Destabilization of bitumen-coated fine solids in oil through water-assisted flocculation using biomolecules extracted from guar beans

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Received: 2 April 2020 / Published online: 17 August 2020 © The Author(s) 2020

Abstract

Non-aqueous extraction (NAE) of bitumen from oil sands has been gaining great attention from both the industry and academia as an alternative to the water-based extraction. A fine solids removal step is important for a NAE process in order to obtain high-quality bitumen product, which, however, remains a great challenge to reduce the fine solids content to the desired level. Here, we introduce a strategy of destabilizing the bitumen-coated silica particles in toluene with the addition of water and biomolecules extracted from Cyamopsis tetragonolobus (L.) Taup., i.e., high molecular weight guar gum (HGG) and low molecular weight guar gum (LGG), respectively. By virtue of sedimentation tests and focused beam reflectance measurement analysis, we demonstrate that the introduced water droplets modified with these biomolecules can facilitate the settling of the solid particles in toluene although the underlying mechanisms differ between these two biomolecule cases. Specifically, in the case of LGG, the added water droplets with the interfacial amphiphilic LGG can strengthen the attachment of solid particles from bulk toluene to the LGG surface. This research work provides useful insight into the development of effective approaches for destabilization and removal of bitumen-coated fine solids from NAE bitumen.

Keywords Non-aqueous extraction · Guar gum · Fine solids · Aggregates · Solid content · Chord length

1 Introduction

Canada holds the third-largest proven oil reserves in the world, only after Venezuela and Saudi Arabia, most of which exists as oil sands. According to the Alberta Energy and Utilities Board (AEUB), the reserves of oil sands are over 174 billion barrels and the crude oil production was 2.83 million barrels per day (bbl/d) in 2017 (Alberta Government 2018). Oil sands, a mixture of minerals matters, bitumen and water, are an important source of unconventional fossil fuel and require special extraction technologies to acquire petroleum and petrochemical products. In 1929, Dr. Clark established a model plant to extract the oil using hot water and a chemical agent, and by 1969, the hot water extraction (HWE) process was commercially applied for the shallow oil sands deposits. It was found that the surface of minerals was typically surrounded by a thin film of connate water, which could facilitate the liberation of bitumen from the oil sands ore during the HWE (Hooshiar et al. 2012; Osacky et al. 2015). However, high consumption of freshwater and fast accumulation of toxic and slow setting mature fine tailings inherent to the HWE process have raised growing public concerns about the environmental and ecological sustainability of the oil sands processing. Although nowadays HWE process can recycle a large proportion (~80%) of process water, importation of additional barrels of freshwater from river (i.e., makeup water) is still necessary for producing each barrel of oil. On average, 3.5 barrels of freshwater is required to produce 1 barrel of oil (Pal et al. 2015).
Non-aqueous extraction (NAE) of oil sands is a technique proposed as an alternative to HWE, which uses organic solvents to completely replace water to dissolve and liberate bitumen from oil sands ore. The merits of NAE are that it can significantly reduce the usage of freshwater and avoid dealing with the sludge tailings with good applicability for all kinds of oil sands (Li et al. 2012). Light hydrocarbon solvents such as toluene, cyclohexane, heptane and their mixtures have been examined in the NAE process (Hashmi and Firoozabadi 2012; Li et al. 2012; Pal et al. 2015). Solvents with high aromaticity have the ability to dissolve most of the bitumen components and are beneficial to the improvement of bitumen recovery in NAE (Hashmi and Firoozabadi 2012). The study undertook by Hooshiar et al. (2012a) revealed that bitumen recovery from a “poor processing ore” (by HWE process) linearly increased with increasing the ratio of toluene to heptane in their mixed solvent. However, even under the optimal technological conditions at present, a considerable amount of fine solids can migrate to the mixture of bitumen and organic solvent during the NAE process, rendering the bitumen product unqualified for downstream operations (Liu et al. 2003). Conventional separation methods such as gravitational or centrifugal settling and filtration are found ineffective and costly in reducing the solid content. Recent studies on the separation of fine solids from organic media have demonstrated that reducing aromaticity of the organic solvent through addition of saturated hydrocarbon solvents (e.g., heptane) could induce the coprecipitation of asphaltenes and fine solids, which, however, is at the cost of low bitumen recovery (Akbarzadeh et al. 2005; Coleman and Toll 1995; Liu et al. 2019a, b; Liu et al. 2003; Natarajan et al. 2011; Osacký et al. 2017; Wang et al. 2012).

