# Flocculation performance of anionic starch in oil sand tailings

Nana Zhao, Hani Al Bitar, Yunyin Zhu, Yuming Xu and Zhiqing Shi

## ABSTRACT

A series of carboxymethyl starches (CMSs), with various degrees of substitution from 0.1 to 0.79, were synthesized and selected as a model to study the feasibility of using natural polymers as flocculants for oil sand tailings treatment. The flocculation performance of modified CMS in kaolin clay suspensions and oil sand tailings was evaluated in terms of settling rate, solids content, capillary suction time, and specific resistance to filtration of the sediment phase. It was found that the synthesized CMS effectively accelerates settling of kaolin suspensions and oil sand fine tailings, thus demonstrating the feasibility of this application.

**Key words** | carboxymethyl starch, dewatering, flocculants, oil sand tailings, settling rate

**Nana Zhao**
**Hani Al Bitar**
**Zhiqing Shi** (corresponding author)
Energy, Mining & Environment,
National Research Council Canada,
Vancouver, BC,
Canada
V6T 1W5
E-mail: *zhiqing.shi@nrc-cnrc.gc.ca*

**Yunyin Zhu**
**Yuming Xu**
Natural Resources Canada, CanmetENERGY,
1 Oil Patch Drive, Devon, AB,
Canada
T9G 1A8

## INTRODUCTION

The efficient and environmentally safe management of large volumes of high-water-content tailings from bitumen extraction of mined oil sands is posing critical challenges for the continued production of oil sands resources. In the past few decades, several major technologies, including composite/consolidated tailings, thickened tailings (paste technology), inline thickening with thin lift, and centrifugation, have been developed to accelerate the settling of fine tailings (Zhu *et al.* 2017).

Thickening of tailings prior to disposal is one of the more efficient ways of separating solids from liquid, reducing the required volume of tailings storage and allowing increased water recycling. This thickening process is facilitated by the addition of chemicals, usually flocculants, to increase the settling rate of suspended fine minerals. Currently, some of the most effective flocculants for flocculation of fine tailings are synthetic polyacrylamide-based polymers or copolymers (Renault *et al.* 2009; Lu *et al.* 2016). For example, Percoll 727 (also known as Magnafloc 1011), an anionic polyacrylamide with high molecular weight and medium charge, was reported to be one of the most efficient flocculants for fine tailings (Xu & Cymerman 1999). Magnafloc 1011 produces fast-settling flocs at relatively low dosages and a supernatant containing about 1.5 wt% solids. However, there is a concern regarding the carcinogenic nature of the monomer, acrylamide, as commercial-grade polyacrylamide (PAM) can contain up to 500 ppm monomer (Woodrow *et al.* 2008). For reference, the maximum allowable level of residual acrylamide in drinking water is 0.5 µg/L (Kiritsakis & Shahidi 2017). More concerns have been raised about acrylamide releases during the degradation of PAM under certain conditions (Levitt *et al.* 2011). Due to increasing demand for environment-friendly materials for treating industrial effluents, natural organic flocculants have emerged as promising alternatives to conventional flocculants. They are safe and biodegradable, fairly shear-stable, readily available from reproducible agricultural resources, and do not result in secondary pollution (Khalil & Aly 2002; Shogren 2009; Lee *et al.* 2014; Yang *et al.* 2014; Dao *et al.* 2016).

Natural polymers including starch, lignin, and chitosan have been developed as flocculants in industrial dewatering processes (Fan *et al.* 2005; Sableviciene *et al.* 2005; Aly 2006; Song *et al.* 2009; You *et al.* 2009; Liu 2011; Ziółkowska & Shyichuk 2011; Ziółkowska *et al.* 2011; Lin *et al.* 2012; Spychaj *et al.* 2013; Razali & Ariffin 2015). Natural polymer modification is one of the most effective strategies for improving the physical and chemical properties of the polymer. Recently, modified starches have attracted attention since they have been shown to be able to efficiently flocculate kaolin suspensions in the laboratory. For example, a series of highly substituted carboxymethyl

starches (CMSs) were prepared and evaluated by Spychaj *et al.* (2013). They found that CMS worked well as a flocculant for kaolin clay suspensions. Pang *et al.* (2013) reported that a cationic-modified starch had a flocculation capacity similar to that of PAM for 0.25% (w/v) kaolin suspensions. The polymer-grafted starch synthesized by Wang *et al.* (2013) gave better flocculation performance in kaolin suspension than PAM under very alkaline conditions (e.g., pH 10.0). However, very limited information is currently available on the application of starches as 'green flocculants' in dewatering oil sand tailings. We therefore conducted the present research work to explore the potential application of modified starches as flocculants in oil sand tailings treatment.

