particles. Commonly, upon the coagulant/ flocculant addition to the system, the zeta potential exhibits an increase toward the zero point of charge. Thus, the particles will come closer to each other and aggregate, giving flocs with a larger diameter. The median diameter (D_{50}) of the flocculated particles is determined from the cumulative distribution curve at 50%. Untreated bentonite suspension possesses micro-particles with a D_{50} of $2.4\mu m$. Fig. 3 represents the changes in D_{50} and CST associated with adding NADES or PAM to the bentonite suspension as a function of their optimum dosage. An evident variation in the floc size and CST values is
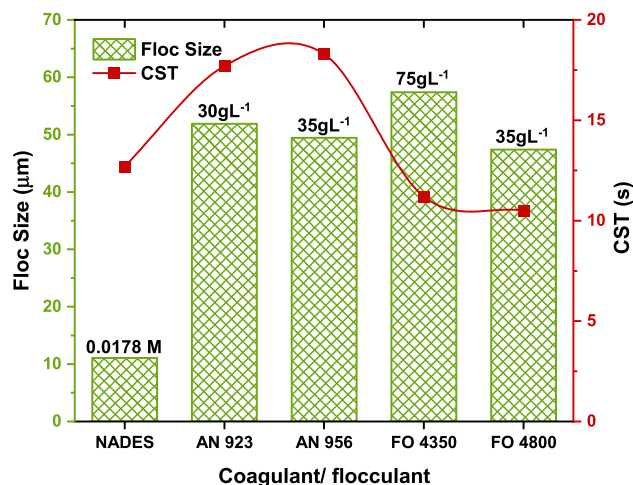
Fig. 3. Floc size and CST as a function of the optimum dosage for single systems.

observed depending on the used coagulant/ flocculant type. The largest flocs were obtained when PAMs were being used as flocculants for bentonite suspension. CPAMs and APAMs are high MW charged polymers with highly branched chains. The long branched chains of the polymer allow it to get attached to several points on the surface of more than one bentonite particle [21]. Hence, the dispersed particles will come closer to each other and agglomerate, forming large flocs. The opposite charges in the CPAM chains and the surface of the particles demonstrate an advantage for the flocculation process. To further explain, the attraction between the CPAM and the particles will destabilize the system and flocculation will occur through charge neutralization, bridging, and adsorption. However, the strong adsorption affinity of CPAM chains toward the bentonite particles can cause surface saturation, limiting the available sites for bridging interactions. From Fig. 3, the sediment produced from flocculated bentonite with FO 4350 SH and FO 4800 SH possessed flocs with a D_{50} of $57.4 \mu m$ and $47.4 \mu m$, respectively. The higher floc size obtained by the low CD CPAM (i.e., FO 4350 SH) compared to the high CD CPAM (i.e., FO 4800 SH) is attributed to the higher dosage required to attain acceptable flocculation efficiency in terms of the turbidity removal and zeta potential. In addition, the lower adsorption affinity of FO 4350 SH to the bentonite particles compared to FO 4800 SH (i.e., 1.0 $mg.g^{-1}$ bentonite and 1.7 $mg.g^{-1}$ bentonite, respectively) contributes to the formation of larger flocs [21].

On the other hand, APAM exhibits low adsorption affinity to the bentonite particles due to the repulsion forces between them. Hence, bridging is the dominant flocculation mechanism when APAM is used. Observations after the flocculation process revealed some differences between the characteristics of the formed flocs using CPAMs and those using APAMs. For instance, at the optimum dosage, flocs with a uniform shape were produced with CPAMs, while APAMs resulted in loosely bounded flocs. The difference in the structure of the systems can be observed from the peaks of the cumulative distribution curves shown in our previous work [21]. Flocculated bentonite suspension with NADES at its optimum dosage achieved the smallest flocs with a D_{50} of $11.1 \mu m$. The slight increase in the D_{50} of the produced flocs using NADES is attributed to its size and the number of charges on it. Compared to CPAMs and APAMs, NADES is a small compound with low MW and only one positive charge on each molecule. Consequently, the destabilization mechanism exhibited does not involve bridging or charge neutralization but follows the electrostatic patch coagulation mechanism which explains the small loose flocs obtained [37].

The size of the flocs and the characteristics of the settled sediments play a significant role in determining the CST. Commonly, the CST required for the trapped water to filter out of the sediment is inversely proportional to the size of the interstices within it. Meaning that when the sediment consists of small compacted flocs, the crevices will be small and narrow, resulting in a longer CST. On the other hand, larger flocs will form less dense sediment with wide interstices; hence, the water will easily flow, giving shorter CST [40,41]. As shown in Fig. 3, the highest CST values of 18.3 s and 17.7 s were obtained by AN 956 SH and AN 923 SH, respectively. The long CST is attributed to the loosely bounded flocs resulting in compacted sediment, making it difficult for the nonbounded water to flow out. Flocculated bentonite suspension with NADES and CPAMs demonstrated a noticeable decrease in the CST to 12.7 s for NADES treated suspensions and to 11.2 s and 10.5 s for FO 4350 SH and FO 4800 SH, respectively. The variation in the CST values is attributed to the difference in the sediment structure. To elaborate, when FO 4800 SH is utilized, the formed flocs are large with a well-defined shape resulting in low compactness sediment with large interstices, thus, the low CST. The sediment produced using NADES as a coagulant resulted in a more dense structure due to the formation of small flocs. Hence, higher CST is obtained compared to CPAMs.

3.2. Degree of flocculation for hybrid NADES/ PAM systems

3.2.1. Turbidity and zeta potential

In the following section, the influence of hybrid NADES/ PAMs systems on the electrokinetics properties of bentonite suspension is investigated. The study's primary purpose is to improve the treatment efficiency of bentonite suspension with hybrid systems. In addition, it was desired to analyze the ability of the hybrid system to minimize the amount of the utilized PAM compared to single systems. The applied NADES dosage was defined at a constant value of 1.78×10^{-2} M which represents the optimum NADES dosage, while the PAM dosage, charge type, and charge density were varied. Two cationic and two anionic PAMs were tested in hybrid systems, which are FO 4800 SH, FO 4350 SH, AN 956 SH, and AN 923 SH, respectively. The optimum PAM dosage and the most effective hybrid system were determined according to the highest reduction in the stability of bentonite suspension. Fig. 4 represents the changes in turbidity and zeta potential for hybrid NADES/ PAM systems as a function of the PAM type, dosage, and CD.

As shown in Fig. 4a, unlike in single systems, CPAMs (i.e., FO 4350 SH, and FO 4800 SH) in a hybrid system cause the suspension to exhibit an extreme charge reversal. To elaborate, the zeta potential increases from $-18 mV$ for suspension treated with NADES only (Fig. 3) to greater than $+20 mV$. Upon the addition of NADES to the suspension the bentonite particles become partially covered with positive charges. As a result, when CPAM is introduced, it adsorbs on the uncovered batches only via hydrogen bonding between the amide groups ($-NH_2$) on the chains and the aluminol (Al-OH) and silanol (Si-OH) groups on the bentonite particles. Consequently, charge reversal and re-suspension of the system occur due to the high density of the cationic charges on the bentonite particles.