The challenge of separating fine solids from organic phase mainly arises from the small size of the fine solids and their hydrophobic nature due to adsorbed bitumen (Liu et al. 2019a, b). Great efforts have been made to study the adsorption of bitumen to mineral solids in an organic solvent (Li et al. 2012; Nadeau 1987). In general, clay minerals such as kaolinite, illite and chlorite, known as non-swelling clay minerals, retain organic residue in a form of patches on the surface of the minerals, whereas smectite, known as swelling clay minerals, retains organic residue in their interlayer space (Osacký et al. 2017). A previous study showed that the presence of the connate water layer on the mineral surface can reduce the adsorption of organic residues to some degree (Sparks et al. 1988). In addition, various techniques such as atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS) and force tensiometer have been used to characterize the surface of the fine solids, finding out that they are only partially covered with bitumen (Liu et al. 2017). It was also found that the hydrophilic and amphiphilic fine solids suspended in oil underwent agglomeration with small amount of added water, which benefited the subsequent solid–oil separations during NAE process (Sparks et al. 1988; Sparks and Meadus 1981; Tan et al. 2009a, b; Yan et al. 2001). Our previous work attempted to modify the surface wettability of fine solids using the amphiphilic polymer PEG-PPG-PEG and claimed that the settling of the modified fine solids in cyclohexane could be enhanced with addition of small amount of water (Liu et al. 2019a, b).

Therefore, in the present research we aim to reduce the stability of fine solids in organic phase by taking the advantage of water and, for the first time, by introducing the biomolecule flocculants guar gums to the system. Guar gum is an economical and environmentally friendly option and has been extensively used for centuries in the food industry as a thickener and in wastewater treatment as a flocculant (Gupta and Ako 2005; Sharma et al. 2018; Singh et al. 2000; Tan et al. 2013; Thombare et al. 2016; Yousif et al. 2017). There are two well-known guar gum products, viz. sodium((2R,3S,5R)-5-(6-amino-9H-purin-9-yl)-3-hydroxytetrahydrofuran-2-yl)methyl dihydrogentriphosphate with low molecular weight (LMW) and a type of polysaccharide with high molecular weight (HMW), both of which are extracted from the plant Cyamopsis tragonolobus L. Taup. For simplification, LGG and HGG are regarded as the representative of LMW guar gum and HMW guar gum, respectively. Figure 1 displays the chemical structures of these two gums. LGG has a hydrophilic phosphate group and it behaves completely ionic in water. HGG is a kind of galactomannan, showing a hydrophilic nature due to the numerous hydroxyl groups across the chain (Pal et al. 2007; Thombare et al. 2016). It has been proved that hydrogen bonding is the main adsorption mechanism of HGG on oxide minerals and kaolinite (Ma and Pawlik 2007).

![Guar gum structures. a low molecular weight guar gum (LGG) and b high molecular weight guar gum (HGG).](image-url)
The objective of this work is to systematically analyze the sedimentation of bitumen-coated silica particles in toluene with the presence of guar gum and water. The stability of suspended fine solids is significantly influenced by the collision frequency, and any aggregates formed upon external stimulus (e.g., additives) will in turn impact the collision frequency (Jeldres et al. 2018; Jin et al. 2011). Previous studies have revealed that the collision frequency and growth of aggregates principally depend on the size of the colliding particles, particle concentration, surface charge and hydrodynamic conditions (Chakraborti et al. 2003; Hashmi and Firoozabadi 2012; Jeldres et al. 2015; Li et al. 2012; Liu et al. 2003). To track the size of colliding fine solids during a settling process, focused beam reflectance measurement (FBRM) was applied in this work. FBRM has been a powerful technique to follow the size distribution of particles, which can provide the information of particle count and chord length in real time (Schäfer et al. 2002; Tadayyon and Rohani 1998). Barret and Glennon explained the working principle of FBRM and demonstrated its potential of monitoring particle size distribution in a multi-particulate and agitated suspension (Park et al. 2014). The use of FBRM can also help monitor the aggregation process of fine solids and enable process control and optimization (Lu et al. 2016). This research work will shed light on the development of efficient and economical approaches to remove intractable fine solids from the NAE bitumen.