CMS is one of the simplest modified anionic starches, having a similar functional group as Magnafloc 1011. It is also commercially available. Therefore, CMS was selected as a model for natural polymers as flocculants for oil sand tailings. The objectives of this work are to better understand the basic interaction mechanisms among anionic starch, water and bitumen in oil sand tailings at laboratory scale, and to develop high-efficiency, economical and environmentally friendly flocculants based on natural polymers, which are suitable for oil sand tailing treatment, i.e., increase the settling rate of fine tailings and allow more water to be released for recycling. In this paper, a series of CMSs with various degrees of substitution from 0.1 to 0.79 were synthesized and their flocculation performances were measured in kaolin suspension and oil sand flotation tailings. The following parameters were used to evaluate the flocculation performance: settling rate, solids content, capillary suction time (CST), and specific resistance to filtration (SRF) of the sediment phase. Evaluation of the flocculation performance of natural polymers in real tailings could provide oil sand operators with some valuable scientific insights, not only into the challenges currently faced by modified natural polymer, but also into the chemical structural design of so-called green flocculants.

## MATERIAL AND METHODS

### Materials

Starch, sodium monochloroacetate (SMCA), glycidyltrimethylammonium chloride (2,3-epoxypropyltrimethylammonium chloride) and PAM were purchased from Sigma-Aldrich. All the reagents were used directly without further purification. Kaolin clay was obtained from
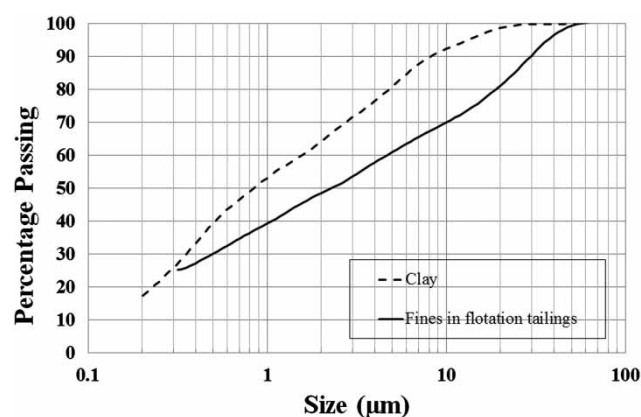


**Figure 1** | Particle size distribution of kaolin clay and fines fraction of cyclone overflow tailings solids (from commercial oil sand operation in Northern Alberta) with the Sedigraphy method.

Greenbarn Potters Supply Ltd. The particle size distribution (PSD) of the clay measured by the Sedigraphy method is displayed in Figure 1. Flotation tailings collected from a commercial oil sand operation in Northern Alberta had a sand (>44 μm) to fines (<44 μm) ratio of 0.48 and the PSD of the fines was also measured by the Sedigraphy method and is reported in Figure 1.

### Synthesis of CMS

Starch was etherified in mixed solvents in a one-step process: 13.7 g SMCA was dissolved in 120 mL of mixed solvents in a reactor. Then 10 mL of 30 wt% sodium hydroxide (NaOH) solution was added to the mixture. After homogenization 9.5 g starch was added into the mixture, which had become white in color. The mixture was left for 2.5 h at 50 °C. The product was then filtered and washed with 80% ethanol solution until the washed liquid was about pH 7.0. The product was finally washed with pure ethanol and dried in an oven at 50 °C for 10 h. The total yield of CMS reached up to 90% based on mass of starting material.

### The degree of substitution of CMS

Back-titration was employed to determine the degree of substitution of CMS (Stojanović *et al.* 2005). The sodium salt of the polymer was converted to the free acid form. Twenty millilitres of 0.2 M NaOH was then added to a known amount of the free acid form, leading to the formation of sodium carboxylate. The excess NaOH was then back titrated, permitting calculation of degree of

substitution using Equation (1):

$$DS = \frac{162 \times nCOOH}{M_{dry} - 58 \times nCOOH} \tag{1}$$

$$M_{dry} = \frac{1 - W_{water}}{100} \times M$$

where DS is the degree of substitution; 162 is the molar mass of AGU (anhydroglucose unit) (g/mol); 58 is the net increase in the mass of an AGU for each carboxymethyl group substituted (g/mol); $nCOOH$ (mol) represents the amount of COOH; $M_{dry}$ (g) is the mass of dry CMS sample; $M$ (g) is the mass of CMS sample; and $W_{water}$ (%) is water content.

## Jar test

As the most extensively used flocculant for wastewater treatment, PAM (molecular weight $5 \times 10^6$) was selected as a control to evaluate the flocculation performance of CMS in our study. Flocculation performances of starch, PAM, and CMS were evaluated using 5.0 wt% of kaolin suspensions, and oil sand tailings (flotation overflow) containing 5.5 wt% solids, respectively. Firstly, half of a given dosage of polymer solution was added into 500 mL kaolin suspension (or tailings) in a graduated cylinder. The cylinder was then sealed and inverted three times for vigorous shaking. The second half dose of the polymer solution was then added into kaolin suspension followed by inverting the graduated cylinder once. After the cylinder was placed on the top of the bench and allowed to stay motionlessly, the settling test started. When the flocculated solids interface crossed the 500-mL mark, a stopwatch timer was started. The times for the interface crossing different heights were recorded. The interfaces were monitored for 1 hour. After 5 minutes settling, a sample of the supernatant was collected for the solids content measurements. At 60 min, the final interface height was recorded and the supernatant was decanted. The underflow sediment was collected into a pre-weighed aluminum dish for solids content measurement. The interface heights were plotted against the settling time to give a settling curve. The initial part of the settling curve was almost straight. The slope of the line was taken as the initial settling rate in mL/sec, which was then converted to m/h knowing the distance between the volume marks on the cylinder.