Furthermore, the variation in the zeta potential of the suspension has a slight influence on its residual turbidity, as illustrated in Fig. 4b. For instance, when the zeta potential increases from 34.3 mV to 40.8 mV upon increasing the FO 4800 SH dosage from 1 mgL^{-1} to 10 mgL^{-1}, the turbidity increases from 0.54 NTU to 1.74 NTU. Increasing the applied dosage and CD of CPAMs in a hybrid system adversely affects its flocculation efficiency. The drop in the flocculation efficiency is attributed to the increase in the density of the cationic charges in the system leading to a further increase in the zeta potential, turbidity, and suspension stability.

Hybrid NADES/APAMs systems showed an exceptional improvement in the treatment efficiency compared to single APAM systems. From Fig. 4, it can be observed that the addition of APAM to the bentonite suspension following the NADES addition results in highly unstable suspension with zeta potential greater than $-8 mV$ and a residual turbidity below 5 NTU. Increasing the applied APAM dosage up to a certain point further enhanced the treatment efficiency of the hybrid
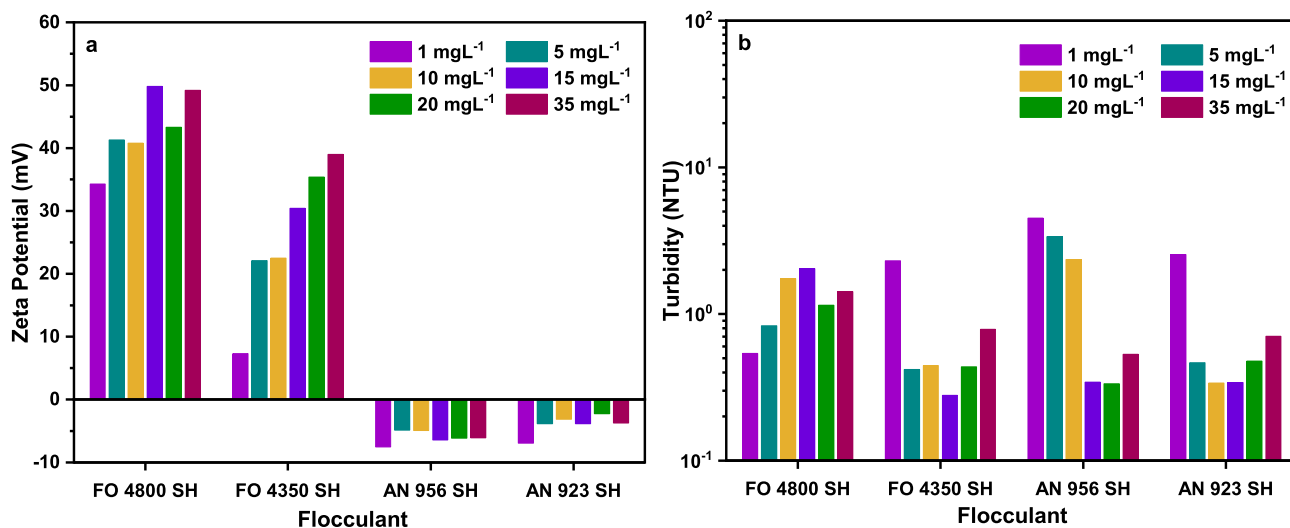
Fig. 4. Zeta potential and turbidity of bentonite suspension as a function of (a) AN 923 SH and (b) AN 956 SH concentration with ChCl:LA NADES as a coagulation aid.

systems. The highest flocculation efficiency was achieved at a dosage of $10 mgL^{-1}$ and $15 mgL^{-1}$ with more than 99% reduction in the residual turbidity and zeta potential of $-3.1 mV$ and $-6.4 mV$ for NADES/ AN 923 SH and NADES/ AN 956 SH, respectively. As illustrated in Fig. 4, a slight increase in the residual turbidity and negative zeta potential is exhibited upon increasing the dosage beyond the optimum values (i.e., $10 mgL^{-1}$ and $15 mgL^{-1}$). The same observation is true for increasing the CD of the APAM. For example, at a fixed dosage of $10 mgL^{-1}$, the negative zeta potential increases from $-3.1 mV$ and $-4.9 mV$ with a 7 times higher turbidity when AN 956 SH with 50% CD is utilized instead of AN 956 SH with 20% CD. The observed trends can be explained through the flocculation mechanisms and interactions within the system. In a hybrid NADES/ APAM system, charge neutralization occurs as the negatively charged APAMs chains get attracted to the NADES covered batches on the bentonite particles. In addition, the bridging mechanism occurs more efficiently on the uncovered patched as the repulsive forces between the chains and the particles are reduced due to the presence of cationic NADES on the particles' surface, which promotes high treatment efficiency. Higher dosage and CD cause higher negative charges in the system, which elevate the repulsion forces between the polymer chains and the uncovered batches on the bentonite particles and hence, increase the system's stability.

3.2.2. Floc size distribution (FSD)

The influence of hybrid NADES/ PAM systems on the flocculation efficiency for bentonite suspensions was investigated through floc size analysis. As mentioned earlier, the utilized NADES concentration was fixed at $1.78 \times 10^{-2} M$ while the PAM dosage and type were varied to determine the optimum conditions. Fig. 5 illustrates the changes in the median floc diameter (D_{50}) for treated bentonite suspensions as a function of the PAM dosage, charge type, and charge density. Generally, increasing the PAM dosage in hybrid systems led to the formation of flocs with greater D_{50}. The impact associated with the different charge types and densities can be distinguished. For example, at a constant dosage of $10 mgL^{-1}$, a D_{50} of $39.4 \mu m$, $42.6 \mu m$, $53.5 \mu m$, and $70.4 \mu m$ for FO 4800 SH, FO 4350 SH, AN 956 SH, and AN 923 SH hybrid systems, respectively were obtained. The variation in the floc size is attributed to the difference in charge type and density and the adopted flocculation mechanism. Flocculation with CPAM occurs through adsorption, bridging, and charge neutralization. However, the presence of the cationic coagulant (i.e., NADES) on some batches of the bentonite particles creates repulsion forces with the CPAMs chains hindering their bridging capabilities. In addition, the available adsorption sites on the
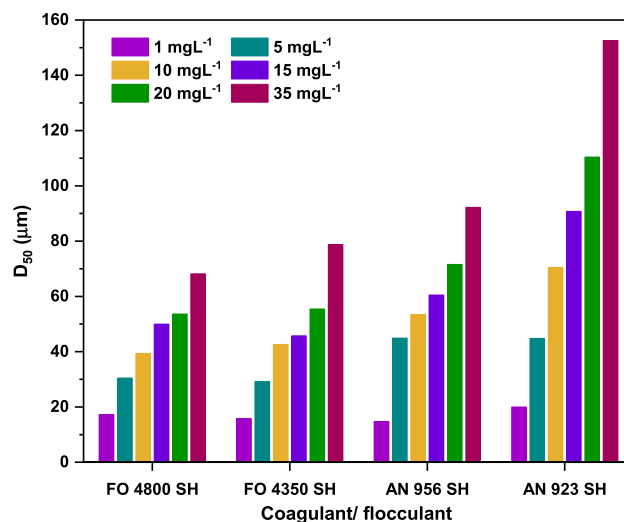

Fig. 5. Variation of the floc size with PAM dosage for NADES/ PAM hybrid systems.

surface of the particles for CPAMs in hybrid systems are limited, reducing the ability to produce large flocs. On the other hand, APAM exhibits low adsorption affinity toward the bentonite particles due to the repulsion between the two negatively charged bodies in the suspension, and hence, flocculation mainly occurs through bridging [21]. Nevertheless, in hybrid systems, the attractive forces between the covered patches with NADES on the surface of the bentonite particles and the APAM chains promote effective bridging and charge neutralization. As a result, the flocculation efficiency increases significantly, and large flocs are produced with D_{50} more significant than those produced by NADES/ CPAMs hybrid systems.