2 Materials and methods

2.1 Materials

Silica particles with diameter of ~0.5–10 µm (Sigma-Aldrich) were used as the model fine solids. Athabasca bitumen (contains ~0.55 wt% solids) provided by Syncrude Canada Ltd was used to prepare bitumen coatings on the silica particles. HPLC-grade toluene (Fisher Scientific) was used as the organic solvent to disperse the silica particles. LGG (C_{10}H_{14}N_{2}Na_{2}O_{12}P_{3}, Mn ~ 536, Fisher Scientific) and HGG (Mn ~ 500 K, Everland, Natural Canadian products) were used as the additives in the sedimentation tests. Milli-Q water (Millipore deionized with a resistance of ≥ 18.2 MΩ cm) was used as to dissolve the guar gums to prepare guar gum aqueous solutions (200 mg/L).

2.2 Preparation of bitumen-coated silica particles

Bitumen-coated silica particles were prepared to mimic the indigenous fine solids found in NAE bitumen. Briefly, bitumen was first diluted with toluene and centrifuged at 9000 RCF for 1 h to eliminate the trace number of solids (0.55 wt%) contained in bitumen, after which toluene was removed from the bitumen via evaporation in vacuum. The treated bitumen was dissolved in toluene again to prepare the bitumen-in-toluene solution (0.2 wt%), and the solution was mixed in the ultrasonic bath for 10 min. Then, clean silica particles were mixed with the bitumen solution at mass ratio of bitumen solution to particles of 1:5. The mixture was sonicated for 5 min to separate any solid aggregates, agitated for 10 min using a magnetic stirrer (1000 rpm) and thoroughly washed with toluene through centrifugation (6000 rpm) for multiple times until the supernatant was clear. The resultant particles were recovered and dried in a fume hood for 8 h. Such bitumen-coated silica particles have a newfound diameter around ~1–5 µm, as demonstrated by FBRM (Fig. S1).

2.3 Sedimentation tests for bitumen-coated silica particles

Controlled sedimentation of silica particles in organic solvent was previously reported by Jin et al. (2011). Briefly, the bitumen-coated silica particles were mixed with toluene at ~2 wt% coated particles. The mixture was sonicated for 5 min and agitated using a magnetic stirrer (1100 rpm) for 10 min. Then, a certain amount of additive was introduced to the mixture, after which the mixture was stirred at 1100 rpm for 1 min and transferred to a 100-mL graduated cylinder. The dosage of all additives was expressed based on the amount of toluene. To better homogenize the mixture of solid slurry and LGG or HGG, the guar gum additive was dissolved in toluene with weight ratio of 90% prior to the sedimentation test. During the sedimentation process, the changes of mudline location in the cylinder (mL) were recorded as a function of settling time (s). Figure 2 shows examples of sedimentation curves where the mudline location was plotted versus time and initial settling rate (ISR) is determined from the initial slope of the curve. Turbidity of the supernatant sample (~70 mL) after 30 min settling was measured using Micro-100 Turbidimeter (Fisher Scientific, Canada) and expressed in NTU (nephelometric turbidity unit). Solid content in the supernatant was measured by centrifuging the supernatant at 5000 RCF for 10 min to separate the solid particles from toluene, then drying the solids in a fume hood for 3 h and finally weighing the resulting particles (Liu et al. 2019a, b).

2.4 FBRM measurement of water droplet size and silica particle size in toluene

To determine the size of water droplets and solid particles, the FBRM probe was immersed in a 250-mL beaker containing either water or a uniform suspension of bitumen-coated silica particles in toluene. A certain amount
of additives were then added to the suspension. During the measurements, the scanning laser of the FBRM probe was focused on a fine spot at the sapphire window interface and the reflected optical signal was processed. The corresponding straight line between any two points on the edge of a water droplet, a particle or particle agglomerate, known as chord length ($s$) was calculated as the product of the measured crossing time ($\Delta t$) and the beam velocity ($V_b$). Chord length counts are summed up in a finite number (number weight: number density) of chord length intervals, yielding the chords length distribution graphically (Tadayyon and Rohani 1998). Since the lens at the tip of the probe was 2.5 cm above the bottom of the beaker, continuous stirring (1100 rpm) was used during the measurements to avoid the settling of solid aggregates to the bottom.