## Specific resistance to filtration

SRF was determined with a pressure filtration apparatus supplied by Micro Filtration Systems. It consists of a stainless steel cylinder with 200 cm$^3$ capacity and a control panel, which permits a pressure of up to 700 kPa to be applied to the top of the tailings in the cylinder. The filter medium used was Whatman No. 17 chromatographic paper with a filtration area of 12.5 cm$^2$. Tailings or paste was placed in the cylinder. After a pressure of 150 kPa was applied, the filtrate (water) was drained out from the bottom of the cylinder and collected in a beaker resting on a balance (PM 2000, Fisher Scientific). The balance was interfaced to a computer recording the weight of the filtrate at intervals of 3 s. For each filtration measurement, a graph of time/volume versus volume was plotted and the slope of the graph was used to calculate the SRF by the following equation:

$$SRF = \frac{2p\,A^2\,b}{c\mu} \tag{2}$$

where p is pressure in Pa, $A$ is area of filtration in cm$^2$, $b$ is slope of time/volume versus volume in s/mL$^2$, $c$ is solids concentration of tailings in g/mL of filtrate, $\mu$ is viscosity of filtrate in Pa.s, and SRF is in units of cm/g.

## Capillary suction time

CST measurements were performed using a Triton TW166 CST apparatus. It consists of a filtration unit and an automatic time recording unit. The filtration unit includes a rectangular piece of filter paper (Whatman chromatographic paper No. 17, $70 \times 90$ mm), a slurry reservoir (a stainless steel cylinder of 18 mm diameter), and two pieces of rectangular Perspex. The filter paper is held between the two blocks of Perspex. In the centre of the top block there is a circular hole. The cylinder, fitting loosely in the hole and resting on the paper, serves as the slurry reservoir. The time recording unit is actually a probe-controlled timer. Engraved in the underside of the upper Perspex block are two circles, 32 and 45 mm in diameter, concentric with the reservoir cylinder. One probe is located in each circle and contacts the absorbent paper. After the cylinder is filled with slurry the water spreads out by the capillary pressure of the filter paper. When the filtrate reaches the first probe the timer starts and when the filtrate reaches the second probe the timer stops. The time interval recorded measures the filterability of the tailings and is referred to as CST in a unit of second.
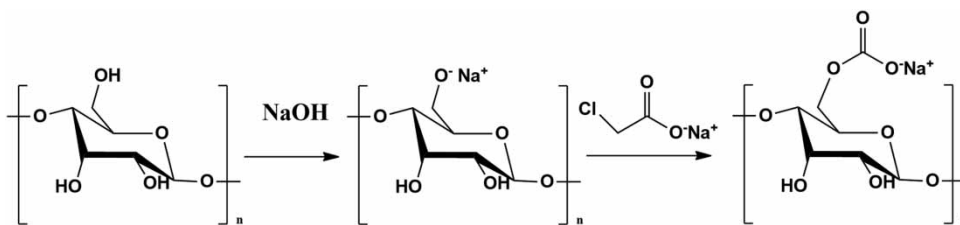
**Figure 2** | Synthetic route for carboxymethyl starch by carboxymethylation reaction between native starch and chloroacetic acid in an alkaline condition.

## RESULTS AND DISCUSSION

### Synthesis of CMS

Figure 2 shows the synthetic route for CMS by carboxymethylation reaction between native starch and chloroacetic acid in an alkaline condition. It is a two-step process: alkalization, where NaOH reacts with the hydroxyl groups of the starch, followed by etherification. Sodium chloride and glycolates are formed as byproducts.

Figure 3 shows the Fourier transform infrared spectra of potato starch before and after modification. The spectra had the characteristic peaks at $3,293 \text{ cm}^{-1}$ and $2,929 \text{ cm}^{-1}$, which are due to O-H stretching vibration and C-H stretching. The band at $1,649 \text{ cm}^{-1}$ originates from tightly bound water present in the starch (water content associated with starch). Compared to native starch, the appearance of two new peaks at $1,605 \text{ cm}^{-1}$ and $1,419 \text{ cm}^{-1}$, which are due to C=O stretching of carbonyl group and $-CH_2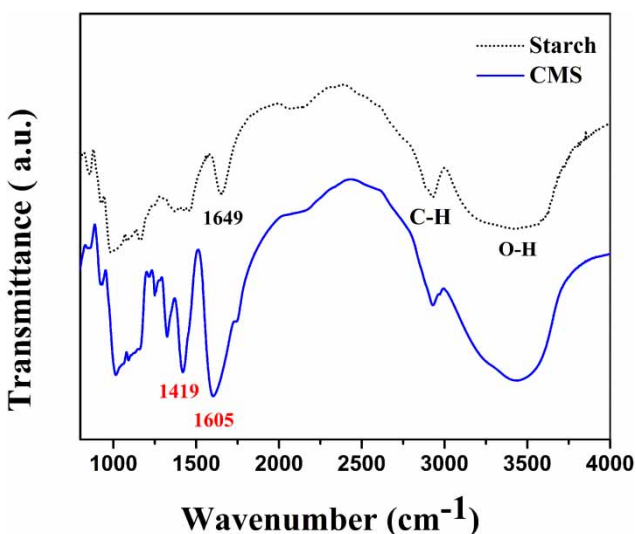$ scissoring, confirmed the successful substitution of $-COO\text{-}Na^+$ group on the starch molecular chains. Furthermore, the band at $1,324 \text{ cm}^{-1}$ is attributed to the overlapping of $-CH_2$ and O-H in-plane bending.

