

Review Paper

Mechanisms for clay-polymer interactions in the treatment of mature fine tailings: A review

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ARTICLE INFO

Article history:

Received 12 March 2024

Received in revised form

6 September 2024

Accepted 9 October 2024

Available online 10 October 2024

Edited by Jia-Jia Fei and Teng Zhu

Keywords:

Mature fine tailings

Polymer flocculants

Clay particles

Asphaltene

ABSTRACT

Chemical flocculants are widely used in treating mature fine tailings (MFT) produced during bitumen extraction processes, among which polymers with high molecular weight (HMW) have demonstrated efficacy in dewatering and clay flocculation. The long polymer chains carry sufficient functional groups to simultaneously interact with multiple clay surfaces, thereby modulating clay surface properties and facilitating the aggregation of clay particles. Significant efforts have been devoted to enhancing the flocculation and dewatering performance of polymer reagents. Despite some successes, the design of new and effective polymer flocculants with desired performance is hindered by the limited fundamental understanding of clay-polymer interaction mechanisms. In this work, interaction mechanisms between polymer flocculants and clay particles are reviewed. Solid flocculation by polymers can be driven by multiple mechanisms, either independently or in combination, due to the diverse properties and solution chemistry involved. Factors that affect the interactions are analyzed, with a particular focus on the effects of clay surface features, pH, ions, and asphaltene. Addressing ongoing debates regarding the synergy of multiple types of polymer segments, the influence of multi-valent ions, and the effects of amphiphilic asphaltene can significantly expedite the design of more effective flocculants and flocculation processes. © 2024 The Authors. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co. Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Oil sands are unconventional petroleum resources from which bitumen could be extracted (Omari et al., 2021). More than three-quarters of the global oil sands deposit are located in Canada, and the rest are mainly in the United States and Venezuela (Fu et al., 2017; Omari et al., 2021). In the bitumen exploitation process, water, sand, silt, and fine particles are usually brought together to the surface as a by-product, which is known as tailings. A gel-like mature fine tailings (MFT) would form after the coarse fraction of these by-products segregate quickly in the settling basin (Alberta Government, 2017a). The fine particles in oil sands tailings settle very slowly, and it usually takes 2–3 years for them to reach a concentration of about 30–40 wt% (Farkish and Fall 2013). Long-term storage structures are required, referred to as tailings ponds. The tailings ponds are settling basins that enable water separation, storage, and recycling, as shown in Fig. 1(a). The environmental

impacts brought by oil sands tailings cannot be neglected, e.g., chemicals leaching due to structure flaws (Moradi et al., 2023) and toxic material seeping into groundwater (McCerery et al., 2024; Tian et al., 2024). However, the total volume of tailings will keep increasing due to the very slow consolidation of untreated MFT and the continuous bitumen production activities. For example, in the Alberta province of Canada, there were approximately 976 million cubic meters of fluid tailings stored within tailings ponds in 2013 and the number increased to about 1500 million in 2019 (Alberta Government, 2017b, 2020). Accelerating the water recovery and land reclamation from tailings has become an urgent need.

Enhancing solid-water separation is the key to water recovery and land reclamation from tailings, which is limited by the fine clay particles in MFT (Wang et al., 2024). Fig. 1(b) shows a consolidated MFT cake after mechanical compression which mainly consists of clay particles. Solid particles with a size equal to or less than 44 µm are considered as fines (Alberta Government, 2017b). In MFT, about 4% of the clay particles are larger than 44 µm, 46% between 6.5 and 44 µm, and 50% less than 6.5 µm (Alamgir et al., 2012). For example, Fig. 1(c) shows a size distribution of clay particles in a MFT suspension. The clay particles in MFT are usually entrained in slightly

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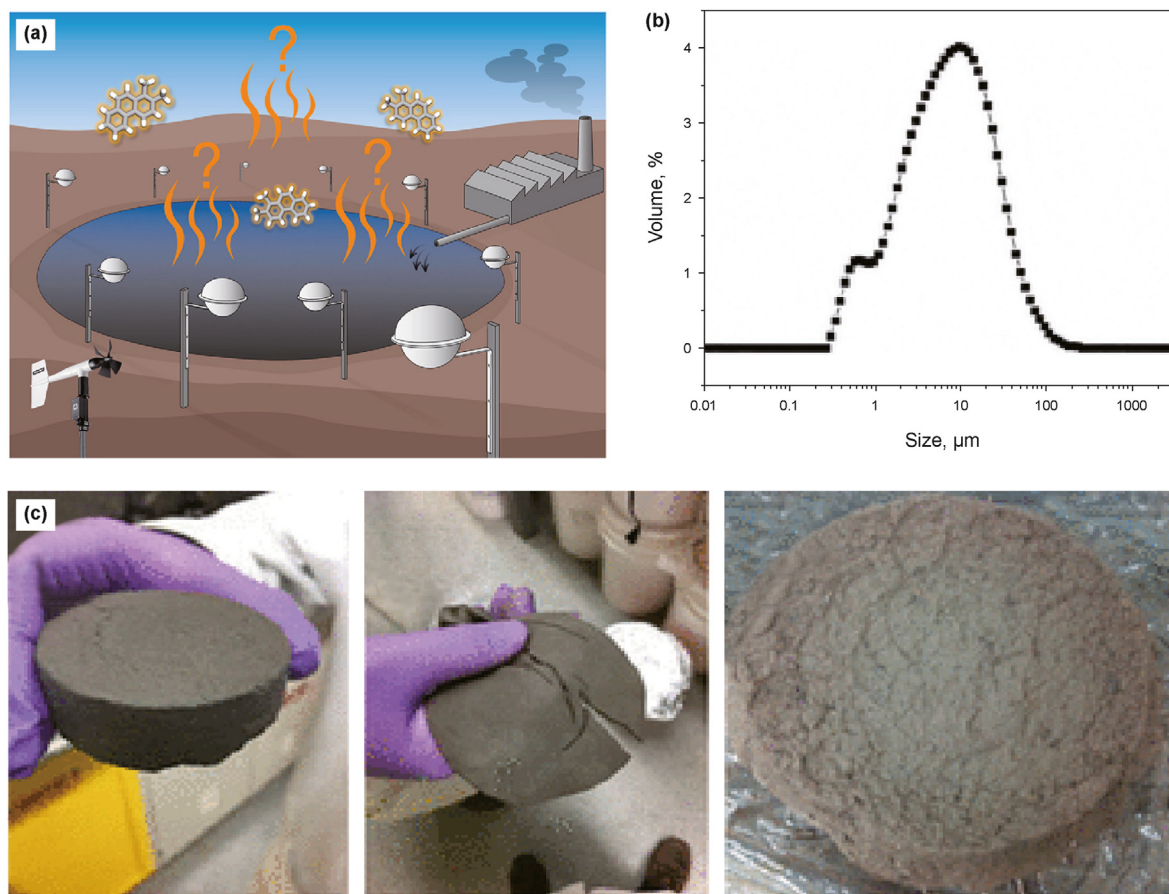


Fig. 1. (a) Illustration of tailings pond, Canada. Reprinted with permission from (Moradi et al., 2023). Copyright 2023 Elsevier. (b) Consolidated MFT cake after mechanical compression. Reprinted with permission from (Yan et al., 2019). Copyright 2019 American Chemical Society. (c) Particle size distribution of MFT suspension measured by Mastersizer. Reprinted with permission from (Yan et al., 2019). Copyright 2019 American Chemical Society.

alkaline process water of which the pH is between 7.7 and 8.8 (Allen, 2008). A small amount of calcium, magnesium, chloride, and sulfate ions are also contained in the process water (Arslan et al., 2023). The clay particles are usually negatively charged in aqueous solutions (Schofield and Samson, 1954), and the electrostatic repulsion between the particles makes them very stable in MFT.

Developing effective methods to destabilize the dispersion of fine particles in MFT has been the research focus for many decades, as told in Fig. 2. After natural drying and sedimentation that help the coarse sands consolidate first, physical and chemical treatment

are employed to treat the fine clay particles. Physical methods include freeze-thaw cycles, filtration, centrifugation, electric treatment, or their combinations, helping dewater the tailings (Hogg, 2000; Vedoy and Soares, 2015; Guo et al., 2020; Santander et al., 2021; Kabwe et al., 2024). Chemicals are also widely used to improve the solid aggregation and dewatering of MFT, including inorganic salts as well as low molecular weight polymers that promote coagulation, as well as macromolecular additives that function as flocculants (Zhang et al., 2019; Yang et al., 2022). Despite some successes, much remains to be done on the selection and synthesis of polymers for MFT. Firstly, the addition of some

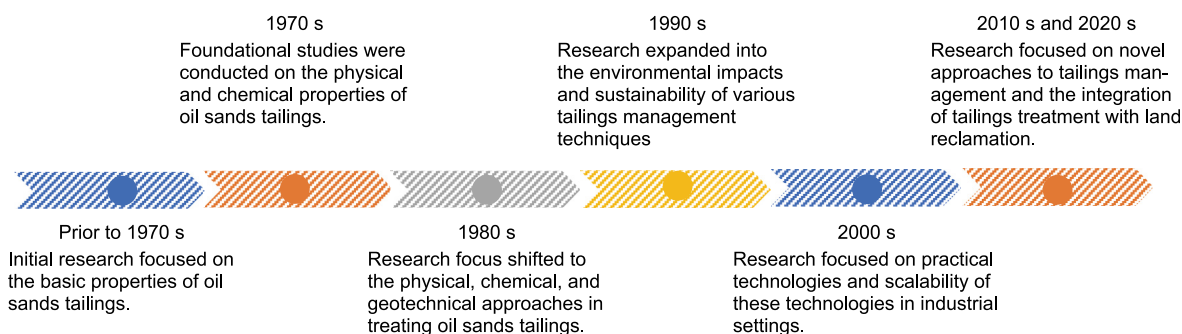


Fig. 2. Evolution of research focus in oil sands tailings treatment. Examples of each stage are given in the works of (Ageton, 1945; Raymond, 1969; Bakhshi et al., 1975; Burchfield and Hepler, 1979; Kessick, 1979; Rao, 1980; MacKinnon and Boerger, 1986; Nix and Martin, 1992; Chalaturnyk et al., 2002; Badiozamani and Askari-Nasab, 2014; Saborimanes, 2021; Gong et al., 2024; Li et al., 2024).

ionic polymers would result in high ion strength in the recovered water, which is not economically and environmentally acceptable. Secondly, most commercial polymer flocculants are developed for other industries, e.g. mining and paper making, and cannot flocculate MFT in high efficiency (Vedoy and Soares, 2015). In addition, bitumen in oil sands tailings could interact with the fine particles, affecting the performance of the added flocculants. The interaction could also impede water release from the pores of clay aggregates, hindering the consolidation (Klein et al., 2013). Above all, understanding the interaction mechanisms between polymers and clay particles can greatly benefit the application of polymers in treating MFT.

This work provides a review of the interaction mechanisms between clay and polymers, in the context of MFT treatment. Previous reviews addressing similar topics are listed in Table 1. Compared to these previous works, the current review specifically focuses on the mechanisms of clay-polymer interactions at a fundamental level. It emphasizes the molecular characteristics of clay minerals and polymer flocculants, and considers the impact of common environmental factors in MFT such as pH, ions, and asphaltene, aiming to provide insights from a molecular viewpoint. Limitations of existing research and future perspectives are also provided.