2.5 Modification of FBRM measurement to track the sedimentation of aggregates

Although under continuous stirring, tracking the settled aggregates of solid particles by FBRM measurements was still difficult due to the elevation of the probe. Therefore, the slurry of bitumen-coated silica particles and toluene with the addition of all additives at a dosage of 1.5 vol%, was first stirred at 1100 rpm for 10 min, and then, the stirring speed was decreased to 20 rpm (minimum speed of the stirrer) in order to follow the aggregation process in a dynamic settling environment. The size of the aggregates was measured over time. When the FBRM probe could not detect the particles anymore, the settling was considered completed.

3 Results and discussion

3.1 Settling curve

To investigate the effectiveness of guar gum additives as well as water in destabilizing bitumen-coated silica particles in toluene, sedimentation tests were conducted following the previously reported method (Jin et al. 2011; Liu et al. 2019a, b). Figure 2 shows the settling curves, mudline position versus settling time, for the bare and bitumen-coated silica particles. Most of the bare particles immediately settled to the bottom of the graduated cylinder and the change of mudline reached an equilibrium state around 1 min, whereas bitumen-coated silica particles required almost 10 times longer time to complete the sedimentation. Previous work ascribed the fast sedimentation of bare particles to the particle aggregates because hydrophilic silica particles tend to attract to each other in hydrocarbon solvent (Liu et al. 2003). Conversely, the hydrophobic bitumen-coated silica particles that have steric repulsion between particles due to the swelling of bitumen layer in toluene could keep the particles apart (Natarajan et al. 2011, 2014; Zhang et al. 2016). Therefore, the suspension of bitumen-coated silica particles was more stable than that of the bare silica particles.

3.2 Sedimentation tests

3.2.1 Effects of water

Sedimentation tests with the addition of only water were conducted to investigate the effects of added water on destabilizing the bitumen-coated silica particles in toluene, and the results are shown in Fig. 3a. An immediate increase in ISR and accompanying drop in supernatant turbidity were observed after a small amount of water (1 vol%) was introduced. The ISR continued to increase with the water dosage and then leveled off at about 5 vol% water. This result is attributed to the formation of hydrogen bonding between water and some interfacially active components exposed on the bitumen coatings, which could enable the water droplets to capture some of the particles (Jian et al. 2016; Tan et al. 2009a, b). On the other hand, the supernatant turbidity reverted to the decreasing trend when the water dosage was higher than 1.5 vol% and continuously increased with increasing water dosage.

Besides the degree of bitumen coatings, the size of water droplets could also affect the collision frequency of particles and the aggregation of particles with water droplets. FBRM measurements were applied to analyze the size distribution of water drops in toluene with varied water
contents from 0.5 vol% to 5 vol%, and the corresponding results are shown in Fig. 3b. At low water dosage of 0.5 vol%, the size of water drops was undetectable, and the counts were negligible. When water dosage was increased to 1 vol%, a broad size distribution from 4 to 30 µm was detected with a peak at ~12 µm. Such broad peak shifted to the higher chord length (i.e., as high as 18 µm) and the corresponding number counts increased simultaneously as the water dosage further increased from 1 vol% to 4 vol%, indicating an increase in both the size and the number of water droplets in the system. Further increase in water dosage (to 5 vol%) led to a sudden drop in both the size and the number of water droplets, likely due to increased coalescence of the water droplets. Based on the FBRM results, we speculate that the high turbidity values in the sedimentation tests specially as water content > 4 vol% could be ascribed to the rapid coalescence of water droplets. Therefore, the added water ineffectively destabilized the particles since the formed large water droplets could instantly settle down to the bottom.