Different solvents (ethanol, isopropanol, and mixtures of the two) were utilized to obtain CMS having various degrees of substitution. The DS of the sample prepared in ethanol was 0.11 (Table 1). With an increase in the ratio of isopropanol/ethanol in the mixed solvents from 3:7 to 7:3, the DS increased from 0.37 to 0.79, implying that isopropanol leads to higher substitution because of the better selectivity for etherification of starch. Jie et al. (2004) also reported that organic solvents strongly affect the reaction efficiency, and that isopropanol was a better solvent than methanol or ethanol for the carboxymethylation of cassava starch.

### Flocculation performance in kaolin suspension

Because it is used extensively as a flocculant for wastewater treatment, PAM was selected as a control to evaluate the flocculation performance of CMS. Flocculation performances of starch, PAM, and CMS were evaluated in 5.0 wt% kaolin suspensions using the cylinder settling tests procedure reported by Xu & Cymerman (1999). Briefly, 5% kaolin clay suspension was prepared using tap water, whose pH is 7.92, ORP is 413 mv and conductivity is 37.3 μs/cm. The settling of flocculated clay suspension in a 500-mL cylinder was monitored and the times for the interface to cross different heights were recorded. The



**Figure 3** | Fourier transform infrared spectra of potato starch before and after modification.

**Table 1** | Effects of reaction solvents (ethanol, isopropanol, and mixtures of the two) on DS of CMS

| Samples | Reaction solvents | Degree of substitution |
|---------|-------------------|------------------------|
| Starch | N/A | 0 |
| CMS#1 | ethanol | 0.11 |
| CMS#2 | isopropanol/ethanol 7:3 (wt%) | 0.79 |
| CMS#3 | isopropanol/ethanol 3:7 (wt%) | 0.37 |

sediment was collected for measurement of solids content, SRF, and CST.

Figure 4(a) shows the settling rate of CMS (DS 0.79) as a function of dosage in the kaolin suspension. The settling rate is defined as the descent velocity of the upper interface, which is estimated from the slope of the initial straight-line portion of the plot of interface height vs settling time (Xu & Cymerman 1999; Zahabi et al. 2010). It was found that the un-flocculated kaolin (i.e., 0 ppm polymer dosage) gave a low initial settling rate of 0.87 m/h. When CMS was added to the suspension the settling rate increased to 2 m/h and 6 m/h with dosages of 10 ppm and 60 ppm, respectively. The settling rate then reached a plateau of 7 m/h with