The charge density of the utilized PAM has an important role in determining the size of the generated flocs. PAM CD in hybrid systems is inversely proportional to the floc size, meaning that the floc size decreases with increasing the CD. To further explain, in NADES/ APAMs hybrid systems and at a constant PAM dosage of $10 mgL^{-1}$, increasing the CD of the APAM from 20% to 50% decreased the D_{50} by 24% (i.e., from $70.4 \mu m$ by AN 923 SH to $53.5 \mu m$ by AN 956 SH). Furthermore, at the exact dosage, flocculated suspension with NADES/ FO 4800 SH (80% CD) achieved a D_{50} of $39.4 \mu m$ while NADES/ FO 4350 SH (25% CD)

attained flocs with a D_{50} of 42.6μm. The obtained results from bentonite suspensions treated with hybrid NADES/ PAM systems were reversed from those obtained from single PAM systems. To elaborate, in single systems, CPAMs demonstrated a better flocculation efficiency with larger and stronger flocs compared to the hybrid NADES/CPAM systems. On the other hand, hybrid NADES/ APAM systems a superior performance and high treatment efficiency compared to single APAM systems. Furthermore, in terms of the charge density, lower CD was more effective in hybrid systems, while the opposite is true for single systems.

From the zeta potential, turbidity, and floc size data in Section 3.2, NADES/ APAMs hybrid systems showed superior performance compared to NADES/ CPAMs. In addition, higher flocculation efficiency was obtained for low CD PAMs. Thus, the treatment efficiency for hybrid systems was in the following order: NADES/ AN 923 SH > NADES/ AN 956 SH > NADES/ FO 4530 SH > NADES/ FO 4800 SH. At a constant NADES dosage of 1.78×10^{-2} M, the optimum PAM dosage for each hybrid system associated with the zeta potential, turbidity, and floc size results are illustrated in Table 2

3.3. Rheological behavior of the dense phase

3.3.1. Shear flow behavior

The flowability of any fluid is assessed by measuring its dynamic viscosity (μ, Pa.s). Viscosity measurements are commonly conducted to evaluate the fluids' fundamental properties, including the particles' size, shape, rigidity, and the forces between them [42]. Fluids possessing low viscosity demonstrate high flowability, meaning that the molecules of the particles within the system are weakly bonded to each other with free movement. In contrast, high viscosity indicates stronger forces between the molecules/ particles and hence, limited flowability [43]. According to our previous study [44], untreated bentonite suspension is diluted with low solid content hence it illustrates Newtonian behavior with very low viscosity and yield stress. Studying the viscosity of the settled sediments after the coagulation/ flocculation process upon force application is essential in order to determine the appropriate handling technique. Fig. 6 presents a comparison between the changes in the viscosity as a function of the shear rate for bentonite suspension treated with single systems (i.e. NADES, APAMs, and CPAMs) and hybrid systems (i.e., NADES + APAMs and NADES + CPAMs). For both single and hybrid systems, a non-Newtonian behavior is exhibited in coagulated/ flocculated suspensions as the viscosity is dependent on the applied force. A general trend of a decrease in the viscosity upon increasing the shear rate is noted in Fig. 6, indicating a shear-thinning "pseudoplastic" behavior for all studied systems. The observed decrease in the viscosity of the sediment can be translated into a weakening in the strength of its constituent flocs [40]. Therefore, all sediments can be termed as plastic fluids where at low shear the elastic forces are surpassing the viscous forces and the sediments demonstrate a solid-like behavior [25]. On the other hand, at high shear, a liquid-like behavior is observed due to the domination of the viscous forces [25].

The initial viscosities at a minimum shear rate of $0.01 s^{-1}$ of all systems under study are summarized in Table 2. Observations from Fig. 6 and Table 2 reveal the distinct differences between dense phases formed by single systems and hybrid systems at their optimum dosage. For

single PAM systems, low initial viscosities in the magnitude of 500 mPa.s and less are detected at the lowest applied shear rate. The obtained results imply the domination of a liquid-like behavior due to the formation of very loose and shear-sensitive flocs. The viscosities of flocculated suspensions with single PAM were in the following order: FO 4800 SH > AN 956 SH > AN 923 SH > FO 4350 SH. The variations in viscosities achieved by single PAM systems are attributed to the charge type and CD of the polymer in addition to the particle–particle and PAM-particle interaction. For CPAM, FO 4800 SH with a high CD showed a viscosity 15 times higher than FO 4350 SH with a low CD. This occurs as a result of the more efficient adsorption of FO 4800 SH on the bentonite particles leading to charge neutralization and stronger bridging interaction. Hence, the formed flocs are stronger stiffer. On the other hand, flocculated bentonite suspensions with AN 956 SH and AN 923 SH demonstrated initial viscosities of 145 mPa.s and 130 mPa.s, respectively which is around 3 times less than that achieved by high CD CPAM (i.e., FO 4800 SH). The disparities in the obtained rheological behavior confirm the differences in the structural strength of the flocs formed using CPAMs and APAMs. While adsorption, charge neutralization, and bridging are the dominant destabilization mechanisms for CPAMs, the repulsive forces between APAMs' chains and the bentonite particles hinder those mechanisms and promote bridging. Consequently, the resultant flocs are loose with weak interactions between them. Furthermore, as shown in Fig. 6, unlike CPAMs, the variation in the CD for APAMs did not have a clear effect on the initial viscosity of the treated suspension. Among the five tested single systems (FO 4800 SH, FO 4350 SH, AN 956 SH, AN 923 SH, and NADES), the initial viscosity of the dense phase resulted from treating bentonite suspension with NADES was the highest with 11,521 mPa.s. The main reason behind the significant increase in the viscosity is the adopted mechanism and the resultant flocs structure. Although NADES produces small flocs with a D_{50} of 11.1μm, however, the stronger interactions between the particles themselves and with the coagulant results in a well-defined strong flocs and compacted sediment. Thus, high initial viscosity is obtained.