3.2.2 Effects of guar gum

Figure 4a presents the results of sedimentation of bitumen-coated silica in toluene with the addition of only guar gums. In both cases of LGG and HGG, the ISR value drastically increased upon the introduction of a small amount of guar gum (~0.5 vol%), and it then leveled off when the gum content was increased to about 3 vol%. The corresponding turbidity was found to fall sharply to 3.5 NTU and 6 NTU for
HGG and LGG, respectively, at the gum dosage of 2 vol%. However, when the gum dosage further increased from 2 vol% to 15 vol%, the turbidity gradually climbed up to 8 NTU and 15 NTU for HGG and LGG, respectively. The increase in turbidity was possibly due to the increased concentration of residual gum in the suspension. It was noticed that the addition of HGG gave rise to higher ISR and lower turbidity values than the addition of LGG independently of the gum dosage, indicating the better performance of HGG in settling the particles. This high settling rate is attributed to the formation of large solid aggregates containing the high molecular weight gum (HGG), which has been reported previously (Garcia Vidal and Pawlik 2015). FBRM measurement showed that HGG could generate larger particle aggregates than the LGG, obtaining a stable peak in the range of ~29–33 µm independent of the concentration (Fig. 4b).

The results on the initial setting rates of bare silica, bitumen-coated silica, bitumen-coated silica with 0.5 vol% LGG or 0.5 vol% HGG in toluene are summarized in Table 1. It can be observed that the addition of either LGG or HGG significantly improves the settling rate of the bitumen-coated silica particles. Table 1 shows that bitumen-coated silica particles could be settled at almost 3 and 4 times its original settling rates with the addition of 0.5 vol% LGG and 0.5 vol% HGG, respectively.

Figure 5 shows the photographs of bitumen-coated silica in toluene samples after 10 min of settling for untreated case (Fig. 5a) and treated cases with the addition of 0.5 vol% LGG (Fig. 5b) or 0.5 vol% HGG (Fig. 5c). For a better comparison, it is noted that the untreated sample contains 0.02 vol% of DI water, equivalent to the water amount used to dissolve LGG and HGG powders before they were mixed with toluene. The tests show that the clarity of the supernatant is highly dependent on the type of additive added. Figure 5a, b demonstrates the supernatant shows less turbidity due to the addition of LGG. Interestingly, when HGG was added to the bitumen-coated silica in toluene suspension, the clarity of the supernatant remarkably increased (Fig. 5c), even better than the LGG case. The above results demonstrate that the addition of LGG and HGG could effectively destabilize the bitumen-coated silica particles in toluene.

Figure 6 shows the sedimentation results with the addition of the guar gum aqueous solutions. It was noticed that the addition of LGG aqueous solution exhibited the similar settling performance to the use of only LGG (Fig. 4a). In other words, the addition of LGG aqueous solution could reduce the amount of LGG necessary to achieve a desirable result. On the other hand, the addition of LGG aqueous solution exerted an apparent reduction in the turbidity of the supernatant compared with the addition of only water, suggesting that the combined addition of LGG and water could strengthen the interactions between the added water and the bitumen-coated silica particles suspended in toluene. The possible reason is that the LGG, a mildly amphiphilic

| Suspension | ISR, ml/s | Suspension + Additive | ISR, ml/s |
|------------|----------|-----------------------|----------|
| Bare silica | 4.010    | Bitumen-coated silica + 0.5 vol% LGG | 1.140    |
| Bitumen-coated silica | 0.434    | Bitumen-coated silica + 0.5 vol% HGG | 1.593    |

Fig. 5 Photographs of settling samples when the bitumen-coated silica in toluene solution is a untreated and treated with 0.5 vol% of b LGG and c HGG are added, after 10 min of settling

Fig. 6 Measured ISR and turbidity in sedimentation tests with varied content of LGG aqueous solution (solid square) and HGG aqueous solution (void square) in toluene
chemical, in accordance with the structure, could migrate to the water/oil interface, and the hydrophobic segments facing the oil phase could induce attractive force between the water droplet and solid particles. On the contrary, the addition of HGG aqueous solution caused a slight decline in ISR in comparison with the addition of HGG alone. The effectiveness of the HGG aqueous solution on decreasing the supernatant turbidity was also inferior to that of the LGG aqueous solution, and the minimum turbidity was found to be \( \sim 8 \) NTU for the HGG aqueous solution and \( \sim 3.5 \) NTU for HGG only. These results are reasonable because the total dosage of HGG was lower in the case of HGG aqueous solution than in the case of HGG only. The other possible reason is that the HGG can be easily hydrated by water through hydrogen bonding due to numerous hydroxyl groups across the chain of HGG, which therefore might weaken the flocculation of solid particles by HGG (Hasan and Abdel-Raouf 2018).