2. Classification of clay minerals in MFT

Electron microscopic pictures of clay particles in MFT showed that they are mainly comprised of stacked clay mineral layers (Barnhisel and Bertsch, 1989; Kang et al., 2019). The clay layers are mostly phyllosilicates with planer structure (as shown in Fig. 3(a)), and each layer is usually in the form of either 1:1 (Fig. 3(b)) or 2:1 atomic layers (Fig. 3(c)). The clay minerals in MFT that belong to 2:1 class are mostly montmorillonite (Chalaturnyk et al., 2002; Kaminsky et al., 2009), smectite consisting of one alumina octahedral sheet sandwiched by two silica tetrahedral sheets, as shown in Fig. 3(c). Thus, the 2:1 structure is also referred to as TOT layer. The structure of montmorillonite is similar to pyrophyllite, yet with

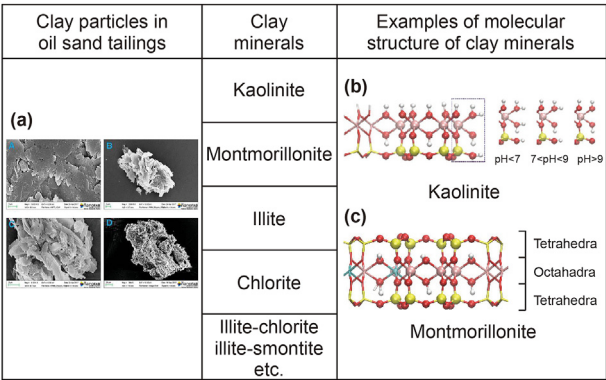


Fig. 3. Classification of clay minerals in oil sand tailings. (a) Cryo-FE-Scanning Electron Microscopy (Cryo-FE-SEM) image of raw MFT (A), sediments obtained after flocculation (B), internal structure of a flocc (C) and sediments obtained after polymer hydrolysis (D). Reprinted with permission from (Gumfekar et al., 2017). Copyright 2017 American Chemical Society. (b) Molecular structure of kaolinite. (c) Molecular structure of montmorillonite. Color scheme: oxygen (red), silicon (yellow), aluminum (pink), magnesium (cyan), and hydrogen (white).

a layer charge arising from isomorphous atom substitution (Stubican and Roy, 1961). The isomorphous substitution is more likely to happen in the octahedral sheet than in the tetrahedral ones. For example, in Fig. 3(c), three aluminum atoms in the octahedral sheet of montmorillonite are substituted by three magnesium atoms (only two are visible in the front view), giving rise to a permanent layer charge of -3 . The negative charge is balanced by ions such as Na^+ and Ca^{2+} in the interlayer space, which can swell underwater, making it possible to accommodate a wide range of guest molecules. Thus, montmorillonite is widely adopted in many applications involving clay-polymer interactions, such as the fabrication of nanocomposite (Altat et al., 2021) and waste removal (Moja et al., 2020).

Kaolinite is a representative 1:1 clay mineral layer in MFT (Tunega et al., 2004), also referred to as TO layer. As shown in

Table 1
Summary of existing reviews addressing similar topics.

References	Focus	Topics
Wang et al., 2014	Theory and practice in MFT treatment	- Techniques for accelerating the sedimentation of fine solids - Techniques for consolidation and dewatering - Application of external energy to induce sludge desaturation - Methods for water recovery
Kossoff et al., 2014	Characteristics, failure, environmental impacts and remediation of mine tailings dams	- Physical, chemical, and mechanical properties of tailings - Storage of tailings in dammed impoundments - Causes of tailings dam failures - Environmental impacts and remediation of tailings dam failures
Rao and Liu, 2015	Geopolymerization technology in mine tailings treatment	- Geopolymer development for treating oil sands MFT - Raw aluminosilicate materials and alkali activators in geopolymerization - Factors affecting geopolymerization
Qi and Fourie, 2019	Cemented paste backfill (a type of thickened tailings) for mineral tailings management	- Polymer flocculation, mechanisms and factors affecting flocculation - Design of cemented paste backfill mix and factors affecting its strength - Pipe transport of cemented paste backfill
Zhao et al., 2021	Iron ore tailings characteristics and concrete properties	- Physical properties, chemical and mineral composition, mechanical and compound activation of iron ore tailings - Properties of concrete incorporating iron ore tailings
He et al., 2022	Production of mine tailings-based geopolymer composites	- Economic and production perspectives of mine tailings-geopolymer composites - Preparation of mine tailings-based geopolymers - Physical and mechanical properties of tailing-based geopolymer composites
Furnell et al., 2022	Dewatered and stacked mine tailings	- Different types of tailings (e.g. conventional, thickened/paste, stacked) - Design and construction of stacked tailings facilities - Transportation of dewatered tailings to final storages - Geotechnical stability
This work	Molecular mechanisms for clay-polymer interactions	- Characteristics of clay minerals in MFT - Clay-polymer interacting mechanisms - External factors affecting molecular interactions between clay and polymer

Fig. 3(b), a common plane of oxygen atoms connects two sheets in a kaolinite layer, one consisting of SiO_4 tetrahedra and the other consisting of AlO_6 octahedra. The chance for atom substitution in kaolinite is small (Bolland et al., 1976), and thus the charge density of kaolinite basal surface is not comparable with montmorillonite. Meanwhile, the edge surface can occupy as much as 50% of the total surface area of a kaolinite particle, while the corresponding value is less than 5% for montmorillonite (Brady et al., 1996). The charge of the edge surface is pH-dependent, which regulates the colloidal properties of clay minerals (Bergaya et al., 2006). Taking kaolinite as an example, when the solution pH is about 7, each edge surface was terminated by one $\text{Al}(\text{OH}_2)(\text{OH})$ group and one $\text{Si}(\text{OH})$ group, as shown in Fig. 3(b). The surface charge under this environment is zero. In an acidic environment with $\text{pH} < 7$, hydroxyl of $\text{Al}(\text{O}-\text{H}_2)(\text{OH})$ groups tends to be protonated, resulting in an $\text{Al}(\text{O}-\text{H}_2)(\text{OH}_2^+)$ group with a +1 charge. When $\text{pH} > 7$, the water bound to the Al atom will deprotonate, generating an $\text{Al}(\text{OH})_2$ group with a charge of −1. When the environment becomes highly alkaline with $\text{pH} > 9$, the $\text{Si}(\text{OH})$ group will also become deprotonated, turning into a $\text{Si}-\text{O}^-$ terminal, and the surface charge becomes −2 per unit.

Other clay minerals such as illite and chlorite also exist in MFT. They usually share similar molecular structures with montmorillonite or kaolinite but vary in isomorphous substitution or interlayer materials. For example, illite belongs to 2:1 class, similar to the structure of montmorillonite except that the isomorphous substitution usually takes place in both the tetrahedral and the octahedral sheets (Theng, 2012; Hao et al., 2018). Chlorite is also of 2:1 type, with hydroxide sheets intercalated in the interlayer spaces (Barnhisel and Bertsch, 1989).

3. Features of clay mineral surfaces

To modulate solid interactions in colloid systems such as clay suspensions in MFT, it is of great importance to understand the surface properties of different clay minerals. In many theoretical models such as the Gouy-Chapman relation and DLVO theory, the surfaces of fine solids were simplified into uniform spheres or planes (Israelachvili, 2011). However, the surface structures of real fine clays are more complex. As introduced in Section 2, there are basically three types of clay surfaces in MFT, the siloxane basal surface, the alumina basal surface, and the pH-dependent edge surface. The geometry, charge condition, and functional groups vary with the types of surfaces, which affect the surface properties such as the surface potential (Zhao et al., 2008; Tournassat et al., 2016) and wettability (Tunega et al., 2004; Zhang et al., 2016), resulting in complex flocculation and dewatering behaviors.

The surface potential usually varies with the type of clay surface due to the different isomorphous substitution or protonation. Even within the same clay mineral layer, the surface potential can still display anisotropy, which challenges the fundamental understanding of surface behaviors. Liu et al. (2002) measured the average zeta potential of kaolinite and montmorillonite suspensions under different pH. The zeta potential of kaolinite in 1 mM KCl solution decreased from about 0 mV at $\text{pH} = 3$ to about −30 mV at $\text{pH} = 10$, while the zeta potential of montmorillonite remained almost unchanged at different pH. Tournassat et al. (2016) employed a two-dimensional Poisson-Boltzmann equation (Bourg et al., 2007) to calculate the surface potential near two different edges of a montmorillonite particle (Fig. 4(a)). As shown in Fig. 4(b) and (c), the [010] edge surface became positive when the pH reduced to 5 while the [110] edge surface remained negative until the pH became less than 3.5, suggesting that the crystallographic orientation significantly affect the surface charge. Performing

molecular dynamics (MD) simulation, Quezada et al. (2021) studied the binding ability of anionic polymers to the surfaces of three clay minerals in water at $\text{pH} = 11$. The results showed that the affinity was in the order of brucite, kaolinite, and quartz. Muscovite micas were cleaved differently by Zhao et al. (2008) to study the surface potential of basal and edge surfaces of 2:1 phyllosilicate. The forces between a silica particle attached to the end of an atomic force microscopy (AFM) cantilever and two different crystallographic planes of mica were measured in an aqueous solution, and pH of the solution was varied. As shown in Fig. 4(d), the long-range force for the basal plane remained repulsive when pH changed from 6 to 10. On the other hand, for the edge surface, the repulsive force decreased as pH was lowered, and reversed to be attractive when $\text{pH} < 6$. According to the work of Zhao et al. (2008), the edge surface had higher surface roughness than the basal surface, which made its surface force more complicated. Fig. 4(e) shows the change of basal and edge surface charges with pH for kaolinite in 0.004 M LiNO_3 . The experimental data was consistent with the theoretical prediction of edge charge, as edge charge was pH-dependent and basal charge was not (Tofighi and Rahnamaie, 2023).

The wettability of a clay surface is tightly related to its type. Through MD simulations, Sun et al. (2023) simulated the adsorptions of an amphiphilic molecule, N-(1-hexylheptyl)-N'-(5-carboxylicdodecyl) perylene-3,4,9,10-tetracarboxylic bisimide (C5Pe) on the tetrahedral layer and octahedral layer of a kaolinite plate, respectively. The adsorption of C5Pe on the tetrahedral layer was through its hydrophobic part (a polyaromatic core) while on the octahedral layer, it was through the hydrophilic part (a carboxylate group). The tetrahedral layer was thus shown to be more hydrophobic than the octahedral layer. Tunega et al. (2004) investigated a water layer on the octahedral and tetrahedral basal surfaces of kaolinite by ab initio molecular dynamics (AIMD) simulations. The results showed that water molecules could form strong hydrogen bonds with all hydroxyl groups on the octahedral surface, via the proton of water and the oxygen of surface OH as well as the oxygen of water and the surface proton. While on the tetrahedral surface, water molecules have a slow rotation motion above the ditrigonal hole, forming and breaking weak hydrogen bonds with the basal oxygen atoms. The octahedral layer is, therefore, more hydrophilic than the tetrahedral layer, consistent with the finding of Sun et al. (2023).

Moreover, for the same type of surface, the wettability can also be different when the surface carries different charges. Zhang et al. (2016) investigated the wettability of the basal surface of montmorillonite with different surface charges by MD simulation. The different charged montmorillonites were solvated by mixtures of decane and water. As the surface charge increased, the contact area between the basal surface and decane gradually decreased until the surface became fully water wet. It was proposed that the increased surface charge attracted more counterions (Na^+ and Ca^{2+}) to the surface. The hydration of the counterions accumulated more water molecules in proximity to the surface and thus increased the wettability. X-ray diffraction as well as water adsorption measurement by Saada et al. (1995) showed that the surface of illite was overall more hydrophilic than kaolinite. As a result, kaolinite had a higher affinity for asphaltene while illite had a higher affinity for water.

To summarize, three main types of clay surfaces exist in MFT: the siloxane basal surface, the alumina basal surface, and the pH-dependent edge surface. These surfaces vary in geometry, charge condition, and functional groups, which affect properties such as surface potential and wettability, leading to complex flocculation and dewatering behaviors.