To analyze the benefits of combining PAM and NADES in terms of the size and strength of the floc, the rheological behavior of the hybrid systems of NADES was studied. As shown in Fig. 6, hybrid systems demonstrated very high initial viscosities ($\mu \gg 10^4$ mPa.s) at low shear values. Furthermore, Fig. 6 and Table 2 divulge the reversed results attained by hybrid systems of NADES + PAM compared to single PAM systems. To further explain, sediments with higher initial viscosities were produced using NADES with APAMs. This trend occurs due to the introduction of ChCl based NADES with a positive charge to the bentonite suspension prior to the PAM addition. As a result, the negatively charged particles will be partially covered with NADES which increases the system's zeta potential (Fig. 2). Consequently, the repulsive forces between the particles and the APAMs' chains diminish, which enhances the adsorption and bridging mechanism within the system. Accordingly, a less negative zeta potential with larger and stiffer flocs is attained (Section 3.2) and therefore, a high initial viscosity. Moreover, APAM with low CD (i.e., AN 923 SH) resulted in sediment with initial viscosity 3 times higher than APAM with a high CD (i.e., AN 956 SH). The highest viscosity of 223,340 mPa.s was attained by NADES/ AN 923 SH while NADES/ AN 956 SH produced sediment with a viscosity of 72,985 mPa.s at their optimum PAM dosage of $10 mgL^{-1}$ and $15 mgL^{-1}$, respectively. The different outcomes between the two APAMs arise from the variation in their CD. As can be seen from Fig. 4 in Section 3.2, Higher anionic CD increases the negative zeta potential compared to AN 923 SH implying higher repulsive force within the system; hence, smaller flocs with weaker interactions and lower viscosity. Hybrid systems of NADES/ CPAMs demonstrated a significant improvement in the viscosity of the produced sediment compared to the single systems. Although the hybrid systems exhibited lower flocculation efficiencies and charge reversal, however, the generated flocs were stronger and more uniform in terms of shape and size, giving denser and more
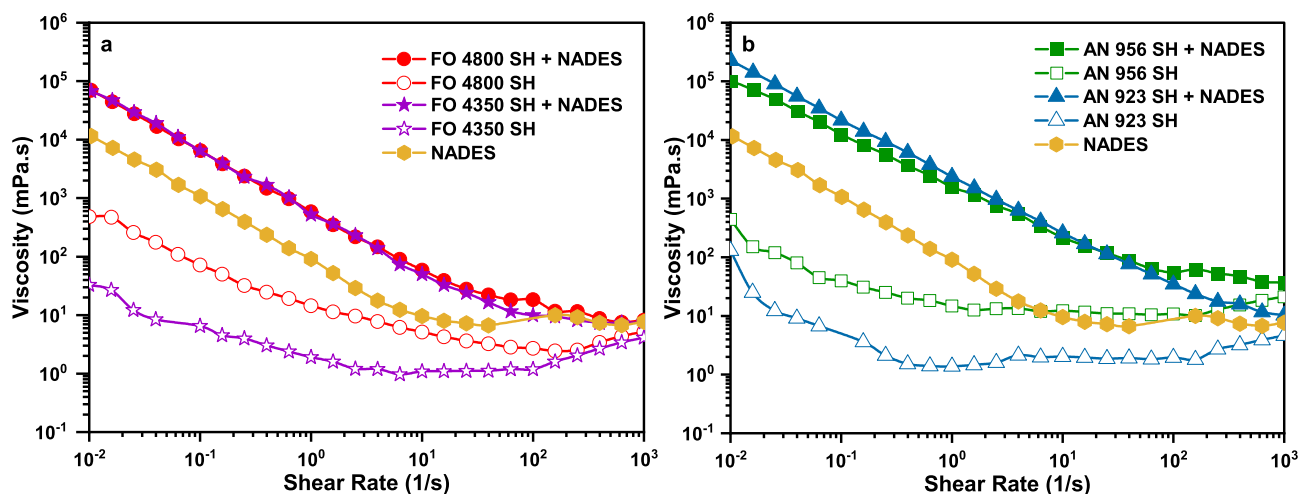
Table 2
Optimum PAM dosage in hybrid systems and the corresponding turbidity zeta potential, and. D_{50}

Polyacrylamide	Optimum dosage (mgL^{-1})	Residual Turbidity (NTU)	Zeta Potential (mV)	D_{50} (μm)
AN 923 SH	10	0.34	−3.1	70.4
AN 956 SH	15	0.34	−6.4	60.5
FO 4350 SH	15	0.28	30.4	46.74
FO 4800 SH	5	0.83	41.3	30.47

Fig. 6. Variation in the viscosity for bentonite suspension treated with (a) CPAM and (b) APAM under varying shear rate.

compacted sediment. Unlike hybrid systems with APAMs, suspensions treated with hybrid NADES/ CPAMs systems with different CD did not show a clear deviation in their viscosity trend. The stated remark indicates that regardless of the lower flocculation efficiency of FO 4800 SH with a high CD, sediments with similar characteristics were produced.

Increasing the applied shear rate has an adverse impact on the structural strength of the treated suspension. Higher shear rate values promote a rapid structural breakdown of the interactions between the flocs in the sediment, which is revealed by the exhibited drop in the viscosities of all systems under study. At a shear of $100 s^{-1}$ and above, the viscosities of treated suspensions were reduced to similar values implying a destructure of the networks between the flocs. However, bentonite suspension flocculated using single PAM systems demonstrate a slight increase in the viscosities, indicating network restructuring.

The viscosity data shown in Fig. 6 were fitted to Herschel-Bulkley model (Eq. (1)) with a regression coefficient (R^2) $\geq$ 98%. τ_0, n, γ, and k in Eq. (1) represent the yield stress (Pa), the flow behavior index (–), shear rate (s^{-1}), and the flow consistency index (Pa.s^n), respectively.

$$\tau = \tau_0 + k\gamma^n \qquad (1)$$

The yield stress is the maximum point after which the material will shift from exhibiting elastic deformation to plastic deformation. The yield stress magnitude for the produced sediment for each system is illustrated in Fig. 7. Hybrid NADES/ PAMs systems demonstrated a significant improvement in the yield stress compared to single systems.
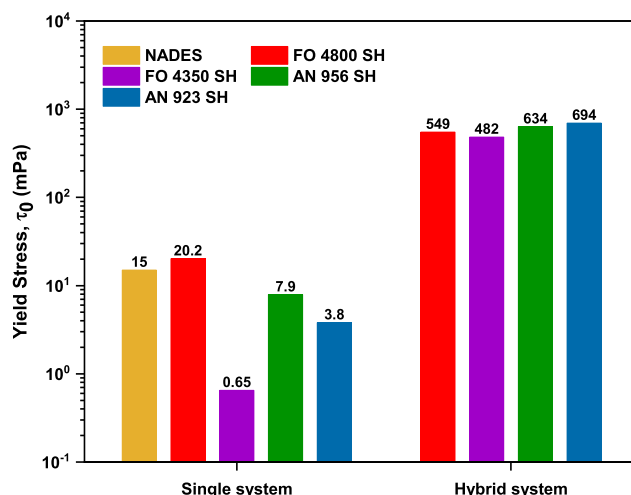
In addition, similar to the viscosity trends, the highest yield stress was obtained by low CD AN 923 SH followed by AN 956 SH. The enhancement in τ_0 is attributed to the higher interaction strength between the particles and the coagulant/ flocculant forming larger and stronger flocs with high shear resistivity, which is explained in detail in Section 3.2.2.

Besides, at a constant shear rate of $1 s^{-1}$, the viscosities of both NADES single system and NADES/ PAM hybrid systems decreased over time as illustrated in Fig. 8. Hence, the produced sediment from the coagulation/ flocculation process possesses a time-dependent thixotropic behavior. Furthermore, after 10 min of continuous shearing and under equilibrium conditions, the final viscosity is different from that in a single NADES system implying that the systems do not go back to their initial state. This proves that the generated flocs by hybrid systems were never reduced to their primary aggregate, confirming the improvement in the structural strength of the sediment. The four hybrid systems under study resulted in different initial and equilibrium viscosities, which denotes a variation in the interaction strength within the sediment. The reduction percentage in the viscosities upon shearing varied between 60% and 90%. The highest reduction corresponded to FO 4350 SH and FO 4800 SH followed by AN 956 SH while AN 923 SH achieved the lowest reduction.