further increases in dosage to 80 ppm and 120 ppm, indicating that there was a limit to the extent to which CMS improved settling (Gregory & Gubai 1991). Hogg (1984) suggested that optimal flocculation occurs when half the area of the solid is covered with the polymer. Therefore, at lower dosages (e.g., 10 or 20 ppm), the relatively inferior flocculation performance is probably due to the insufficient amounts of CMS for bridging clay particles to form flocs. With increasing dosages, the settling rate increased to 6 m/h since more clay particles bridged together to form flocs. When CMS provided adequate bridging links between particles to form flocs, it reached its optimal dosage and settling rate (7 m/h). However, there was no further
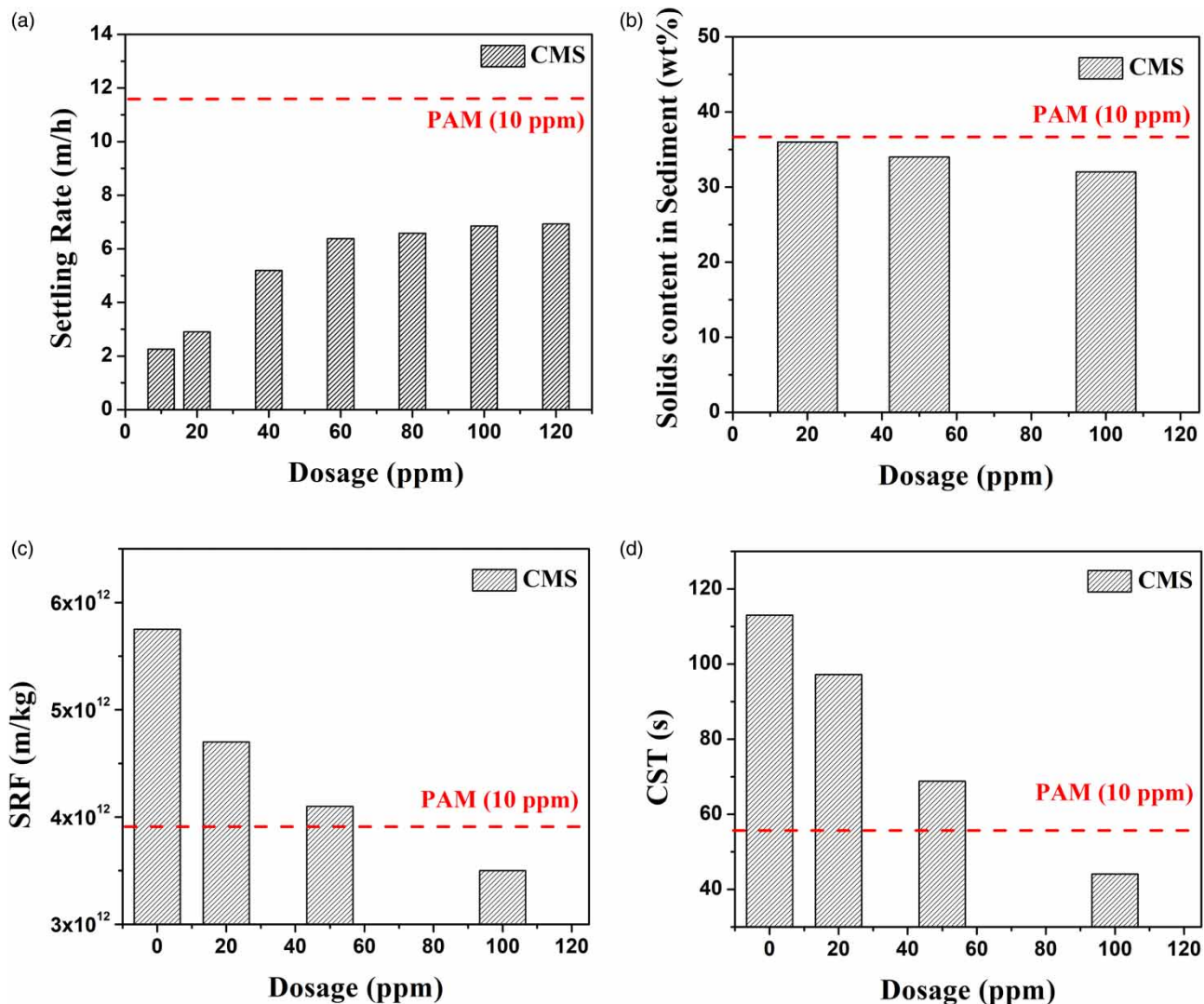


**Figure 4** | Effects of CMS (DS 0.79) dosage for a kaolin clay suspension on settling rate measured by graduated cylinder test (a), solids content in sediment calculated by underflow sediment (b), specific resistance to filtration (SRF) determined with a pressure filtration apparatus supplied by Micro Filtration Systems (c), and capillary suction time (CST) performed using a Triton TW166 CST apparatus (d).

improvement in settling rates beyond the dosage of 80 ppm. The maximum settling rate of CMS (DS 0.79) was 7 m/h, which is reasonably comparable to 10 m/h for PAM with a dosage of 8 ppm.

The settling rates of CMS with different DS (0.11, 0.37 and 0.79) were also evaluated. As an example, at the dosage of 40 ppm in kaolin suspension the settling rates for CMS with DS 0.11 and 0.37 were 3.5 m/h and 3.8 m/h, respectively, which are lower than the settling rate for the CMS with DS 0.79 (5 m/h). This clearly indicates the dependence of the flocculation performance of CMS on the number of acidic groups in the starch. Therefore, CMS with DS 0.79 was selected for further tests.

Figure 4(b) shows the solids content in sediment as a function of dosage of modified starch for kaolin clay. The solids content obtained using CMS in kaolin clay decreased only by 4% with increasing dosage from 20 ppm to 100 ppm, suggesting that the dosage of CMS does not have a significant impact on solids content of the sediment. The maximum solids content for CMS was 36 wt%, compared to 36.9 wt% for commercial PAM, indicating CMS gave similar compaction performance to that of PAM for kaolin clay.

The dewatering ability of the sediment obtained from flocculation using the modified starch was evaluated in terms of SRF and CST. SRF is widely used to evaluate the dewatering ability of a sediment, and smaller SRF values indicate better dewatering potential. The effect of the dosage of modified starch on SRF for kaolin clay suspension is shown in Figure 4(c). It was found that the un-flocculated kaolin (i.e., 0 ppm polymer dosage) showed a high SRF of $5.8 \times 10^{12}$ m/kg. When CMS was added the SRF of the sediment phase decreased to $4.7 \times 10^{12}$ m/kg at a dosage of 20 ppm. With increasing dosage from 20 ppm to 100 ppm, SRF decreased by 25%. The lowest SRF value of the sediment phase was $3.5 \times 10^{12}$ m/kg, obtained using CMS (DS 0.79) at a dosage of 100 ppm, which was comparable to that for commercial PAM ($3.9 \times 10^{12}$ m/kg).