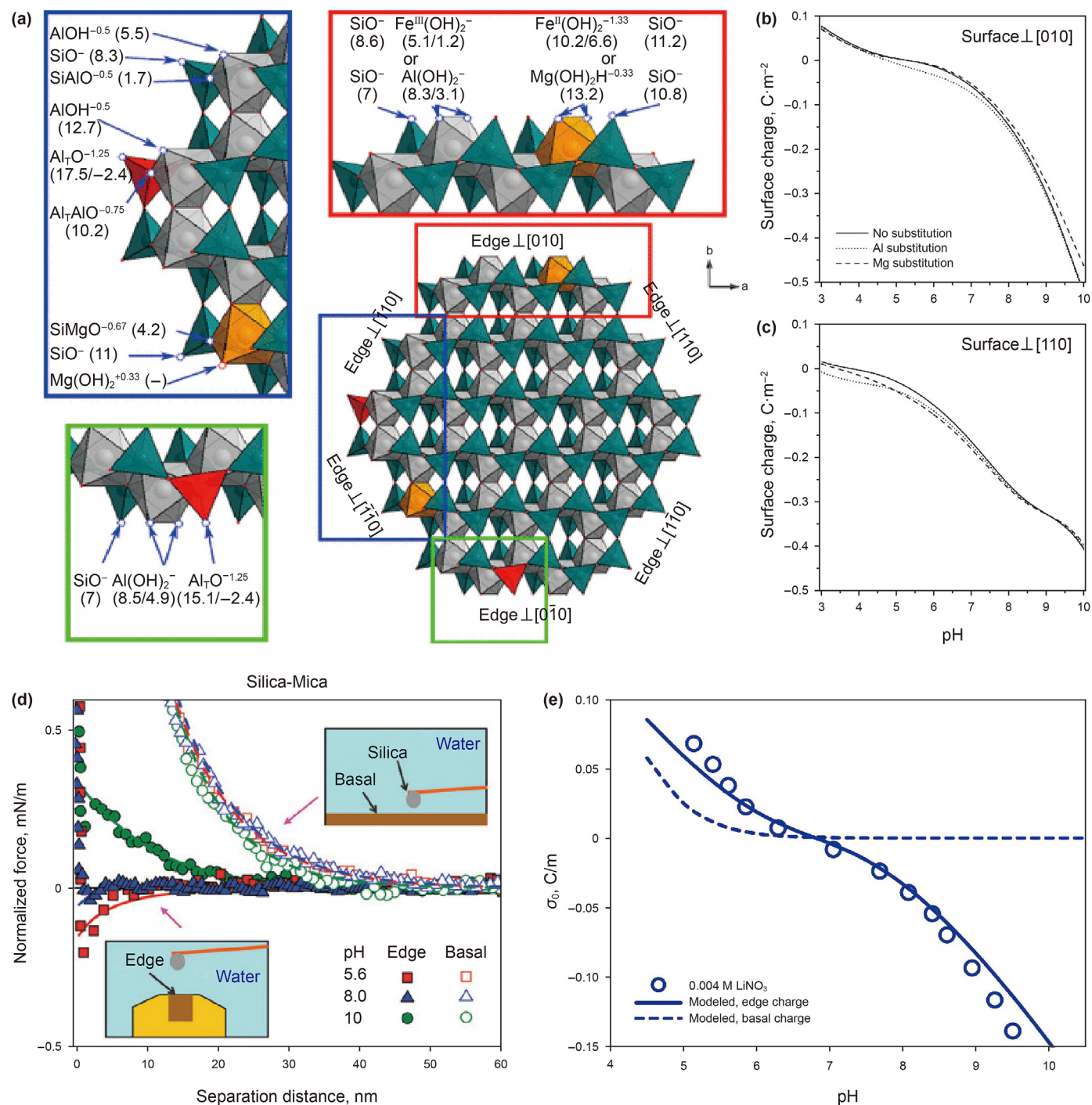


Fig. 4. (a) Edge surface sites of a model montmorillonite particle. (b) and (c) Predicted surface charge as a function of pH for a montmorillonite particle. Reprinted with permission from (Tournassat et al., 2016). Copyright 2016 American Chemical Society. (d) Forces between silica probe of AFM and edge surface of mica, as well as between silica and basal surface of mica. Reprint with permission from (Zhao et al., 2008). Copyright 2008 American Chemical Society. (e) Experimental and modeled data for the surface charges of kaolinite in 0.004 M LiNO_3 solution. Reprinted with permission from (Tofighi and Rahnamaie, 2023). Copyright 2023 Elsevier.

4. Roles of polymer flocculants in modulating clay interactions

The efficacy of many polymers with high molecular weight (HMW) in modulating the solids interactions has been widely proved, either in clay mineral suspensions or MFT. The long polymer chains carry sufficient functional groups to simultaneously interact with multiple solid surfaces, so that the solids can be

flocculated together, achieving desirable flocculation performances. The modulation can be driven by multiple mechanisms, independently or together, due to the variety of surface properties. In the studies to be reviewed below, the techniques used to characterize clay-polymer interactions can be divided into the following categories: (1) techniques that measure the polymer's flocculation ability, such as the sedimentation test, dewatering test, and focused beam reflectance measurement (FBRM); (2) measurements of

polymer adsorption, such as quartz crystal microbalance with dissipation monitoring (QCM-D); (3) surface charge analyses to assess the electrostatic interactions between clay particles and polymers, represented by zeta potential measurement; (4) microscopy techniques that visualize morphological changes of the solid surfaces resulting from polymer adsorption, such as SEM, AFM; (5) force measurements between clay surfaces and polymers, such as AFM and surface force apparatus (SFA); and (6) theoretical modeling that reveals clay-polymer interactions at molecular scale, such as MD and AIMD simulations. It is worth noting that due to the difference in lab and industrial scales, the results reported from lab-scale characterizations (e.g., settling rate or amount from sedimentation tests) could be lower than desired in real oil sands MFT treatments. Nevertheless, these experiments still allow for interpretation of the clay-polymer interaction mechanisms and performance comparison between different polymers.

4.1. Suppressing electric double layer force

Charged polymers can mediate solid interactions by altering their electrostatic properties. In aqueous solutions, the negatively charged solids attract the counter-ions and co-ions to distribute around the solid surface, forming the diffuse electric double layer (EDL) (Israelachvili, 2011). The aggregation of similarly charged solids is hindered by the repulsive electric double-layer forces. The addition of anionic polymers with high molecular weight serves the same function as inorganic salts: to compress the thickness of EDL and thus suppress the repulsive forces between solids. The solids are thus easier to approach each other and aggregate together. The aggregation of solids induced by inorganic salts or low molecular weight polymers through the same mechanism is usually referred to as coagulation (Wang et al., 2014). For example, Robert et al. (2012) synthesized several nitrogen-containing polymers (PEIs (MW = 600 g/mol), PDAMA (MW = 5000 g/mol), AFPAAAs (MW = 5×10^4 g/mol), AFPMMA (MW = 1.2×10^5 g/mol), AFPMMA-co-PS (MW = 1.17×10^5 g/mol)) as switchable ionogens for kaolinite and montmorillonite treatment. The nitrogen-containing polymers could form ammonium bicarbonate salts with the addition of CO₂. The initial settling rate (ISR) was improved, and the supernatant turbidity was reduced when the polymers and CO₂ were added, which indicated that fine particles in the suspension started to aggregate. Meanwhile, the zeta potential of the clays increased, suggesting the suppression of EDL of kaolinite/montmorillonite particles by the ammonium bicarbonate salts, leading to less repulsion between the particles and initiation of aggregation and settling. The polymers were recycled after removing the CO₂ by injecting inert Ar gas into the extracted supernatant. Kaolinite particles were later added into the supernatant after recycling, and barely settled, which manifested that the polymers stayed in the aqueous phase of the supernatant without binding to the clay particles.

4.2. Neutralizing surface charge

In the regulation of the electrostatic properties of the solids, charge neutralization or charge patching of the solids by cationic polymers is also commonly employed to promote flocculation. The oppositely charged polymers reduce the surface charge of solids through adsorption, making the solids less repulsive to each other. Chen et al. (2020) measured the zeta potential of clay particles in coal/kaolinite mixed tailings at various concentrations of cationic stearyl trimethyl ammonium chloride (STAC). The zeta potential increased from −47 mV at 0 ppm to 66 mV at 200 ppm, suggesting that STAC could neutralize and even reverse the surface charge of clay particles. Meanwhile, MD results proved that the adsorption of

STAC on coal and kaolinite in water was driven by electrostatic interactions between the oppositely charged polymers and clay particles. Gumfekar et al. (2017) compared the flocculation behavior of two types of cationic polymers: poly(TMAEMC) with a higher charge density and poly PCL₂ChMA with a lower charge density, as well as their copolymers. For the same tailings, poly(-TMAEMC) and its copolymers were found to lead to higher ISR (as illustrated in Fig. 5), lower supernatant turbidity, and lower capillary suction time (CST). This stronger flocculation ability of poly(-TMAEMC) was attributed to more significant charge neutralization caused by polymer adsorption. A similar conclusion was also drawn by Vajihinejad et al. (2017), who tested the MFT flocculation behavior of copolymers AAm-co-DADMAC consisting of acrylamide and cationic poly (diallyldimethylammonium chloride). The charge density and average molecular weight (ranging from 9×10^4 to 1.4×10^6 g/mol) of the copolymer were controlled during polymer synthesis. The results showed better dewatering ability, represented by smaller CST and stronger specific resistance to filtration (SRF), with increasing charge density of the copolymer, while the molecular weight showed little influence. Better flocculation ability of polymers with high cationic charge density was also observed by other experimental work (Pennetta de Oliveira et al., 2018).

4.3. Bridging via hydrogen bonds

Besides modifying the surface charges and EDL thickness, HMW polymers are more often designed to bind to solid surfaces. The solids are thus flocculated together by the long polymer chain that they are bound to simultaneously. Chemical or physical bonds could form between surface groups of clay particles and certain residues on the polymers. For example, Lu et al. (2016) investigated the adsorption of neutral glycopolymers (PLAEMA, 2-lactobionamidoethyl methacrylamide) onto mica sheets, which share a similar structure as kaolinite. The mica sheets were dipped into the polymer solution for 1 h allowing for adsorption, and then rinsed to remove unattached polymers. Increased roughness of the mica surface characterized by AFM image proved that the polymers could attach to mica (Fig. 6(a)). SFA measurements showed adhesive force between two micas in the polymer solutions (Fig. 6(b)), which suggested that the polymers bridged the solids via hydrogen bonding between the hydroxyl groups from the pendant sugar residues of the glycopolymer and from the mica surface (Fig. 6(c)). Li et al. (2005) measured the long-range electrostatic force and short-range adhesion force between a spherical model silica and tailing samples by AFM. The tailing samples were treated by negatively charged HPAM (hydrolyzed polyacrylamide) of various dosages. The electrostatic force remained repulsive irrespective of the dosage of HPAM, while an adhesion force of 0.4 mN/m was obtained when the HPAM was added at 15 and 30 ppm, along with an increase in ISR. Based on the results, it was proposed that HPAM promoted the flocculation mainly through the bridging effect through the hydrogen bonding between hydroxyl groups of HPAM and solid surfaces, rather than altering the electrostatic properties of the solids.