3.3.2. Viscoelastic behavior

The strength of the treated suspension was evaluated by performing oscillatory measurements and determining the viscous (G'') and elastic
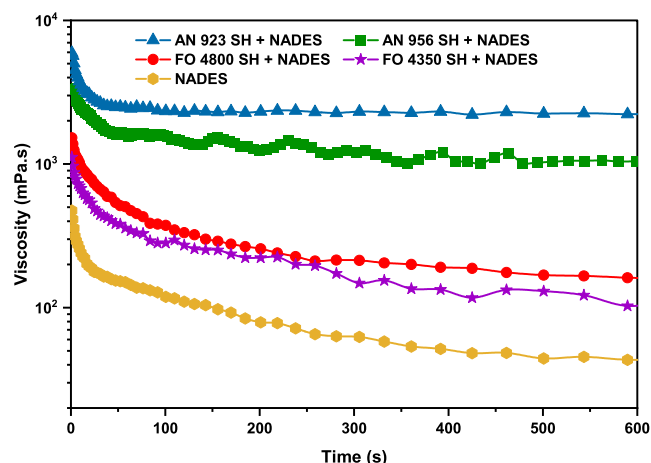

Fig. 7. Yield stress as a function of the coagulant/ flocculant type.

Fig. 8. Viscosity as a function of time for hybrid systems at their optimum dosage.

(G') modulus. G' and G'' represent the amount of energy stored in the material and dissipated from it, respectively, when undergoing deformation. The viscous and elastic modulus of bentonite suspension treated with single and hybrid systems are illustrated in Fig. 9. As shown in Fig. 9, G' and G'' values were constant over a wide range of frequencies implying the independency of the viscous and elastic behavior on the frequency. Nevertheless, at a specific frequency, known as the critical frequency (ω_c), the G' for most systems exhibit a sudden sharp drop until it reaches a minimum while G'' starts increasing. The observed trend indicate the transition in the material behavior from solid-like to liquid-like. The decrease in G' can be explained through the breakdown of the interactions between the flocs forming the sediment, hence, reducing its structural strength [40,45,46]. The later increase in G' suggests some restructuring upon higher frequencies which is a typical behavior for flocculated suspensions [45]. Treated suspensions with hybrid systems of NADES/ AN 956 SH, NADES/ AN 923 SH, and NADES/ FO 4350 SH did not demonstrate a sharp decrease at higher frequencies; instead, an increase in the G' was exhibited (Fig. 9a). The observed behavior implies that these systems result in sediments with a more rubbery-like behavior [45].

The G' and G'' values were obtained at an oscillatory frequency of $0.1 Rad.s^{-1}$ in addition to the critical frequency (ω_c) for each system are summarized in Table 3. From the oscillatory test results for all systems, the elastic modulus (G') always exceeded the viscous modulus (G''). Greater G' in comparison to G'' indicates the superiority of the solid-like behavior of the treated suspensions over viscous-like. Furthermore, the

Table 3
Initial viscosities of treated bentonite suspension at the optimum dosage of the utilized coagulant/ flocculant.

Coagulant/ flocculant	Optimum dosage(mgL^{-1})	Initial viscosity(mPa.s)
NADES	1.75×10^{-2}*	11,521
FO 4800 SH	35	480
FO 4350 SH	75	32
AN 956 SH	35	145
AN 923 SH	30	130
FO 4800 SH + NADES	5	69,638
FO 4350 SH + NADES	15	67,176
AN 956 SH + NADES	15	72,985
AN 923 SH + NADES	10	223,340

* the optimum dosage of NADES is in molar (M)

higher ω_c values prove the high structural gel-like strength of the generated flocs. Observations from Fig. 9 and Table 3 show that hybrid systems of NADES/ PAMs surpassed the single systems in terms of the sediments' capacity to store mechanical energy. For example, the highest G' attained from a single system was for suspensions treated using NADES with a capacity of $3078 mPa$ followed by FO 4800 SH, AN 965 SH, AN 965 SH, and lastly FO 4350 SH. CPAM with high CD (i.e., FO 4800 SH) achieved a capacity almost 35 times higher than low CD FO 4350 SH. On the other hand, APAMs with low and medium CD demonstrated similar elastic and viscous modulus trends. The differences between the single systems in G' and G'' can be attributed to the
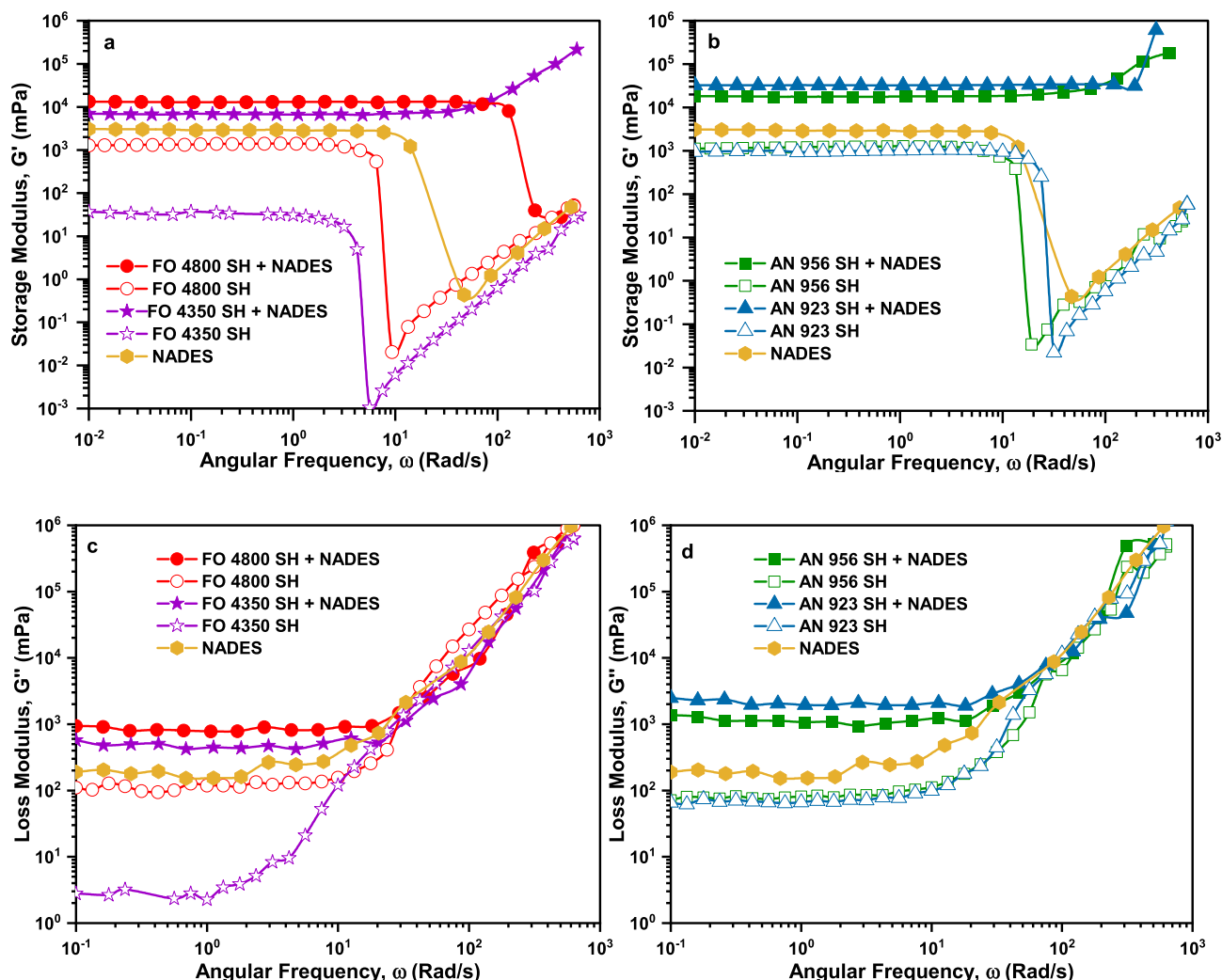