CST, which is an empirical measure of the resistance offered by a sediment to the withdrawal of water, is another useful index for determining dewaterability. Lower CST values mean higher dewatering rates. Figure 4(d) compares the CST values between CMS and commercial PAM in kaolin clay. It was observed that the un-flocculated kaolin gave a high CST of 113 s and then the CST value decreased to 97 s and 42 s with additions of 20 ppm and 100 ppm CMS, respectively. The difference between CST values for CMS at a dosage of 50 ppm and PAM at 10 ppm was less than 12 s, implying that the kaolin clay sediment flocculated by CMS had filterability similar to that for PAM.

## Flocculation performance in oil sand tailings

The effectiveness of CMS in flocculating oil sand tailings was evaluated since CMS showed promising flocculation performance for kaolin. The flocculation tests using CMS (DS 0.79) were conducted on the cyclone overflow, obtained from oil sand fine tailings, from a commercial oil sand mine operation. The tailings used in this work contained 5.5 wt% mineral solids that had a sand-to-fines ratio of 0.48. In other words, the solids in the tailings contained about 68 wt% fines (<44 μm in size) and 32 wt% sand (>44 μm in size). The PSD of the fines fraction is shown in Figure 1.

Figure 5(a) presents the settling rates of CMS in oil sand tailings for various dosages. It was found that the settling rate of CMS increased from 2.6 m/h to 6.3 m/h with increasing dosages from 50 ppm to 200 ppm, which is comparable to commercial PAM with a dosage of 50 ppm (6.8 m/h). Figure 5(b) shows the solids content in sediment (1 h settling in a cylinder) as a function of dosage of modified starch. CMS in the dosage range of 50 ppm to 75 ppm gave comparable or better settling and compaction performance than 50 ppm PAM. For example, the solids content in sediment using 50 ppm CMS reached 36 wt%, higher than that for PAM (24.5 wt%) at the same dosage.

Figure 5(c) shows SRF values of the sediment as a function of dosage of CMS. Similar trends can be observed to that for kaolin suspension: the SRF of the sediment decreases with increasing polymer dosage. For example, the SRF decreased by 38% when the dosage increased from 50 ppm to 100 ppm. The lowest SRF value of the sediment using CMS was $3.0 \times 10^{13}$ m/kg, similar to that obtained using PAM at a dosage of 50 ppm ($3.1 \times 10^{13}$ m/kg). Figure 5(d) shows CST values of the sediment for CMS and PAM. The CST value decreased from 138 s to 67 s when CMS dosage increased from 50 ppm to 100 ppm. The CST value of CMS-treated sediment at a dosage of 100 ppm was shorter than that for PAM at a dosage of 50 ppm. The results indicate that CMS gives filterability similar to that for PAM for tailings sediment, further confirming the results obtained from SRF measurement.