In addition to experiments, the formation of hydrogen bonds between polymer flocculant and clay surfaces was also supported by MD simulations (Wang et al., 2015b; Chen et al., 2020; Sun et al., 2020; Cheng et al., 2021; Shi et al., 2023). At the molecular scale, the properties of hydrogen bonds were thoroughly studied, which could provide theoretical guidance to the experimental design of polymer flocculants. For example, Sun et al. (2021) showed that the number of hydrogen bonds between anionic PAM and montmorillonite correlated positively with the number of Ca²⁺-polymer complexes on the montmorillonite surface. Cheng et al. (2021) showed that the amino groups of 3-dodecyloxypropanamine or

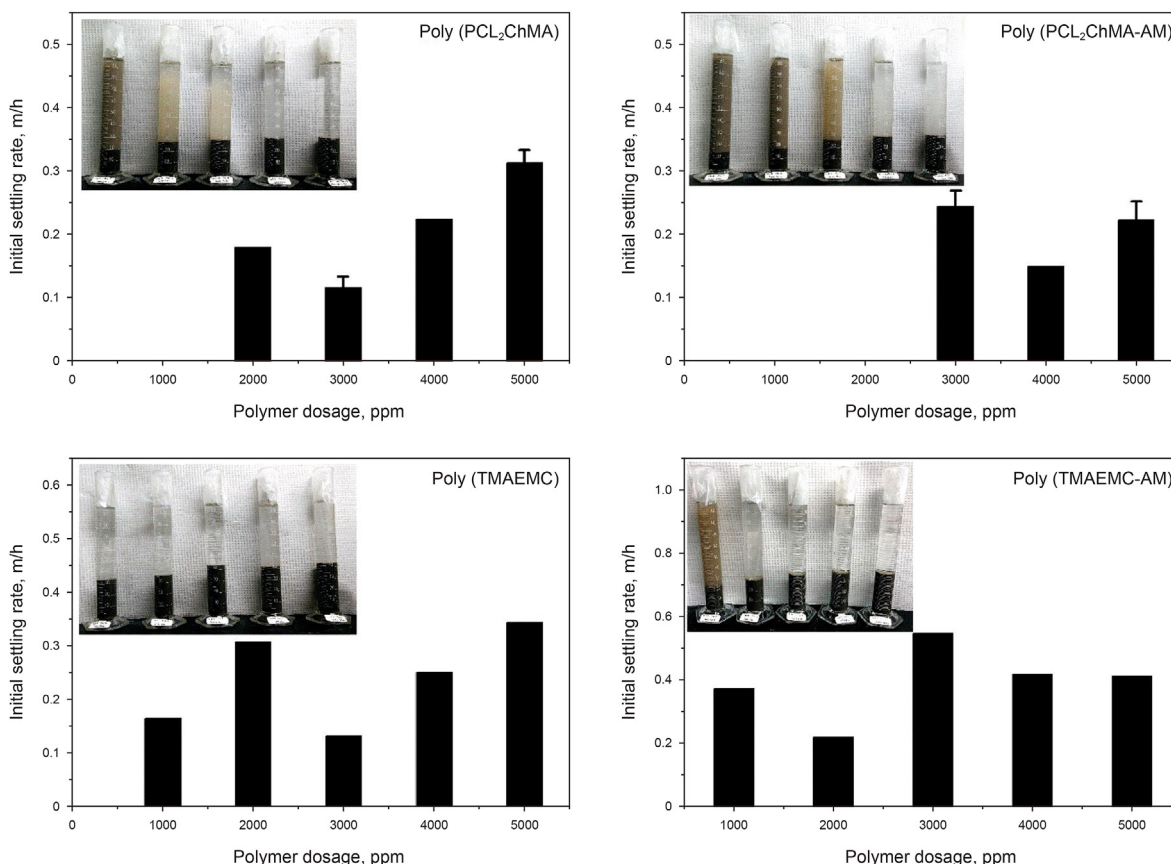


Fig. 5. ISR using PCL₂ChMA and TMAEMC-based polymers and copolymers at varying dosages with 5 wt% MFT. Reprinted with permission from (Gumfekar et al., 2017). Copyright 2017 American Chemical Society.

3-tetradecyloxypropylamine were more inclined to give protons than to accept protons when forming hydrogen bonds with silica.

4.4. Modulating surface wettability

Hydrophobic effects play an important role in tuning solid-water interaction, promoting water release from MFT. Polymers with hydrophobic segments were adopted to improve solid flocculation and reduce water entrapment (Reis et al., 2016; Zou et al., 2019; Chen et al., 2020; Hethnawi et al., 2022; Shi et al., 2023). For example, through settlement and filtration experiments, Shi et al. (2023) showed that the dewaterability and sedimentation of montmorillonite suspension increased with the concentration of a cationic surfactant, cetyl trimethyl ammonium bromide (CTAB). Additionally, the contact angle of water on montmorillonite particles increased with CTAB concentration, indicating an increase in hydrophobicity. MD results also supported the increase of hydrophobicity as the thickness of the water layer on the basal surface of montmorillonite was reduced by CTAB. It was proposed that the cationic CTAB adsorbed on montmorillonite through electrostatic attraction, leaving the hydrophobic long alkyl chains extending into the bulk, altering the surface wettability of the montmorillonite particles. The increase in surface hydrophobicity therefore led to better dewaterability. The adhesion of montmorillonite particles was also promoted, as the interaction between the particles shifted primarily from electrostatic repulsion to hydrophobic interactions. In addition to testing the performance of commercial polymers, new synthesis strategies by incorporating hydrophobic segments into commercial polymer flocculants, particularly PAM, is widely

adopted to enhance flocculation and dewaterability performance (Reis et al., 2016; Du et al., 2021; Hethnawi et al., 2022). For example, Reis et al. (2016) evaluated the CST, turbidity, and centrifugation performance of polymers synthesized by copolymerizing different amounts of polypropylene oxide (PPO) macromonomers with acrylamide, effectively incorporating hydrophobic groups into PAM. Hethnawi et al. (2022) synthesized a three-in-one nanoflocculant comprising titanomagnetite nanoparticles grafted with hydrophobically modified PAM and sodium lauryl sulfate, and measured the ISR, supernatant turbidity, sludge volume index, CST, as well as SRF of the treated MFT. The hydrophobically modified polymers were reported to exhibit good sedimentation and dewaterability performances. The role of hydrophilic/hydrophobic interactions between solid particles during flocculation was confirmed by Zhang et al. (2018) through a theoretical model. In the model, the interaction between clay particles included four components, van der Waals force, electrostatic force, Lewis acid-base force (used to capture the hydrophilic/hydrophobic interactions between particles), and lubrication force which became present when two particles approached each other squeezing out the fluid between them. The model was implemented using the Lattice-Boltzmann method to simulate floc growth, and validated by the growth in particle number concentration in experiments (McAnally, 1999).

Recently, thermo-responsive and pH-responsive polymers whose wettability varies with temperature or pH are gaining increasing interests (Li et al., 2015; Lu et al., 2015; Zhang et al., 2017; Zheng and Taylor, 2020; Kajornprai et al., 2023; Pany et al., 2023; Juengchareonpoon et al., 2024; Tchameni et al., 2024). For example,

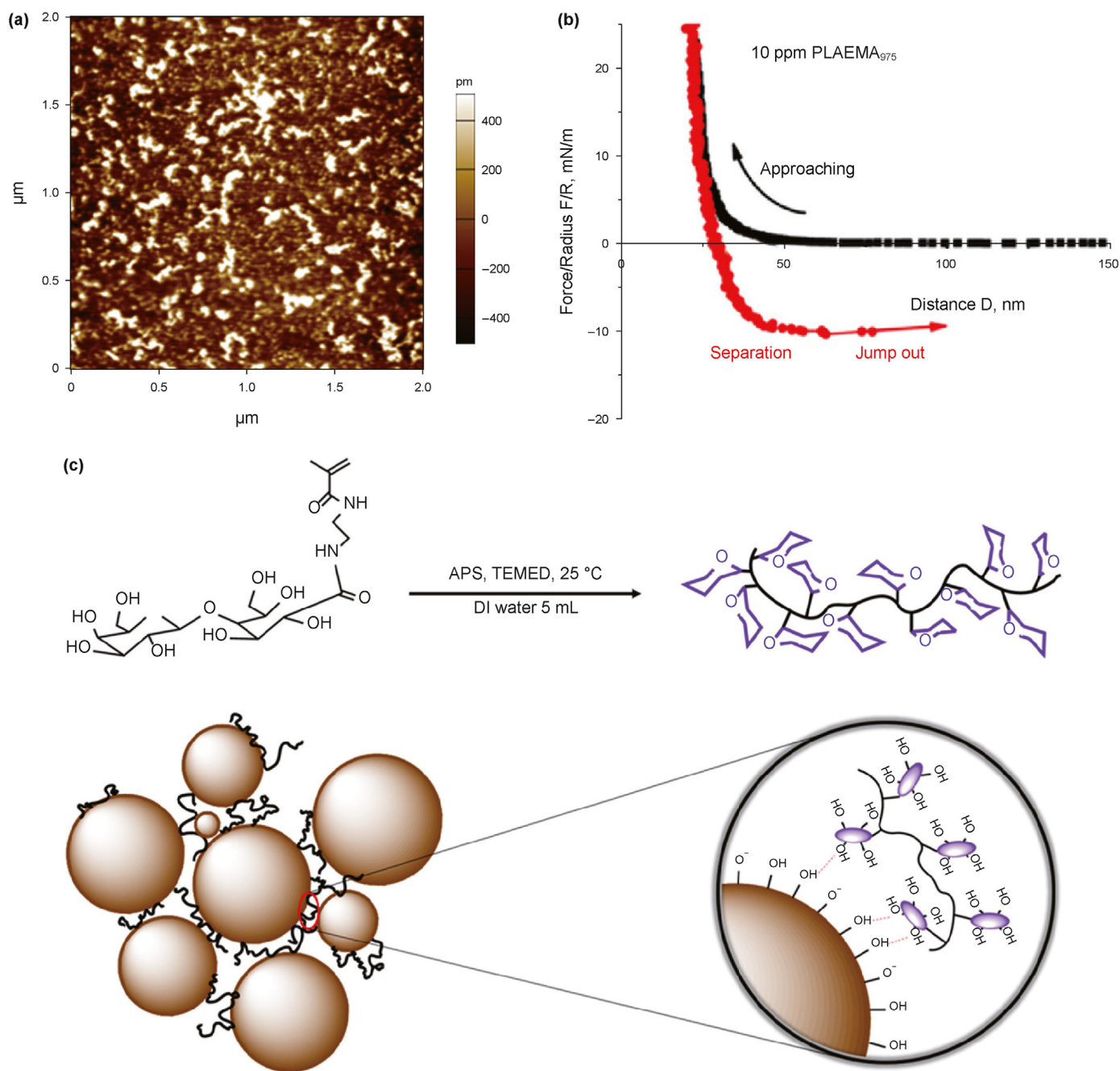


Fig. 6. (a) Topographic AFM images of PLAEMA coating absorbed on mica surfaces. (b) Force vs. distance profiles between the two mica surfaces in 10 ppm of PLAEMA water solutions. (c) Proposed mechanism of the adhesion of the polymer to the particle surface. Reprinted with permission from (Lu et al., 2016a). Copyright 2016 American Chemical Society.

Zhang et al. (2017) utilized the temperature-responsive wettability of poly(NIPAm) to enhance the dewatering of MFT. Working with a cationic polymer (poly(Aam-*st*-DADMAC), it could flocculate the solids first. When the temperature was increased above a critical value, the polymer became hydrophobic and large flocs were formed, resulting into high ISR, as shown in Fig. 7. A two-step consolidation process, where the temperature was changed from 25 to 50 °C and back to 25 °C, could further enhance the dewatering since in the second step (50–25 °C) the hydrophobic interactions were absent, and the large flocs broke up allowing small flocs to fill the gaps. Besides the temperature-responsive wettability, Lu et al. (2015) utilized the pH and temperature responsive properties of

P(AEMA₅₁-*st*-MAAmBo₇₆-*st*-NIPAM₃₈₁) (PAMN) to further improve the flocculation and dewatering of fine kaolinite suspensions. Similar to the report by Zhang et al. (2017), increasing temperature from 25 to 50 °C increased the solubility of the hydrophobic benzoboroxole moieties of PAM, so that the hydrophobic interaction between the benzoboroxole residues and the particles as well as between PAMN-adsorbed particles was enhanced, leading to an increase of ISR. Furthermore, pH was shown to influence the flocculation, by modulating the charge and wettability of benzoboroxole. At both 25 and 50 °C, switching the pH from 7 to 11 improved particle consolidation. At pH = 7, strong adhesion existed between cationic PAMN and anionic kaolinite particles, due to electrostatic