Fig. 9. Variation in the storage modulus and loss modulus for (a)/(c) cationic and (b)/(d) anionic systems with angular frequency.

variation in the size and strength of the flocs in the sediment. As mentioned in Section 3.1.2, the flocs produced using NADES were small in size resulting in a denser and more compacted sediment, hence, a higher capacity to store mechanical energy [40]. Conversely, the poor flocculation efficiency and the loosely bounded flocs formed during the flocculation process with FO 4350 SH are the reasons behind the low G' and G''.

The utilization of hybrid NADES/ PAMs systems resulted in a significant improvement of the settled sediment properties. The bentonite suspension treated NADES/ AN 923 SH hybrid system showed the highest capacity to store mechanical energy and return to its initial configuration upon removing the applied oscillatory shear. Furthermore, the floc size and the interaction strength played a significant role in determining the viscous and elastic behavior of the sediment. Accordingly, hybrid systems were ranked as follows: NADES/ AN 923 SH, NADES/ AN 956 SH, and lastly NADES/ FO 4800 SH along with NADES/ FO 4350 SH. The uniform compacted large flocs of the APAM systems retained less water compared to the CPAM systems and hence, elevated their resistance to structural breakdown with the increasing oscillatory frequency. The differences in CD of CPAMs in hybrid systems did not show a significant impact in terms of enhancing the viscoelastic properties. However, APAM with low CD demonstrated superior behavior compared to high CD. The higher adsorption tendency of AN 923 SH with low CD toward the uncovered batches with NADES on the bentonite particles promotes higher flocculation efficiency and stronger flocs than AN 956 SH. The obtained viscous and elastic modulus for single and hybrid systems were in good agreement with the viscosity and floc size trends. This confirms that hybrid systems contribute to better particle-particles and coagulant/ flocculant-particle interactions. Thus, improving the treatment efficiency and the properties of the treated system which is necessary for the advanced treatment steps.

Furthermore, the complex viscosity (η^*) for single and hybrid systems as a function of the angular frequency was assisted and the outcomes are presented in Fig. 10. Complex viscosity is defined as the material's total resistance to flow [47]. As shown in Fig. 10, for all systems understudy a gradual decrease in the η^* is exhibited upon increasing the angular frequency. At a certain point known as the critical frequency (ω_c), a sharp decrease in the η^* is observed after which the η^* starts increasing gradually with the angular frequency. The demonstrated decrease in the η^* is attributed to the particle–particle and flocculant-particle interactions breakdown due to force application. Furthermore, it is worthy of mentioning that the ω_c of the η^* correspond to the same ω_c detected in the G' data (Table 4). In addition, the observed η^* trends are in good agreement with the G'.

Table 4

G', G'', and critical frequency of treated bentonite suspension at the optimum dosage of the utilized coagulant/ flocculant.

Coagulant/ flocculant	G' (mPa)	G'' (mPa)	ω_c (mPa)
NADES	3,077.8	189.4	46.9
FO 4800 SH	1,269.8	110.1	13.3
FO 4350 SH	36.6	2.8	2.4
AN 956 SH	1,114.5	71.1	13.3
AN 923 SH	925.1	65.1	10.0
FO 4800 SH + NADES	13,255	937.72	86.8
FO 4350 SH + NADES	6,925.9	572.1	–
AN 956 SH + NADES	18,152	1375	–
AN 923 SH + NADES	32,487	2481.6	–

3.4. Destabilization degree vs. rheological behavior

3.4.1. Zeta potential

Commonly, the stability of colloidal suspension is assessed by conducting zeta potential measurements, which determine the magnitude of the electrostatic interactions within the system. In other words, it measures the total net charge of the particles' surfaces [48]. According to the zeta potential value, the colloidal system can be classified as stable or unstable. High zeta potential (i.e., $\zeta > +30$ and $\zeta < -30$) indicates high stability of the system due to the domination of the repulsive forces between the similarly charged particles. When the zeta potential value approaches to zero, the stability of the system decreases as a result of the attractive forces overcoming the repulsive forces [3,49]. Highly stable colloidal systems exhibit very low interactions between the particles while strong coagulant/ flocculant-particle and particle-particle interactions are associated with destabilized systems. Thus, unstable systems with zeta potential close to the zero point of charge demonstrate elevated viscosities, which require the application of high stress to initiate the flow and vice versa for stable systems [40].

The variation in the rheological properties, including the elastic modulus, yield stress, and viscosity with the zeta potential of treated suspensions using hybrid NADES/ PAMs system at their optimum dosage, is illustrated in Fig. 11. The highest elastic modulus, yield stress, and viscosity of $32,487 mPa$, $694 mPa$, $223,340 mPa.s$, respectively attained by bentonite suspension treated using NADES/ AN 923 SH hybrid system at its optimum dosage was associated with a zeta potential of $-3.9 mV$. The reduction in the negative zeta potential to a value close to the zero point of charge, compared to the single systems (Fig. 2), significantly reduced the system's stability. As a result, flocs with strong interactions and high resistance to deformation were formed. Increasing the CD of APAMs induced a more negative zeta potential of $-6.2 mV$
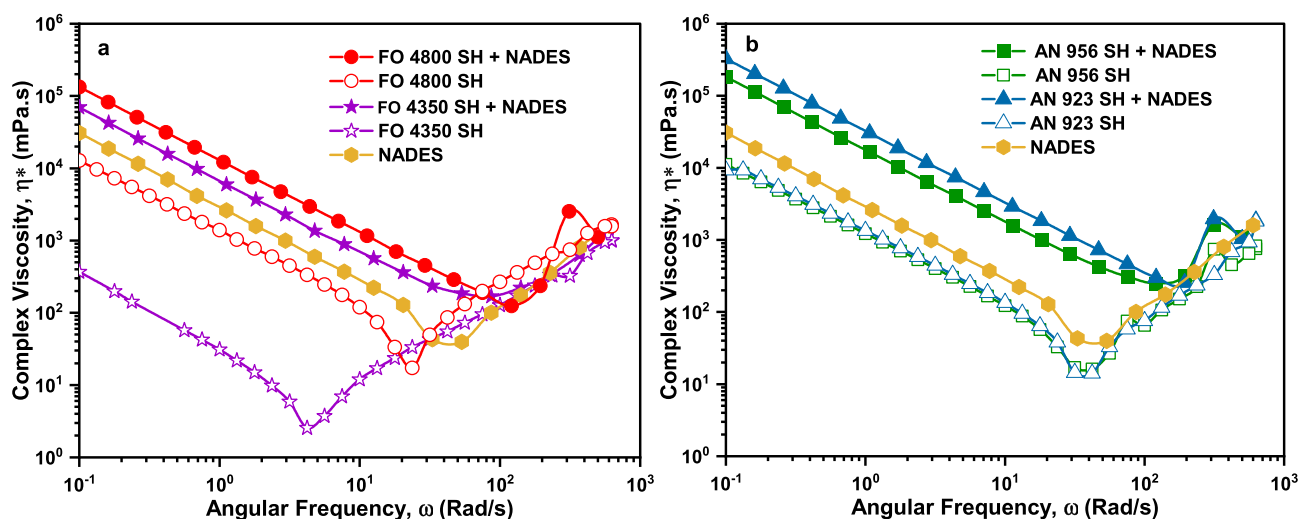