In this work we explored the possibility of applying natural-product-based flocculants to treat oil sand tailings. Our laboratory-scale tests demonstrated the feasibility of using CMS as a flocculant for oil sand tailings. It should be emphasized that, although the flocculation performance of CMS in terms of settling rate is lower and the required dosage is higher than for commercial flocculants, the cost of CMS is also much lower, thus making CMS potentially
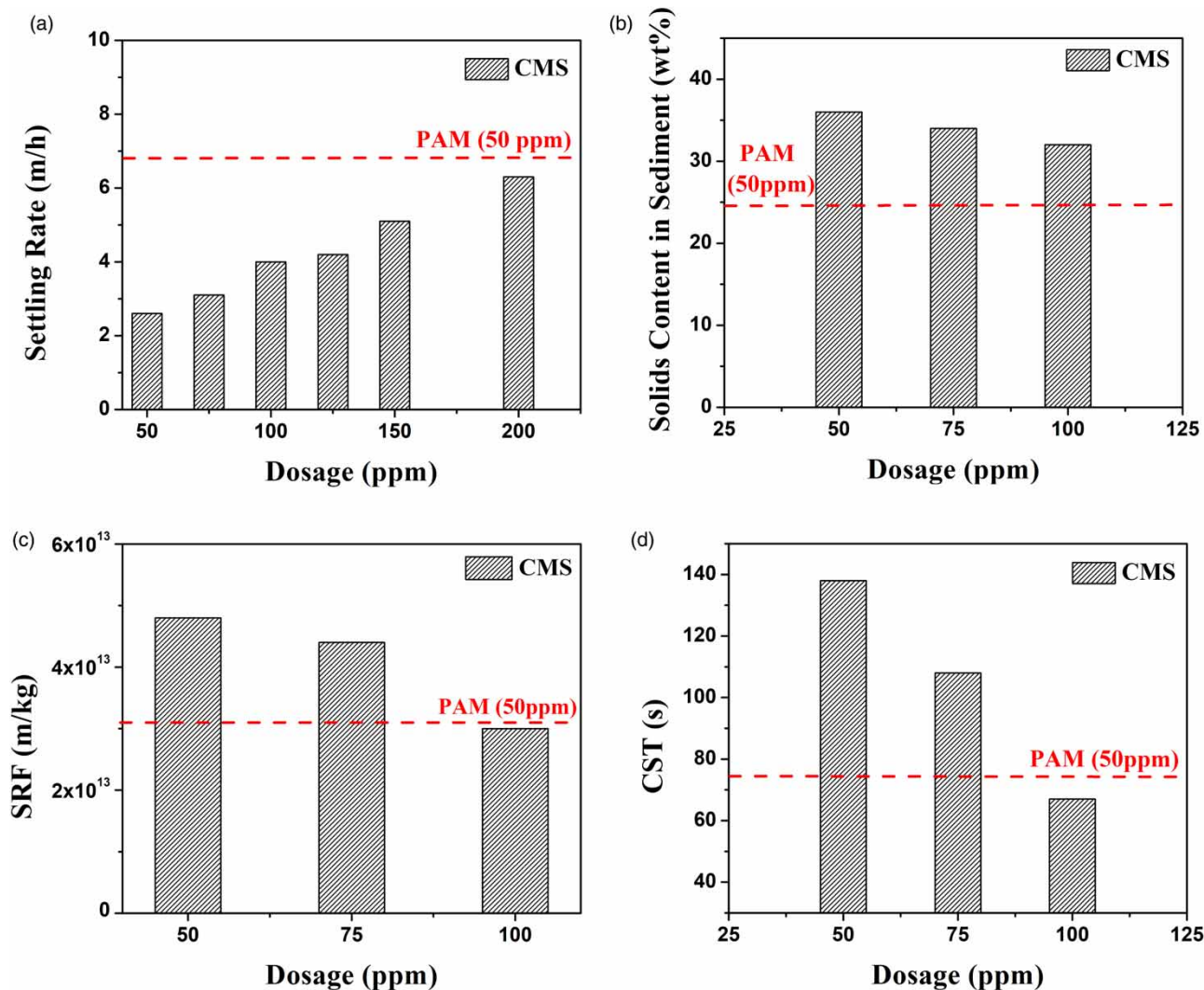
**Figure 5** │ Effects of CMS (DS 0.79) dosage for oil sand tailings on settling rate measured by graduated cylinder test (a), solids content in sediment calculated by underflow sediment (b), specific resistance to filtration (SRF) determined with a pressure filtration apparatus supplied by Micro Filtration Systems (c), and capillary suction time (CST) performed using a Triton TW166 CST apparatus (d).

economically competitive with the added benefit of being environmentally neutral.

## CONCLUSION

Starch was successfully modified by introducing anionic carboxymethyl functional groups. The application of the modified CMSs in flocculation of kaolin clay suspensions and oil sand tailing was investigated and compared with commercial PAM-based flocculants. It was found that the synthesized CMS effectively accelerated settling of kaolin suspensions and oil sand fine tailings. The settling rate increased with increasing dosage until it reached a

plateau. Compared to PAM, the dose of CMS required in order to reach the same settling rate was two to six times that of PAM. This paper also introduced preliminary work using CST for comparing the dewatering performance of kaolin clay suspensions and oil sand tailing conditioned with anionic starch. The CST for kaolin suspension decreased from 113 s to approximately 42 s with the addition of CMS at the dosage of 100 ppm. Increasing the polymer dose resulted in a decrease in the dewatering time. The performance of the natural starch polymer was comparable with selected PAM, indicating good potential for future use in oil sand tailings treatment applications. Pilot-scale evaluation is being planned for the near future.

## REFERENCES

Aly, A. A. 2006 Preparation, characterization and evaluation of anionic starch derivatives as flocculants and for metal removal. *Starch* **58** (8), 391–400.

Dao, V. H., Cameron, N. R. & Saito, K. 2016 Synthesis, properties and performance of organic polymers employed in flocculation applications. *Polym. Chem.* **7** (1), 11–25.

Fan, Q., Ju, B., Zhang, S. & Yang, J. 2005 Preparation of carboxymethyl starch with high degree of substitution and high solution viscosity. *Fine Chem.* **z1**, 112–114.

Gregory, J. & Gubai, L. 1991 Effects of dosing and mixing conditions on polymer flocculation of concentrated suspensions. *Chem. Eng. Commun.* **108** (1), 3–21.

Hogg, R. 1984 Collision efficiency factors for polymer flocculation. *J. Colloid Interf. Sci.* **102** (1), 232–236.

Jie, Y., Chen, W., Manurung, R. M., Ganzerld, K. J. & Heeres, H. J. 2004 Exploratory studies on the carboxymethylation of cassava starch in water-miscible organic media. *Starch* **56** (3–4), 100–107.

Khalil, M. I. & Aly, A. A. 2002 Preparation and evaluation of some anionic starch derivatives as flocculants. *Starch* **54** (3–4), 132–139.