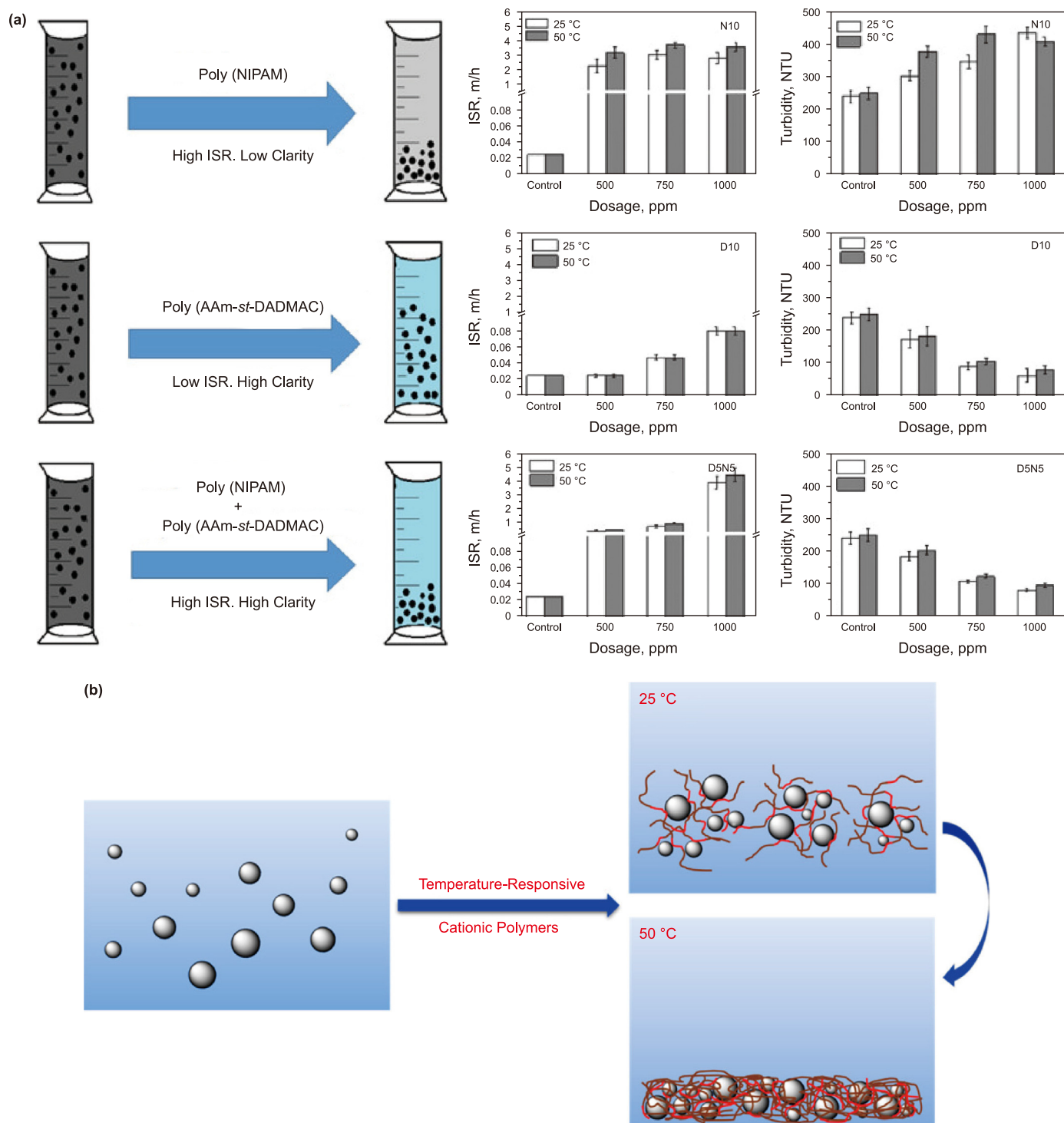


Fig. 7. (a) ISR of 10 wt% MFT treated by poly(NIPAM), poly(AAm-st-DADMAC), as well as both of them at temperature of 25 and 50 °C, respectively. (b) Proposed mechanism for the flocculation of MFT when treated by temperature-responsive polymers. Reprinted with permission from (Zhang et al., 2017). Copyright 2017 American Chemical Society.

attractions, complexation of benzoboroxole of PAMN to hydroxyl groups of particles, hydrogen bonding, and hydrophobic interaction. As pH increased, the benzoboroxole moieties gradually became negatively charged, diminishing the complexation and electrostatic attraction between PAMN and the particles. Benzoboroxole also became more hydrophilic so the hydrophobic interaction was suppressed. As a result, the flocs in the sediment broke up into small flocs, filling the gaps and expelling trapped water,

resulting in a more compact sediment.

4.5. Combined charge neutralization and bridging

Besides enhancing the flocculation via a single mechanism, flocculants commonly functioned through multiple mechanisms to achieve better flocculation performance. For example, polymers carried different types of charges were utilized together to enhance

the adsorption on solid surface (Dixon and Soares, 2024). Lu et al. (2016b) sequentially added two oppositely charged polymer flocculants into MFT, first anionic Magnafloc-1011 (MF-1011, $MW = 1.75 \times 1.75 \times 10^7$ g/mol) and then cationic chitosan ($MW = (6 \sim 8) \times 10^4$ g/mol). The zeta potential of tailings particles changed from -38.6 to -39 mV after the addition of MF alone at 20 ppm but reached about 0 mV when 200 ppm of chitosan was added after MF. An adhesion force of 4 mN/m appeared between two micas in MF solution and became 31 mN/m when chitosan was added. The settling behavior, quantified by ISR, turbidity of supernatant, and floc size, also reached the best when 200 ppm of chitosan was added after 20 ppm of MF (Fig. 8(a)). In these experiments, MF was proposed to first bridge the particles to form flocs, and in the second stage chitosan bonded the negatively charged flocs or remaining particles, resulting in improved flocculation (Fig. 8(b)).

It is worth mentioning that various functioning sequences of two types of flocculants to promote flocculation were reported. Wang et al. (2016) investigated the flocculation behaviors of Zetag ($MW = 12.7 \times 10^6$ g/mol) solution preconditioned by hot water bath and NaOH. Increasing the temperature or pH of the polymer solution could enhance the hydrolysis of Zetag molecules, from which cationic choline ions were produced. The floc size obtained from FBRM indicated that there were two stages of the floc growth, with a significantly increased growth rate in the second stage. It was hypothesized that in the first stage, the released cationic choline ions could attach to the solid surfaces causing charge neutralization and aggregation of some solids, whereas in the second stage, the anionic polyacrylamide backbones bridged the

choline coated solids or uncoated solids. Charge neutralization and initial coagulation in the first stage led to more efficient bridging and increased growth rate in the second stage. The mechanism of the two-step flocculation process was further studied by Sun et al. (2020) who simulated the adsorption of cationic chitosan and neutral PAM, as well as the adsorption of anionic MF and neutral PAM on negatively charged montmorillonite. Their MD results showed that chitosan achieved a fast adsorption rate and displayed a monolayer adsorption on the montmorillonite surface. The monolayer adsorption would hinder the adhesion between chitosan-adsorbed solid particles, implying that many solids would be left in the supernatant, resulting in high turbidity. Contrastingly, PAM/MF formed cluster first in water and then adsorbed on the solid surface in a multi-layer configuration, which might result in a slow flocculation rate and low ISR of MFT. The PAM/MF adsorbed solids could be bridged together through hydrogen bonding, and therefore most solids could settle down and result into low turbidity of the supernatant. When functioned together, chitosan and PAM/MF displayed fast multilayer adsorption, which could achieve both high ISR and low turbidity of supernatant of MFT (Fig. 8(c) and (d)). Zhang et al. (2017) performed a series of settling tests on MFT samples in a mixed solution of two polymers with different ratios, cationic AAm-st-DADMAC ($MW = 2.2 \times 10^6$ g/mol) and neutral NIPAm ($MW = 1.2 \times 10^6$ g/mol) with hydroxyl groups. Pure poly (AAm-st-DADMAC) could absorb onto the solids via charge neutralization, but this only resulted in ISR of less than 1 m/h at all dosages. ISR of MFT treated with pure NIPAm could reach 3 m/h via the bridging effect enabled by the hydroxyl groups. The best ISR result (3.5 m/h) was obtained at an optimum ratio of 30%

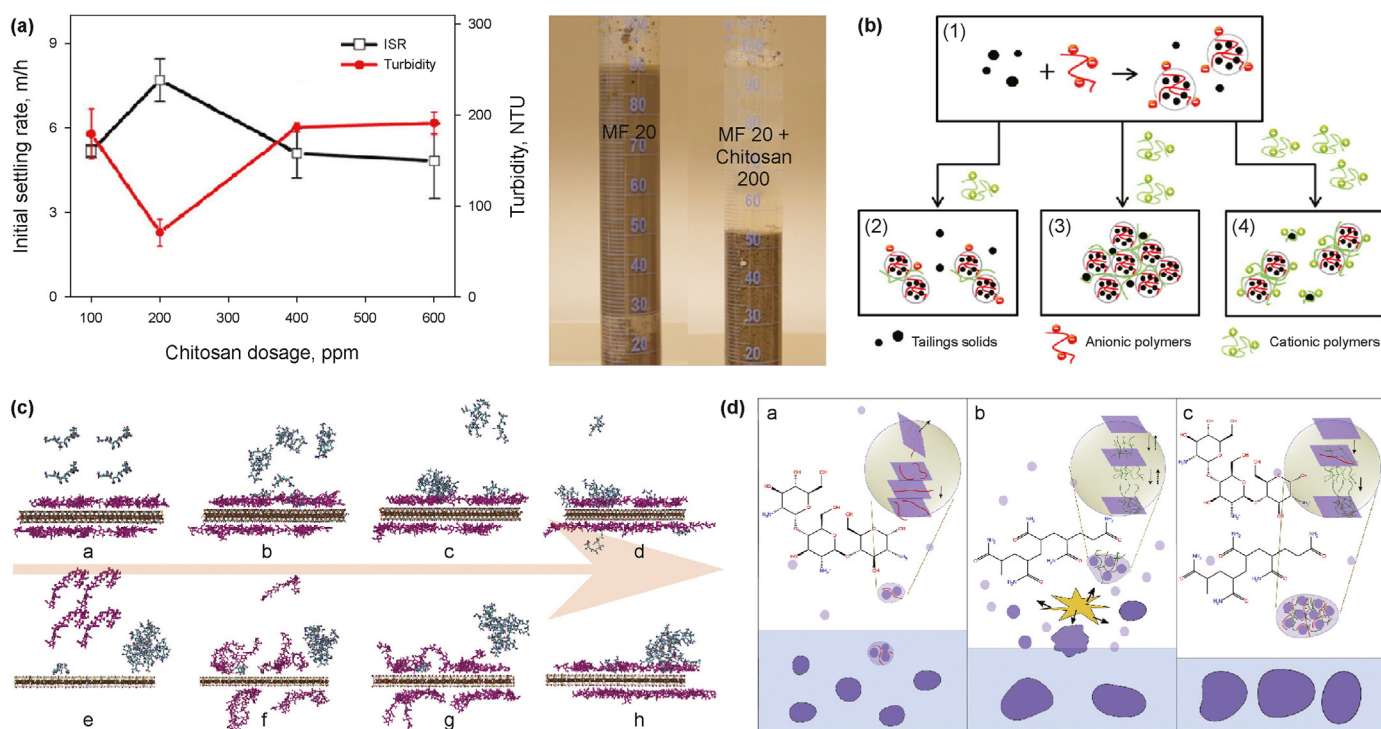


Fig. 8. (a) ISR and turbidity of supernatants of MFT using a two-step flocculation process with 20 ppm of MF followed by different dosages of chitosan. Image shows the clarity of supernatants of extraction tailings after treatment by two different flocculation processes: (left) flocculation using 20 ppm MF and (right) two-step flocculation using 20 ppm of MF and 200 ppm of chitosan. (b) A schematic for proposed flocculation mechanism involved in the two-step flocculation process: (1) small flocs formed from MF bridging (2) adsorption of a small (insufficient) amount of chitosan onto particle surfaces induces incomplete flocculation; (3) complete neutralization by chitosan forms large flocs; (4) excessive positive chitosan re-stabilizes the system through electrical repulsion. (c) MD snapshots of adsorption process of PAM on chitosan coated montmorillonite surface (top), and adsorption process of chitosan on PAM adsorbed montmorillonite surface (bottom). (d) Proposed mechanism for the macroscopic flocculation of montmorillonite by the addition of chitosan, PAM, chitosan and PAM. Plates represent the clay mineral particles; chitosan and PAM are represented by strings. (a) and (b) are reprinted with permission from (Lu et al., 2016b). Copyright 2016 Elsevier. (c) and (d) are reprinted with permission from (Sun et al., 2020). Copyright 2020 Elsevier.