Considering the ISR and turbidity data and gum dosages, it can be concluded that the ability of these additives to destabilize the bitumen-coated silica particles followed the order: water < LGG < LGG aqueous solution < HGG aqueous solution \( \approx \) HGG. The trend can be reasonably explained based on the distinct chemical structures of the two gums and their different destabilization mechanisms. The amphiphilic LGG serves as a modifier to the water/oil interface to induce the strong adhesion between the water drops and the hydrophobic bitumen-coated silica particles. The gum dosage was much higher when the LGG was used alone than when it was used as an aqueous solution, and the inferior results even at the higher dosage was possibly due to the insoluble nature of the LGG in toluene. Therefore, in the case of the added LGG aqueous solution, the water drops provided suitable water/oil interfaces for the LGG, where the gum was enriched which promoted the interactions between the LGG and solid particles. In contrast, the introduction of water to the HGG system would block the active sites of HGG in water drops not improving significantly the flocculation efficiency. To have a better view of the performances of these additives, the residual solid content retained in the supernatant after 30 min settling was determined. Figure 7a presents the collected data from the five types of batch tests with the dosages of additives from 0 vol% to 5 vol%. Overall, the cases of only water and only LGG showed much higher solid contents than other three cases under all dosage conditions. The performance of LGG was obviously enhanced once it was added to the solid toluene slurry in the form of aqueous solution, and the minimum solid contents were found to be \( \sim 1.1 \) wt% and \( \sim 0.6 \) wt% for the LGG and LGG aqueous solution, respectively, which was consistent with the turbidity and ISR results. With regard to the HGG, the introduction of water did not improve the performance significantly. However, at additives dosages of 0.2–1.8 vol%, the solid content was slightly lower in the case of HGG aqueous solution than in the case of only HGG. Interestingly, the performances of LGG aqueous solution, HGG and HGG aqueous solution on reducing the solid content were found to be identical at 2 vol% dosage condition and their supernatant sample exhibited the similar clarity at 1.5 vol% dosage (Fig. 7b).
3.3 FBRM measurements

3.3.1 Size of aggregates during stirring process

FBRM was used to have a clear assessment of the dimension of aggregates of bitumen-coated silica particles formed during the dynamic stirring process. Figure 8a shows the size distribution of aggregates recorded upon the addition of only water, LGG, HGG, LGG aqueous solution and HGG aqueous solution. The dosage of all the additives was fixed to 1.5 vol%. The case of LGG showed a broad size distribution from 5 µm to 45 µm, and most of the aggregates' size was concentrated around ~ 13 µm. In comparison, the addition of LGG aqueous solution resulted in a much stronger and shaper peak with higher counts values, indicating that more solid particles experienced aggregation. The resultant peak location apparently shifted to a higher chord length (~ 18 µm), and most of the peak area overlapped with the peak of water drops, suggesting that most of the particle aggregates were possibly captured by water drops, with the enhancement caused by the appearance of LGG on the water/oil interface. For HGG, the size distribution of adding HGG only exhibited peak location around ~ 35 µm, accounting for the formation of large solid flocs by polysaccharide. The peak location slightly shifted to ~ 40 µm when using the HGG aqueous solution as the additive.

Figure 8b shows the changes in the size of aggregates upon the sequential addition (0.5, 0.75, 1.0, 1.5, 2.0 and 3.0 vol%) of HGG, LGG aqueous solution and HGG aqueous solution, respectively. It was clearly noticed that each subsequent addition of gum or gum aqueous solution at certain time interval led to a significant increase in aggregate size. For example, from 5 min to ~ 20 min, as the dosage of HGG increased from 0.5 vol% to 0.75 vol% to 1 vol%, the chord length apparently changed from 12 µm to 19 µm to 27 µm, indicating an ongoing aggregation of suspended solid particles. In the cases of LGG aqueous solution and HGG aqueous solution, the chord length value at 20 min reached to ~ 29 µm and ~ 31 µm, respectively, attributed to the generation of large water–solid agglomerates. When the dosage was 3 vol%, all three cases did not present further growth in chord length, suggesting the growth of aggregates ceased.