Kiritsakis, A. & Shahidi, F. 2017 *Olives and Olive Oil as Functional Foods: Bioactivity, Chemistry and Processing.* Wiley, Hoboken, NJ, USA.

Lee, C. S., Robinson, J. & Chong, M. F. 2014 A review on application of flocculants in wastewater treatment. *Process Saf. Environ. Prot.* **92** (6), 489–508.

Levitt, D. B., Pope, G. A. & Jouenne, S. 2011 Chemical degradation of polyacrylamide polymers under alkaline conditions. *SPE Reservoir Evaluation & Engineering.* **14**, 281–286.

Lin, Q., Qian, S., Li, C., Pan, H., Wu, Z. & Liu, G. 2012 Synthesis, flocculation and adsorption performance of amphoteric starch. *Carbohydr. Polym.* **90** (1), 275–283.

Liu, H. 2011 Study on preparation and application in flocculants of modified lignin. *Mod. Appl. Sci.* **5** (1), 205–208.

Lu, Q., Yan, B., Xie, L., Huang, J., Liu, Y. & Zeng, H. 2016 A two-step flocculation process on oil sands tailings treatment using oppositely charged polymer flocculants. *Sci. Total Environ.* **565**, 369–375.

Pang, Y., Ding, Y., Chen, J. & Gong, W. 2013 Synthesis and flocculation characteristics of cationic modified corncob: a novel polymeric flocculant. *J. Agric. Sci.* **4** (9B), 23–28.

Razali, M. A. A. & Ariffin, A. 2015 Polymeric flocculant based on cassava starch grafted polydiallyldimethylammonium chloride: flocculation behavior and mechanism. *Appl. Surf. Sci.* **351**, 89–94.

Renault, F., Sancey, B., Badot, P. M. & Crini, G. 2009 Chitosan for coagulation/flocculation processes – an eco-friendly approach. *Eur. Polym. J.* **45** (5), 1337–1348.

Sableviciene, D., Klimaviciute, R., Bendoraitiene, J. & Zemaitaitis, A. 2005 Flocculation properties of high-substituted cationic starches. *Colloids Surf. A* **259** (1–3), 23–30.

Shogren, R. L. 2009 Flocculation of kaolin by waxy maize starch phosphates. *Carbohydr. Polym.* **76** (4), 639–644.

Song, H., Wu, D., Zhang, R. Q., Qiao, L. Y., Zhang, S. H., Lin, S. & Ye, J. 2009 Synthesis and application of amphoteric starch graft polymer. *Carbohydr. Polym.* **78** (2), 253–257.

Spychaj, T., Zdanowicz, M., Kujawa, J. & Schmidt, B. 2013 Carboxymethyl starch with high degree of substitution: synthesis, properties and application. *POLIMERY* **58** (7–8), 503–511.

Stojanović, Z., Jeremić, K., Jovanović, S. & Lechner, M. D. 2005 A comparison of some methods for the determination of the degree of substitution of carboxymethyl starch. *Starch* **5** (2), 79–83.

Wang, J. P., Yuan, S. J., Wang, Y. & Yu, H. Q. 2013 Synthesis, characterization and application of a novel starch-based flocculant with high flocculation and dewatering properties. *Water Res.* **4** (8), 2643–2648.

Woodrow, J. E., Seiber, J. N. & Miller, G. C. 2008 Acrylamide release resulting from sunlight irradiation of aqueous polyacrylamide/iron mixtures. *J. Agric. Food Chem.* **56** (8), 2773–2779.

Xu, Y. & Cymerman, G. 1999 Flocculation of oil sand tailings. In: *Proceeding of 38th Annual Conference of Metallurgists, Polymers in the Mineral Processing Industry*, August 22–26, Quebec, pp. 591–604.

Yang, Z., Wu, H., Yuan, B., Huang, M., Yang, H., Li, A., Bai, J. & Cheng, R. 2014 Synthesis of amphoteric starch-based grafting flocculants for flocculation of both positively and negatively charged colloidal contaminants from water. *Chem. Eng. J.* **244**, 209–217.

You, L., Lu, F., Li, D., Qiao, Z. & Yin, Y. 2009 Preparation and flocculation properties of cationic starch/chitosan crosslinking-copolymer. *J. Hazard. Mater.* **172** (1), 38–45.

Zahabi, A., Gray, M. R., Czarnecki, J. & Dabros, T. 2010 Flocculation of silica particles from a model oil solution: effect of adsorbed asphaltenes. *Energy Fuels* **24** (6), 3616–3623.

Zhu, Y., Tan, X. & Liu, Q. 2017 Dual polymer flocculants for mature fine tailings dewatering. *Can. J. Chem. Eng.* **95** (1), 3–10.

Ziółkowska, D. & Shyichuk, A. 2011 Flocculation abilities of industrial cationic starches. *POLIMERY* **56** (3), 244–246.

Ziółkowska, D., Shyichuk, A., Cysewski, P. & Organiściak, A. 2011 Flocculation efficiency of cationic potato starch in the presence of coagulants. *CHEMIK* **65** (4), 309–314.