AAm-st-DADMAC and 70% neutral NIPAm, which was supposed to be caused by the cooperative effect of hydrogen bonding and charge neutralization.

4.6. Other mechanisms

Though rarely mentioned in MFT research studies, the depletion effect can also cause the adhesion of two hard-sphere particles in colloids. Asakura and Oosawa modeled the phase separation of hard-sphere colloids caused by non-adsorbing polymers (Asakura and Oosawa, 1954, 1958), and showed that two similarly sized colloid particles attracted each other when immersed in a non-adsorbing polymer solution. The attraction was attributed to the so-called “depletion effect”. In particular, the mutually impenetrable particles were surrounded by a depletion zone inaccessible to the polymer coils. When the depletion zones of two particles overlap, the polymers are expelled from the space between the particles, creating an effective osmotic pressure that pushes the particles together. Under this model, the pairwise interaction potential between two colloidal particles was written as: $U(r) = U_0(r) + U_{\text{dep}}(r)$, where $U_0(r)$ was the bare particle interaction potential, and the depletion potential $U_{\text{dep}}(r)$ was in the form of: $U_{\text{dep}}(r) = -P_{\text{osmotic}}V_{\text{overlap}}$, subjecting to $\sigma < r \leq \sigma + 2r_g$. Here σ was twice the particle diameter, r_g was the gyration radius of the polymer, P_{osmotic} was the osmotic pressure that proportional to the number density of all polymers in a pure polymer solution, and V_{overlap} was the volume of the overlapping depletion zones between particles.

Yan et al. (2019) made a hydrogel of MFT by adding two types of polymers, branched poly(ethylenimine) (BPEI) and a cross-linker called difunctional telechelic poly(ethylene oxide) (DFPEO), together to MFT. The cationic BPEI first adhered to the clay surface through electrostatic attraction to form flocs. DFPEO was then added to adhere to the flocs through dynamic Schiff base reactions between aldehyde groups of DFPEO and the amino groups of BPEI. As a result, the aqueous colloidal suspension (MFT with solid content >30 wt%) was converted into a self-healing composite hydrogel with a dynamics double cross-linked network. The hydrogel of MFT showed a good dewatering performance in that 50% of water could be rapidly released within 30 min by vacuum filtration.

When two solid surfaces approach each other closer than a few nanometers, additional short-range forces can arise and become dominant, in particular, the solvation (MacEwan, 1948; Graber and Mingelgrin, 1994) and structural forces (Ji et al., 2013; Lu et al., 2016a; Zhu et al., 2017). They are non-DLVO forces and can be much stronger than the DLVO forces (electric double layer and van der Waals forces) in highly constricted spaces. Graber and Mingelgrin (1994) performed a series of separation tests of Na-montmorillonite in different solutions. The results showed that the clays exhibited maximum separation in the solvent whose solubility was closest to that of the clays. Steric hindrance between the brush-like or mushroom-like polymer chains (tethered to a surface and extending outward) was frequently used to explain the decrease of MFT settling when the polymers were overdosed (Ji et al., 2013; Lu et al., 2016a; Zhu et al., 2017). The maximum collision efficiency between particles is usually achieved when half of the particle surface is covered by flocculants (Besra et al., 2002).

As can be seen from the reviewed studies above, the mechanisms by which polymer flocculants modulate clay interactions are multifaceted, depending on the types, structures, and properties of polymers. Polyelectrolytes can act like inorganic salts, coagulating the solids together via modification of surface charges or EDL. Polymer flocculants can adhere to multiple solids simultaneously and bridge them together through charge neutralization or forming

charge patches (polymers with a net charge), establishing hydrogen bonds (polymers with functional groups that can give or accept protons), or a combination of them. Additionally, novel polymers (thermo-responsive or pH-responsive) that can modulate the wettability of clay surfaces are gaining increasing attention.

5. Effects of solution chemistry

5.1. pH of solution

The effects of pH on flocculation are multifold. By decreasing the pH of the solution, the acid sites on the solid surfaces dissociate less, rendering reduced surface charge and enhanced hydrophobicity. Zhu et al. (2011) pressurized CO₂ into industrial tailings to investigate how CO₂ affected the flocculation. The zeta potential of the particles increased from about −43 to −27 mV when the pH value of the CO₂ treated solution decreased from about 8.5 to 5. The ISR and clarity of the supernatant also increased with the partial pressure of CO₂. Similar findings were also reported by others in MFT or clay suspension (Sworska et al., 2000; Jada et al., 2006). Gu et al. (2003) measured the contact angle of water on kaolinite particles at different pH. As shown in Fig. 9(a), When the pH was greater than 3, the contact angles were less than 20°, while contact angles >120° were obtained for pH < 3 (Fig. 9(a)). The reduced surface charge consequently decreases the electrostatic repulsion between the fine solids. However, the non-monotonic response of solids to pH was also reported. Menon and Wasan (1986) observed a non-monotonic change in the zeta potential of montmorillonite with pH. With increasing pH, the zeta potential first decreased from about −30 mV until a minimum of −70 mV was reached at pH = 3.5 to pH = 4.5. It then increased to a maximum of about −35 mV at pH = 6 to pH = 7 and finally stabilized at about −60 mV when pH was further increased. The non-monotonic change was attributed to the presence of two types of acid sites on the edge surface of montmorillonite (James and Parks, 1982): the strong acid site dissociated at pH ≈ 4.5, while the weak acid site dissociated at pH ≈ 9. Shi et al. (2022) measured the zeta potentials of silica (SiO₂), alumina (Al₂O₃), and kaolinite when pH increased from 2 to 10 in 0.1 mM NaCl. Silica and alumina were used as they shared chemical properties similar to the tetrahedral and octahedral basal surfaces of kaolinite, respectively. For all three particles, zeta potentials decreased with increasing pH. The points of zero charge (PZC) of silica and alumina were approximately at pH = 8 and pH = 2, respectively, indicating different surface properties. PZC of kaolinite was at about pH = 4, which was in between silica and alumina particles, implying that the charge of kaolinite was mediated by both types of surfaces.

The pH-dependent charges on the edge surface can lead to different structures within the clay mineral aggregates. In an acidic medium, since the edge surface would be positively charged and attract a negatively charged basal surface, aggregates with a “card-house” structure would be formed by edge (+)/face (−) contact (Van Olphen, 1963; Vali and Bachmann, 1988). While in an alkaline medium, the edge surface could be neutral or negatively charged. If the ionic strength of the solution was high enough to suppress the EDL repulsive forces between the particles, “card-pack” flocs would be formed by face (−)/face (−) contact due to the residual valence forces between the basal surfaces. Nasser and James (2007) developed a sedimentation-consolidation mechanics model based on the work of Landman and White (1994). Application of the model to kaolinite suspension showed that at pH = 2 and with a low electrolyte concentration, the particles were more likely to form “card-house” aggregates via edge/face interaction, resulting in a voluminous structure. When high ionic strength suppressed the EDL of the basal surfaces, face/face interaction was more favored,

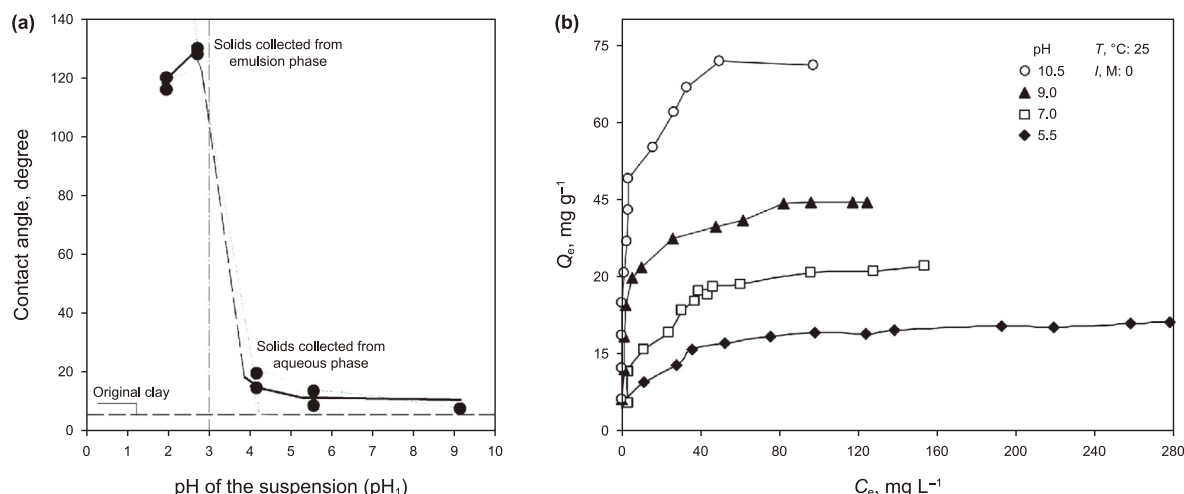


Fig. 9. (a) Contact angle of water on clay particles obtained from the upper emulsion phase for suspensions at pH < 3 and pH > 3, respectively. Reprinted with permission from (Gu et al., 2003). Copyright 2003 Elsevier. (b) The effect of solution pH on the adsorption of PAM onto kaolinite. Reprinted with permission from (Tekin et al., 2005). Copyright 2005 Elsevier.

which led to tightly packed flake-like structures and the formation of denser gels.

Besides the dissociation of acid sites on clay surfaces, pH can also change the configuration and adsorption efficiency of ionic flocculants. Hasan and Fatehi (2018) showed that the clarity and clay loss increased with pH when kaolinite and bentonite suspensions were treated with cationic kraft lignin-AM-DMC polymer. This was contradictory to the decreased zeta potential of the clays upon pH increase, which would have provided more stabilization for the suspension. The discrepancy resulted from the change in polymer adsorption efficiency with pH. The adsorption efficiency of cationic kraft lignin-AM-DMC polymer on kaolinite was limited to 0.6 mg/g under pH = 2 while increased to 2.3 mg/g when pH was larger than 7. Similar pH-dependent adsorption was found by Tekin et al. (2005). In their work, the adsorption efficiency of cationic polyacrylamide PAM to kaolinite samples was determined with the aid of a UV–VIS spectrophotometer, which increased from about 15 to 75 mg/g as pH increased from 5.5 to 10.5 (Fig. 9(b)).

5.2. Salinity and ion valence

The presence of electrolyte ions in MFT is inevitable, resulting from many production activities employing saline solutions (Yang et al., 2015; Huang et al., 2021; Gong et al., 2024). Besides, inorganic salts are widely added to enhance flocculation (Grewer et al., 2010; Gorakhki and Bareither, 2015; Wang et al., 2015a; Govedarica et al., 2020). The presence of salt ions greatly affects the solid interaction in the colloidal systems.

First and foremost, EDL at the solid-water interface can be greatly suppressed by the ions, reducing the electric double-layer forces between the solids. In the presence of polymer flocculants, the ions can impact the EDLs of both solids and polymers, mediating the polymer adsorption and the resulting flocculation. For monovalent ions, increasing the salinity can thus better suppress the EDL repulsion between the particles. The solids are therefore easier to approach and adhere via other local forces such as van der Waals force and hydrogen bonding. Ji et al. (2013) compared the settling behavior of oil sand tailings in fresh water and saline solution, which were both treated by three kinds of polymers: anionic MF, nonionic PAM, and Al-PAM (Al(OH)₃-polyacrylamide). The ISR of fine solids and clarity of supernatant of MF treated tailings was significantly increased in saline solution compared with those in

fresh water (Fig. 10(a)). Zeta potential of the clay particles in the supernatant increased from about −37 mV in fresh water to −15 mV in saline solution, leading to reduced electrostatic repulsion. Meanwhile, the hydrodynamics radii of MF, determined from dynamic light scattering, were much smaller in saline solution. This was because the EDL of the polymer was also suppressed, and the polymer became more coiled (as illustrated in Fig. 10(b)). The smaller radii made the adsorption layer of MF denser, enhancing the strength of the solid-polymer-solid connection. Compared with the anionic MF, for the neutral PAM and Al-PAM, the increased salinity only suppressed the EDL of the fine solids, and thus enhancement of flocculation in saline tailings was less significant. Zhang et al. (2018) also investigated the effects of salinity on particle coagulation in their theoretical model based on extended DLVO theory. The EDL force was calculated from the model and found to decrease with increasing salt concentration. When the salinity (defined by the Practical Salinity Scale (Andedward and Lewis, 1980)) was increased from 0 to 20, the settling velocity (vertical component of the particle's translational velocity) increased rapidly and reached a plateau of 0.16 mm/s at salinity of 2. The result was consistent with the MD simulations of Sun et al. (2021) who simulated APAM adsorption on anionic montmorillonite in the presence of different dosages of NaCl (0, 0.05, 0.1, 0.3, and 0.5 M). Increasing salt concentration promoted polymer adsorption until reaching a plateau, as the increased salinity gradually compensated the negative charges of polymers and surfaces, suppressing their electrostatic repulsion.