Fig. 10. complex viscosity as a function of the angular frequency for (a) cationic and (b) anionic hybrid systems.
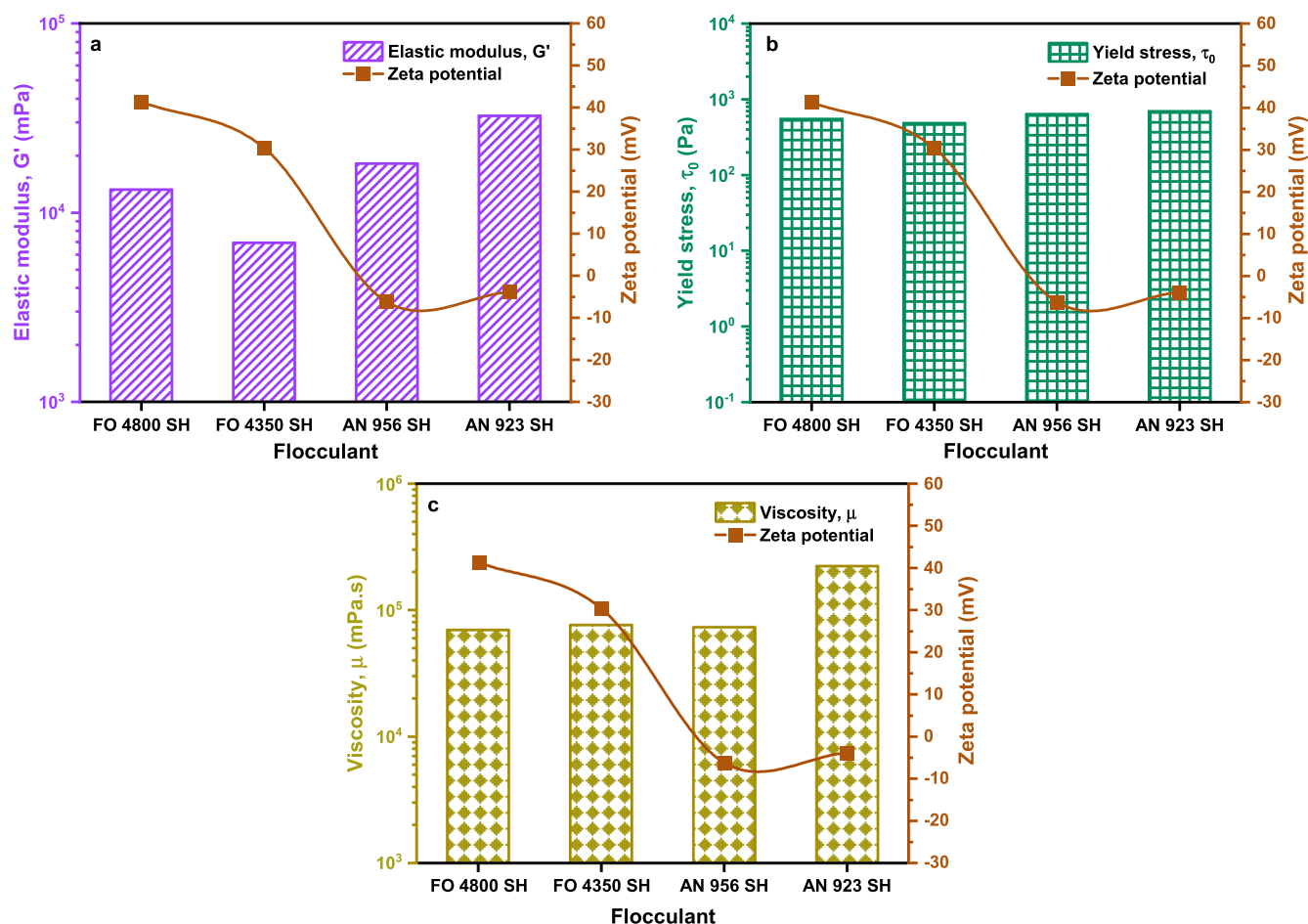
Fig. 11. variation of (a) Elastic modulus, (b) yield stress, and (c) viscosity with a zeta potential of treated bentonite suspension with NADES/ PAMs hybrid systems.

leading to a slight alteration in the rheological behavior of the treated suspension. For example, increasing the CD from 20% to 50% led to a decrease of 44% in the elastic modulus, 9% in the yield stress, and 67% in the viscosity. This can be attributed to the lower bridging ability between the APAM chains and the batches uncovered with NADES on the bentonite particles due to the high repulsion between them. Hence, reducing the strength of the interactions between the particles and their resistance to deformation.

On the other hand, the highly positive zeta potential of $30.4 mV$ and $41.3 mV$ achieved by NADES/ FO 4350 SH and NADES/ FO 4800 SH, respectively affected the rheological properties of the treated suspensions. To elaborate, the presence of excess positive charge due to the addition of cationic NADES and CPAM to the suspension results in a complete saturation of the negatively charged bentonite particles and hence, a charge reversal. Consequently, the resultant flocs demonstrate weak interaction due to the domination of the repulsive forces between them and the reduction of the adsorption capacity and bridging ability of the CPAMs on the bentonite particles. Therefore, the flocs were highly sensitive to applied stress.

3.4.2. Floc size and CST

Correlation of the rheological properties to the floc size and CST results were also conducted. Performing such analysis is important to provide the necessary support to the obtained zeta potential results. The relation between the elastic modulus, yield stress, and viscosity with the floc size and CST for each hybrid system at their optimum dosage is illustrated in Fig. 12. Observations from Fig. 12 reveal that generally, larger flocs yield higher viscosity, elastic modulus, and yield stress with lower CST. The type and CD of the utilized PAM significantly influence

the electrokinetics and rheological properties. For instance, flocs with a greater D_{50} were produced from suspensions treated with APAM hybrid systems. The presence of NADES with a positive charge on the surface of the bentonite particles plays a vital role in reducing the repulsion forces between the negatively charged surfaces and chains and promotes agglomeration. Consequently, the formed flocs exhibit strong interactions resulting in high strength sediment as indicated by the elastic modulus, viscosity, and yield stress results. Furthermore, the size of the flocs induces the structure of the settled sediments and hence, the time required for the free water to filter out. The large flocs produced by NADES/ APAM hybrid systems result in sediment with large interstices in which the free water can easily flow through and thus low CST. The opposite is applicable for suspensions treated with NADES/ CPAMs hybrid systems.