3.3.2 Size of aggregates during sedimentation process

FBRM measurements with low stirring speed (20 rpm) were applied to monitor the in situ size of aggregates during the sedimentation process. Figure 9a shows the changes of chord length as a function of time with the addition of water, LGG, HGG, LGG aqueous solution and HGG aqueous solution. Without the enough agitation, the formed large aggregates would quickly settle. Consequently, the size of aggregates suspended in toluene would continuously decrease and ultimately became negligible once the settling was completed. According to the results in Fig. 9a, two kinds of decline behaviors were observed: a steep decline and a mild decline. Apparently, the addition of HGG, LGG aqueous solution or HGG aqueous solution showed the steep decline in aggregate size, and the settling was completed around 15 min, which were in good agreement with the relatively high ISR values achieved in these three cases. It is interesting to note that although the size of aggregates in the case of LGG

![Fig. 8](image-url)
aqueous solution did not go beyond 35 µm, it had a slightly steeper slope than HGG, suggesting that most of the aggregates formed in this case had the same size and there was little breakage during settling due to the small amount of water confirmed by the size distribution taken during settling shown in Fig. 9b; on the other hand, the size distribution for HGG systems shows a broader size distribution (Fig. S2). For the addition of water only or LGG only which showed low ISR and high residual solid content in sedimentation tests, a mild decline in the size of aggregates was observed. Under such low stirring rate (20 rpm), the pure water droplets would undergo coalescence and became unstable. Consequently, the aggregates formation was only attributed to collision between particles in the case of only water.

4 Conclusions

Destabilizing the fine solids in organic media is the first step for the effective removal of fine solids from bitumen product during the non-aqueous extraction (NAE) of Alberta oil sands in order to meet the specifications of pipeline transport and refinery feed. In this work, we demonstrated a way to destabilize the bitumen-coated silica particles in toluene through addition of water-assisted biomolecules extracted from the natural guar bean. Two kinds of well-known extracted guar gum, a low molecular weight disodium[[[5-(6-aminopurin-9-yl)-3-hydroxyxolan-2-yl]methoxy-hydroxyphosphoryl]oxy-oxidophosphoryl] hydrogen phosphate (LGG) and a high molecular weight polysaccharide (HGG), were examined. It is observed that the performance in fast settling and in lowering solid content of guar gum to destabilize the bitumen-coated silica particles followed the order: water only < LGG only < LGG aqueous solution < HGG aqueous solution ≈ HGG only. The LGG, an amphiphilic chemical, could facilitate the aggregation of bitumen-coated silica particles by modifying the surface of the solids, rendering the solid particles less oleophilic and more hydrophilic. The modification by LGG could be further facilitated by adding water to LGG to the system because the added water provided water/oil interfaces to stabilize and disperse the LGG, significantly increasing the effectiveness of interaction between the gum and solid particles. Simultaneously, the presence of water could trigger the formation of agglomerates with the modified solid particles and remarkably accelerate the settling process. Different from LGG, the HGG acted as a flocculant to destabilize the bitumen-coated silica particles by means of forming large solid flocs which readily settled out by gravitational force. Due to the robust effects of flocculation by HGG, the introduction of water did not improve the settling performance. The results provided insights into the development of methods to destabilize the intractable oleophilic fine solids suspended in oil media. We envision that by adjusting the concentration of gum in aqueous solution, it is possible to remove the indigenous fine solids from NAE bitumen.

Acknowledgements The authors gratefully acknowledge the financial support from Institute for Oil Sands Innovation (IOSI), Imperial Oil, the Natural Sciences and Engineering Research Council of Canada (NSERC) and Alberta Innovates to the research work. The authors also gratefully acknowledge the financial support from the Canada Foundation for Innovation (CFI), the Future Energy Systems under...
the Canada First Research Excellence Fund and the Canada Research Chairs Program.

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