Besides salinity, increasing ion valence was also adopted to mediate the polymer adsorption, and yet the efficacy of multi-valent ions was multifold. First, the EDL could be better suppressed by the increased ion valence. The presence of divalent cations, e.g., Ca²⁺ and Mg²⁺, has a significant effect on the counterion distribution close to a negatively charged surface. Even with a small concentration of divalent cations in the bulk phase, the surface could have a very high local concentration (Israelachvili, 2011), decreasing the surface charge and the surface potential. For example, Long et al. (2006b) showed that the addition of calcium or magnesium to aqueous solutions containing 5 ppm HPAM flocculants and 20 mM KCl significantly increased the adhesion force between a silica particle (sharing a similar structure with the clay fines in MFT) and a silica wafer, measured by AFM. The settling test of MFT was also performed with the same additives of

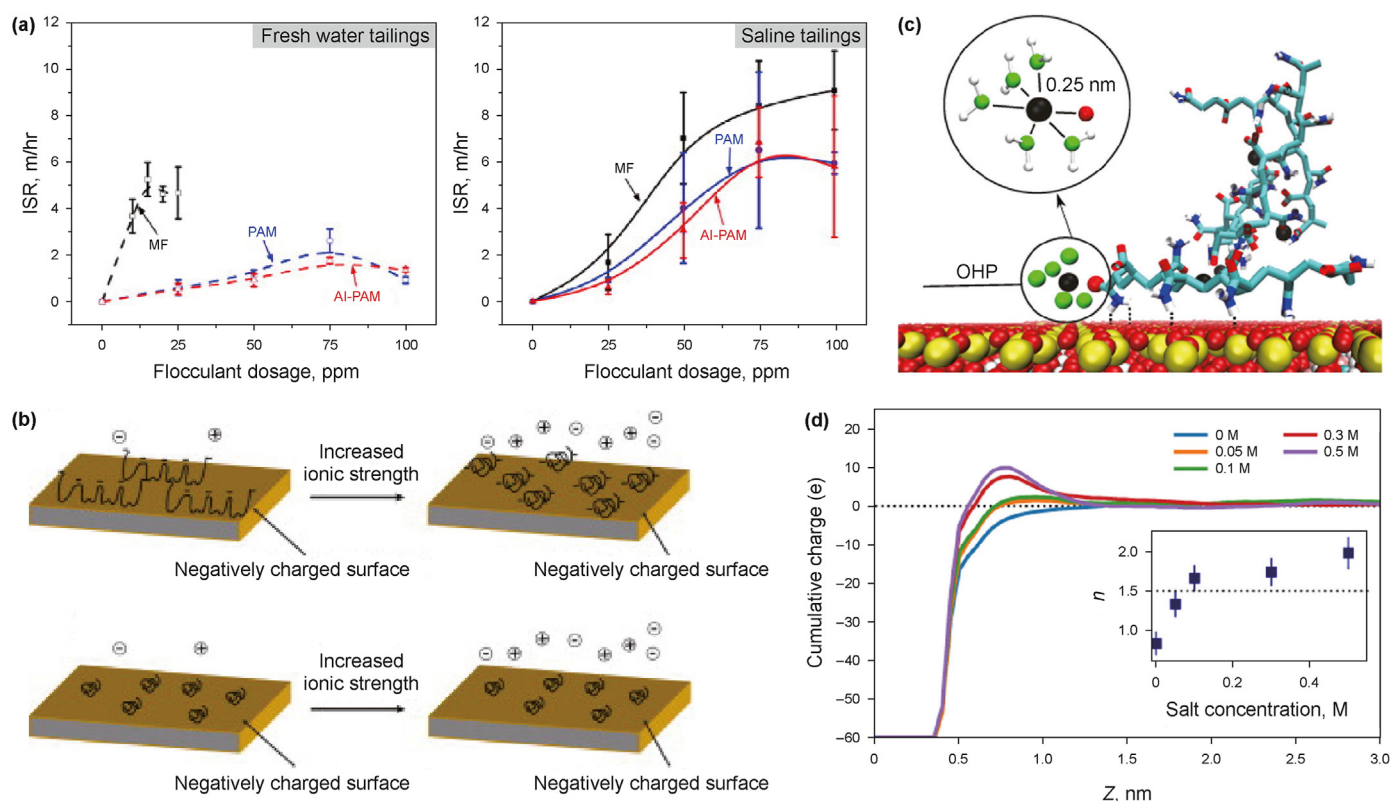


Fig. 10. (a) ISRs of freshwater tailings and saline tailings treated by MF (black, 0–100 ppm), PAM (blue, 0–100 ppm), and Al-PAM (red, 0–100 ppm). (b) Schematic of the impact of ionic strength on the conformation and adsorption of flocculants on negatively charged particle surfaces. (c) Adsorption configuration of APAM on montmorillonite surface. (d) Cumulative charges of montmorillonite, APAM, and ions in systems with varying dosages of CaCl_2 . Average number (n) of Ca^{2+} coordinated to each APAM molecule is shown as an inset. (a) and (b) are reprinted with permission from (Ji et al., 2013). Copyright 2013 Elsevier. (c) and (d) are reprinted with permission from (Sun et al., 2023). Copyright 2023 American Chemical Society.

polymers and ions, and the settling performance correlated well with the adhesion force. A similar finding was also reported by Sivasubramanian et al. (2021). In addition to suppressing the EDL force, multi-valent ions could serve as bridges, connecting the polymer and solids through charge neutralization, further enhancing the polymer adsorption. Li et al. (2005) found that the amount of Ca^{2+} and Mg^{2+} in process water decreased after the addition of HPAM. The above observations were attributed to the cation bridging (HPAM-Ca-clay) effect, where the calcium/magnesium ions simultaneously bound with the polymers and the solids to enhance the polymer adsorption on the solids.

Unlike monovalent ions, increasing the salinity of multi-valent ions may not promote flocculation. First, the surface charge of both polymers and solid surfaces could be over-neutralized by multi-valent ions, introducing new electrostatic repulsions. In MD simulations of Sun et al. (2021), APAM adsorptions displayed a non-monotonic trend with the dosage of CaCl_2 solutions. Characterization of the local molecular structure near Ca^{2+} showed that APAM was coordinated to Ca^{2+} by displacing 1–2 water oxygens in the first solvation shell of Ca^{2+} (as shown in the marked area in Fig. 10(c)). The negative charge of APAM molecule could thus be neutralized when coordinating to Ca^{2+} . The number of Ca^{2+} coordinated to APAM increased with salt concentration, and the negative charge of APAM was gradually neutralized and even reversed. Meanwhile, the surface charge of montmorillonite could also be over-compensated when salt concentration was sufficiently high because of the ion correlation effects (Fig. 10(d)). As a result, the electrostatic repulsion between APAM and montmorillonite was gradually suppressed to zero when salt concentration increased to

a moderate value, and became enhanced again when salt concentration further increased. APAM adsorption was most prominent in the solution where charges of both APAM and montmorillonite was closest to being just neutralized. Similar findings about the optimum dosage of multi-valent salts were also reported by Long et al. (2006b) and Sworska et al. (2000). Secondly, multi-valent ions were proposed to be capable of competing for available binding sites of polymers on clay surfaces, hindering the polymer adsorption. Peng and Di (1994) measured the height of the supernatant of kaolinite suspensions treated by APAM, with CaCl_2 in different concentrations (0, 0.0005, and 0.001 M). The height of the supernatant decreased with CaCl_2 concentration, manifesting a negative correlation between the flocculation of kaolinite particles and CaCl_2 concentration. The negative correlation was attributed to the precipitation of calcium hydroxyl on the surface of kaolinite, blocking the hydroxyl groups on the surface to form hydrogen bonds with the polymers and other surfaces. The polymer adsorption and solids coagulation were thus impeded. A similar phenomenon was reported by Kaarmukhilnilavan et al. (2020), who investigated the flocculation efficiency of avian egg white on the kaolinite suspensions. Quantities of kaolinite in the supernatant were monitored in a standard jar-test apparatus as characteristics of flocculation. It was proposed that the Ca^{2+} gradually compensated the negative charge of kaolinite by adsorbing on the basal plane, resulting in better flocculation, when dosage of CaCl_2 increased from 40 to 100 ppm. When the dosage of CaCl_2 was higher than 100 ppm, negative Cl^- started binding with Ca^{2+} . The charge compensation was thus intervened by the Cl^- . As a result, the flocculation efficiency stopped increasing.

5.3. Effect of asphaltene

Unlike traditional crude oil, bitumen extracted from oil sands has abundant polymeric materials with high molecular weight. The heaviest components, known as asphaltenes, mainly consist of polyaromatic planes with aliphatic side chains as peripherals, and may also contain polar groups (e.g., carboxyl groups) and heteroatoms (e.g., oxygen, nitrogen, and metal atoms). The molecular structure thus enables asphaltene adsorption on fine particles through multiple types of interaction, such as hydrogen bonding, hydrophobic interaction, electrostatic interaction, chemical bonding, and combinations of them (Dubey and Waxman, 1991; Maravilha et al., 2021; Shafieyoun et al., 2024). For example, Sun

et al. (2023) calculated the free energy for the adsorption of model asphaltene (C5Pe) on different kaolinite surfaces in water (Fig. 11(a)), as well as entropy and enthalpy of binding, based on the results of MD simulations. The calculated results showed that C5Pe became adsorbed on the alumina surface of kaolinite driven by hydrogen bonding, and on the siloxane surface by hydrophobic interaction. The adsorption of asphaltene is inevitable and impacts the flocculation process in oil sand tailings.