By comparing the two APAMs hybrid systems (i.e., NADES/ AN 923 SH and NADES/ AN 956 SH), it can be noticed that low CD APAM demonstrates a better performance than high CD APAM. As mentioned above, less repulsion is exhibited between the uncovered batches of the bentonite particles and the low CD APAM chains. Consequently, the produced sediment possesses larger flocs with stronger connections and hence, better rheological properties and lower CST. The obtained outcomes from the zeta potential, floc size, and CST are in good agreement. Systems with a less negative zeta potential give flocs with a greater median diameter and accordingly, higher viscosity, elastic modulus, yield stress, and CST.

4. Conclusions

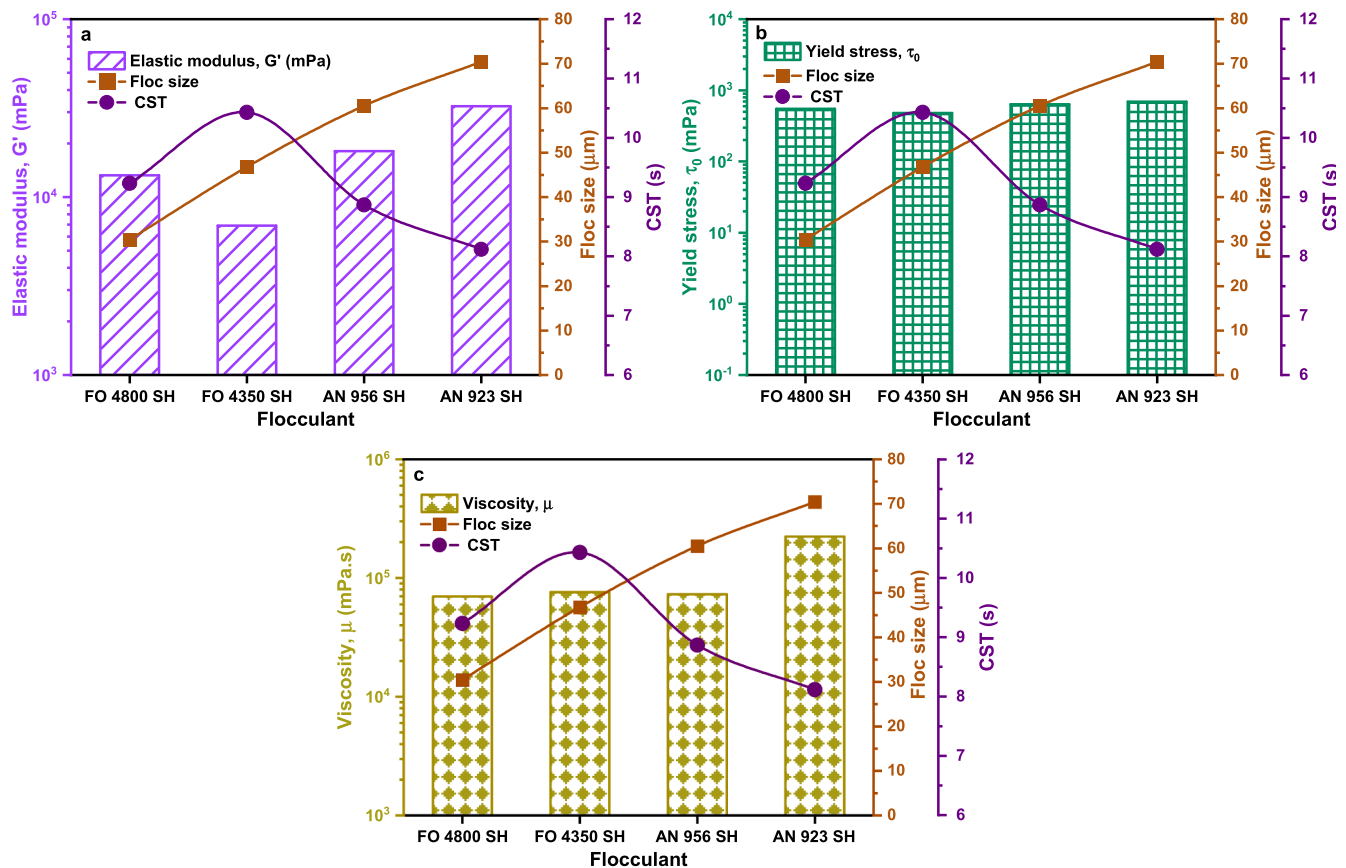The main objective of this paper was to study the potential of uti-

Fig. 12. variation of (a) Elastic modulus, (b) yield stress, and (c) viscosity with the floc size and CST of treated bentonite suspension with NADES/ PAMs hybrid systems.

lizing a hybrid coagulant/ flocculant system to improve the treatment efficiency of bentonite suspension and the rheological properties of the produced sediment. ChCl:LA based NADES at a fixed dosage of $1.78 \times 10^{-2} M$ along with Four PAMs were utilized in the study as the coagulant and flocculants, respectively. The influence of the PAM type, dosage, and charge density on the treatment process was investigated using hybrid systems as well as single systems to benchmark and evaluate the performance of the hybrid systems. The following remarks were concluded from the conducted study:

- Hybrid NADES/ APAMs systems showed an exceptional improvement in the flocculation efficiency of bentonite suspension compared to single APAM systems. The combination of NADES and APAM resulted in a destabilized suspension (i.e., $-10\,\mathrm{mV} < \zeta < 0\,\mathrm{mV}$) with turbidity below 1 NTU and a D_{50} from 20% to 40% greater than single systems.
- The utilization of a hybrid system adversely affected the performance of CPAMs in terms of the degree of stability and floc size. At the optimum CPAM dosage, the floc size achieved by the hybrid systems was 15% to 40% smaller than those produced by single systems. Furthermore, the utilization of hybrid NADES/ CPAMs systems caused a severe charge reversal due to the saturation of the bentonite particles with positive charges.
- Treating bentonite suspension with hybrid NADES/ PAM systems enhanced the rheological properties of the produced sediments, including viscosity, elastic modulus, and yield stress. This occurs due to the strong interaction between the particles' surface and the coagulant/flocculant, stronger and more compacted flocs, and more viscous sediment compared to the single systems.

- All produced sediment from single and hybrid systems demonstrated a non-Newtonian shear-thinning behavior with measurable yield stress and were best described by the Herschel Bulkley model.
- Hybrid systems with anionic PAM demonstrated a higher flocculation efficiency and better rheological properties compared to systems with cationic PAM. Moreover, PAM with a lower CD showed a superior behavior over high CD PAM.
- Among all investigated hybrid systems, NADES combined with a low CD APAM (i.e., AN 923 SH) system resulted in the highest treatment efficiency with the most desirable rheological properties. On the other hand, NADES/ FO 4800 SH hybrid system showed the lowest treatment efficiency.

CRediT authorship contribution statement

Dana I. M. Al-Risheq: Writing – original draft. **Shifa M.R. Shaikh:** Writing – original draft. **Mustafa S Nasser:** Conceptualization, Supervision. **Fares Almomani:** Supervision. **Ibnelwaleed A. Hussein:** Writing – review & editing. **Mohammad K. Hassan:** Writing – review & editing.

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.

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