There have been conflicting reports on the effect of asphaltene on MFT stabilization and settling. On the one hand, the adsorption of asphaltene could introduce a new binding site on the solid surface, or alter the wettability of the surface, promoting solid flocculation. Don Scott et al. (1985) reported that tailings sludge

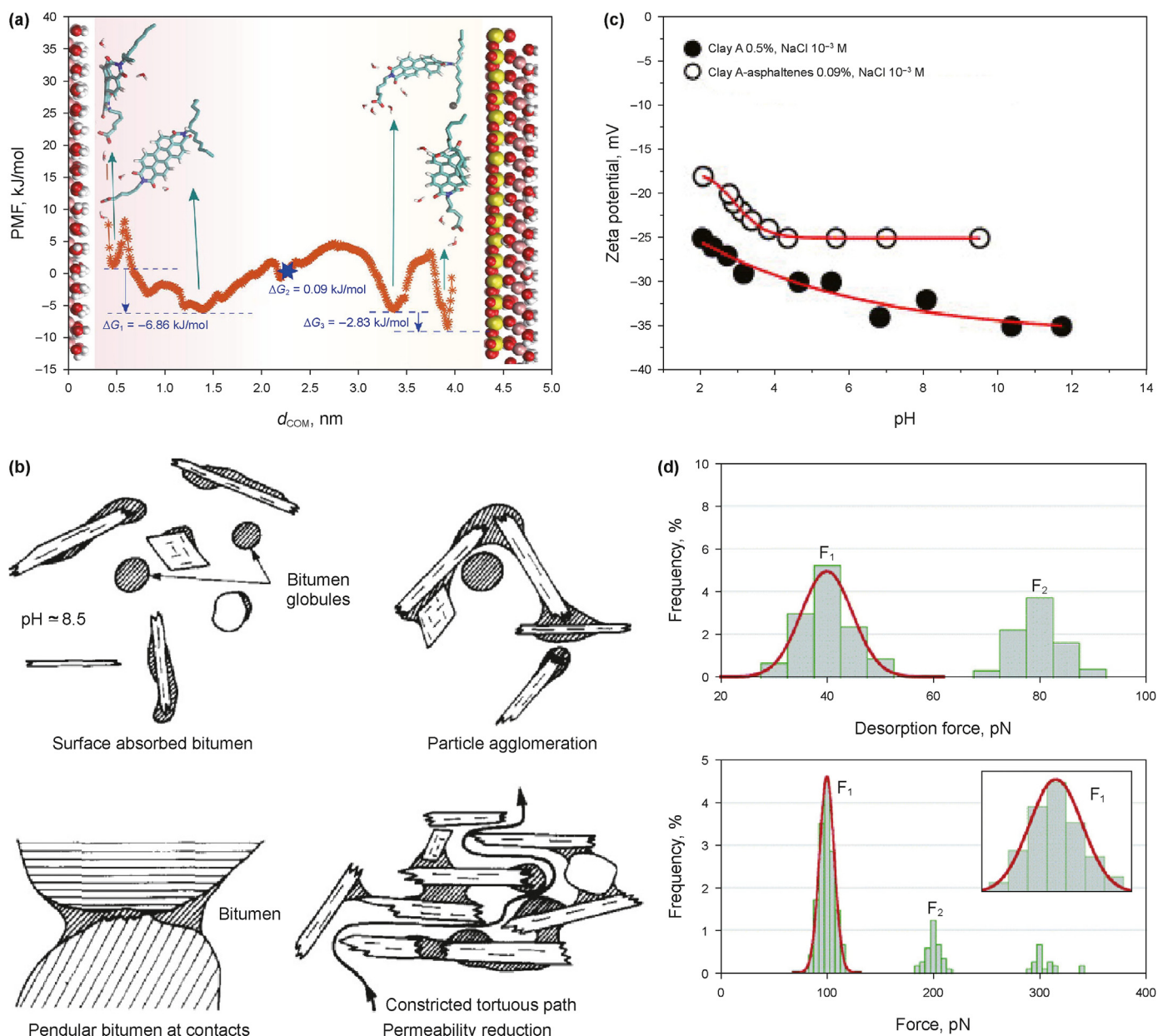


Fig. 11. (a) Free energy profile when the C5Pe was between the alumina (left) and siloxane (right) surfaces of Kaol in water. Reprinted with permission from (Sun et al., 2023). Copyright 2023 Elsevier. (b) Schematic picture where bitumen works as a binding agent to flocculate clay particles together. Reprinted with permission from (Don Scott et al., 1985). Copyright 1985 Elsevier. (c) Zeta potential of bare and asphaltene covered clay particles, as a function of pH of the aqueous medium. Reprinted with permission from (Jada et al., 2006). Copyright 2006 Elsevier. (d) Adsorption and desorption force of HPAM molecules on a mica surface (top) and bitumen surface (bottom). Reprinted with permission from (Long et al., 2006a). Copyright 2006 American Chemical Society.

containing asphaltene could settle with a higher efficiency than bare clays. They hypothesized that asphaltene molecules worked as a binding agent in the flocculation of solids (as illustrated in Fig. 11(b)). Jada et al. (2006) observed that the zeta potential of asphaltene-coated montmorillonite was less negative than the bare sample and independent of pH, which would enhance the clay flocculation (Fig. 11(c)). SEM images from Pourmohammadbagher and Shaw (2016) also showed that the floc size of asphaltene-coated kaolinite and illite was bigger than the uncoated ones. Menon and Wasan (1986) found that asphaltene adsorption changed the wettability of clay particles dramatically: the contact angle between montmorillonite particles and water changed from 70° to 150° when asphaltene concentration changed from 0 to 0.4 g/L, suggesting a transformation from hydrophilic to hydrophobic.

On the other hand, many researchers reported that adsorbed asphaltene enhanced the stability of clays in aqueous solution, mainly through the increase of the negative surface charge. Majid et al. (1991) found that the settling of clays increased linearly with bitumen removal. In the measurements of Liu et al. (2002), at pH = 8 the average zeta potential of asphaltene emulsion in KCl solution was about −80 mV while the corresponding value was about −30 mV for kaolinite and montmorillonite suspension. The more negative surface potential of the asphaltene could lead to stronger electrostatic repulsion and hence more stable suspension if they became adsorbed on the clay particles. Marlow et al. (1987) showed that the zeta potential of illite particles increased from 0 to −40 mV when the bitumen content in the illite suspension increased from 0 to 5 wt%, and the settling rate of illite decreased quickly from 24 to 3 cm/min when the asphaltene adsorption density changed from 0 to 12 mg/g. Electrostatic repulsion between the asphaltene-coated particles was attributed to be the dominant factor for the enhanced stability of the colloidal suspension. However, further increase of asphaltene contents had almost zero effect on the zeta potential. As well, the settling rate was about 2.5 cm/min when asphaltene adsorption density reached 24 mg/g. These were attributed to the steric hindrance between asphaltenes. Menon and Wasan (1986) reported similar findings on montmorillonite suspension, where the zeta potential of montmorillonite changed from about −40 to −50 mV when the asphaltene concentration increased from 0 to 1 g/L and remained at −50 mV when asphaltene was further added.

Asphaltenes can also impact the function of polymer flocculants by interfering with the polymer adsorption onto clay particles. Long et al. (2006b) used single molecule force spectroscopy (SMFS) to investigate the adsorption of an HPAM molecule on clay and bitumen surfaces in process water. The desorption/adsorption forces of HPAM on mica and bitumen surfaces were about 100 and 40 pN respectively (Fig. 11(d)), which implies that asphaltene coated on the solid surface would undermine the adsorption of flocculants. A similar phenomenon was also found by Klein et al. (2013), who studied the absorption of an anionic flocculants AF246 on alumina and bitumen surfaces with quartz QCM-D and observed a reluctant adsorption of the flocculants on bitumen. Li et al. (2005) measured by AFM the long-range electrostatic repulsive force between asphaltene and an anionic HPAM flocculants, as well as the force between mica and HPAM, and found the former to be stronger than the latter. On the other hand, Klein et al. (2013) explored the effect of bitumen content on the flocculation ability of an anionic flocculant AF246. The bitumen content in MFT was controlled by air flotation and blending. When the bitumen content was reduced from 0.45 to 0.18 wt%, the ISR increased from about 2.5 to 7 m/h, and the weighted chord length in FBRM increased from 280 to 350 μm, suggesting an improvement in flocculation. However, by further reducing the bitumen content to 0.08 wt%, the

ISR and FBRM chord length decreased to 1.3 m/h and 300 μm. Similar non-monotonic changes were also reported for the amounts of polymers that entered the settled clays, which first increased and then decreased with the reduction of bitumen.

To summarize, environmental factors such pH, ions, and asphaltene can influence the properties of both the clay surfaces and the polymers, as well as their interactions. Conflicting reports on the performance of polymer flocculants could be caused by the presence of these external factors and their inconsistencies in the experimental settings. Due to the complex surface properties of clay particles and various responses of polymer functional groups to environmental factors, a molecular-level understanding of the clay-polymer interaction mechanisms is critical to resolving the existing debates in the literature.

6. Limitations and future perspectives

In this work, interaction mechanisms between polymer flocculants and clay particles in the treatment of MFT are reviewed. The clay-polymer interactions can be affected by many factors, some related to the intrinsic features of the clay and the polymer (e.g., clay surface groups and flocculant type), while others pertaining to external conditions (e.g., pH, temperature, presence of ions or asphaltenes). Another element of consideration, which is often behind contradicting reports in the literature, is the lack of well-defined and consistently applied experimental methods to evaluate the performance of polymer flocculants. For example, the shear rate, mixing duration, and intensity during the addition of polymer flocculants are usually not standardized, and the delicate difference between different polymers could be reduced or even masked by the poor control of polymer addition process. Likewise, an extended pre-shearing of MFT before polymer addition can cause bitumen release and consequently influence the functioning of polymers. To enhance the robustness of future research, it is crucial to establish standardized, repeatable experimental protocols and design consistent approaches to systematically evaluate the interplay between multiple variables. Some potential strategies include using clearly characterized clay suspensions to eliminate the interference of impurities, consistent control of shear rates and mixing time, and developing better mixers for high-solid MFT.

Although there have been abundant studies on testing the performance of polymers as flocculants, a limited amount of work is done at the molecular level to directly reveal their mechanistic function. As such there still exist knowledge gaps. First of all, while it has been proposed based on experimental measurements that polymers could enhance clay flocculation by mechanisms such as cation exchange, charge neutralization, and hydrogen bonding, stronger evidence at the molecular level is needed. In the experiments, multiple types of functional groups of an HMW polymer could mediate the flocculation differently, making it difficult to provide accurate interpretations. Meanwhile, mixed types of clay mineral surfaces could be present simultaneously and interact differently with the polymers. The real-time “observation” of microscopic systems could well complement the experimental investigation, providing a comprehensive understanding of the function of polymer flocculants. More specifically, some experiments have shown that two polymers working via different mechanisms can have a synergetic effect on MFT flocculation when they are both added. The mechanisms behind the synergies need to be fully understood. The optimum dosage ratio and adding sequence of the polymers need to be clarified, which will allow us to better design the flocculants as well as the process to promote clay flocculation.

The complex clay-clay interaction mediated by flocculants also led to debates in the literature on the role of solution environments

such as pH and ions. For example, seemingly contradictory phenomena were reported regarding the influence of cations on flocculation. Several hypotheses have been proposed such as cation exchange, cation's blocking of the binding sites for polymer, sup-

Petroleum, Grant number: 2462024PTJS002).

Nomenclature

Abbreviation/symbol	Description
AIMD	ab initio molecular dynamics
AFM	atomic force microscopy
BPEI	poly(ethylenimine)
CST	capillary suction time
CTAB	cetyl trimethyl ammonium bromide
C5Pe	N-(1-hexylheptyl)-N'-(5-carboxyicdodecyl) perylene-3,4,9,10-tetracarboxylic bisimide
DFPEO	poly(ethylene oxide)
EDL	electric double layer
FBRM	focused beam reflectance measurement
HMW	high molecular weight
HPAM	hydrolyzed polyacrylamide
PAMN	P(AEMA ₅₁ -st-MAAmBo ₇₆ -st-NIPAM ₃₈₁) (PAMN)
ISR	initial settling rate
MD	molecular dynamics
MF	magnafloc
MFT	mature fine tailings
PPO	polypropylene oxide
PZC	points of zero charge
QCM-D	crystal microbalance with dissipation monitoring
SEM	scanning electron microscopy
SFA	surface force apparatus
SMFS	single molecule force spectroscopy
SRF	specific resistance to filtration
STAC	stearyl trimethyl ammonium chloride

pression of electric double layer force, and the combination of multiple mechanisms. These ambiguities as well as mechanistic insights on the effects of solution environment can be better addressed.

Another challenge is that reports about the effects of asphaltene on MFT treatment vary significantly among existing literature. The presence of asphaltene largely complicates the clay-clay and clay-polymer interactions. The amphiphilic nature of asphaltene renders its high affinities to multiple types of solid surfaces, altering the clay-clay interactions. Besides, the deprotonation/protonation and presence of heteroatoms of asphaltene could interfere with the clay-clay and clay-polymer interactions by mediating the long-range (electrostatic) and short-range (hydrogen bonding) interactions. Since the amount of asphaltene in MFT cannot be neglected, the role of asphaltene in the interaction between clay and polymer needs to be investigated.

CRediT authorship contribution statement

Wen-Yuan Sun: Writing – original draft, Investigation, Formal analysis. **Hongbo Zeng:** Writing – review & editing, Supervision. **Tian Tang:** Writing – review & editing, Supervision.

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.

Acknowledgements

We acknowledge the financial supports from National Natural Science Foundation of China (Grant number: 52304071) and MOE Key Laboratory of Petroleum Engineering (China University of

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