APPLICATION OF RHAMNOLIPID AND MICROBIAL ACTIVITIES FOR IMPROVING THE SEDIMENTATION OF OIL SAND TAILINGS

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Abstract: Densification of oil sand tailings deposited in the tailing ponds and recovering water from them are two major challenges issues in the oil sands industry. A small increase in the tailing settlement rate can improve tailing's densification and significantly, reduce water consumption and the volume of tailing ponds. Currently most of the industrial consolidation methods are based on clay particle flocculation using agents (i.e. gypsum), and polymeric flocculants. In this work, the potential of rhamnolipid as a flocculating agent and microbial activities for increasing the sedimentation of fine tailing was investigated through the sedimentation experiments. It has been found that sedimentation increases by increasing the rhamnolipid concentrations. According to the result of zeta potential and particle size distribution, rhamnolipid increased sedimentation by improving the hydrophobicity of particles. Different concentrations of rhamnolipid together with the two microbial strains isolated from weathered oil lead to increases in sedimentation (by a maximum factor of 3.04), the concentration of larger particles (by a maximum factor of 1.9), particle mean diameter (by a maximum factor of 2.11) and flocculation significantly. The strong activity in this case could be probably due to the interaction of biosurfactant and high molecular weight microbial organics with clay particles (through a bridging mechanism, and improving hydrophobicity) or due to the change in chemistry of pore water as a result of microbial metabolism. This work shows the potential of using rhamnolipid and microbial culture for increasing the oil sand tailing sedimentation in a more environmental friendly and economical process. Further research is needed for the biosurfactant fate in the recycled water and the microbial role in sedimentation.

1 INTRODUCTION

Global demand for unconventional energy sources such as coal bed methane, heavy oil, and bitumen has grown in recent years. Canadian oil sands are mainly located in the Athabasca region in Alberta, with the rest in Peace River and Cold Lake (Government of Alberta 2008). There are two methods for bitumen production from oil sands; surface mining and in situ separation of the bitumen (Patterson 2012). Two to four barrels of fresh water are required per barrel of oil produced from the surface mining method (Alberta Energy 2010). "Tails" or "tailings" are the by-products from the extraction of bitumen from the sand by surface mining method which are pumped into the tailings ponds for storage (Figure 1). This tailing suspension is a mixture of process affected water, sand, clays, salts, metals, residual bitumen and hydrocarbon diluents. It has been reported that between 1992 and 2008, the extent of tailings ponds grew by 422% while the extent of mine pits, facilities, and infrastructure grew by 383% (Timoney and Lee 2009).

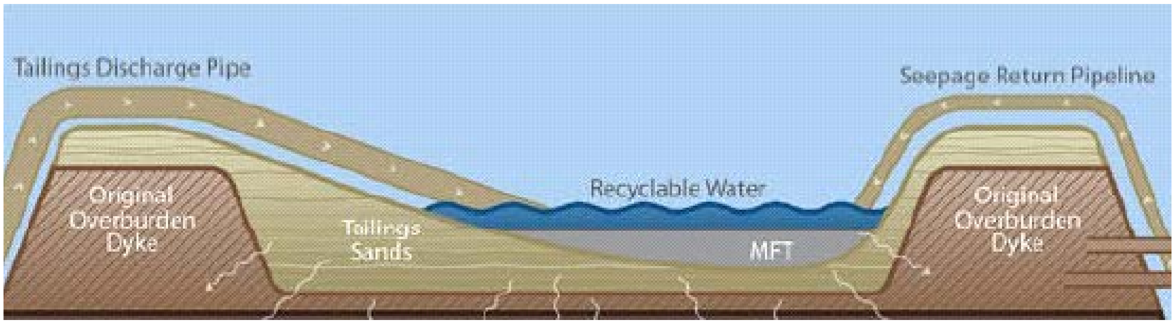

Figure 1 : Schematic Diagram of a Tailings Pond (Government of Alberta 2013)

In the pond there are different layers according to the weight of material, sand, settling to the bottom of the pond. The toxic water rises and forms the top layer which can be recycled into the extraction process (Mamer 2007; Masliyah 2007). Coarse sand grains (larger than 44 microns) settle out quickly. Thin fine tailings (TFT) which are a combination of fines and water with less than 30% solids will start immediately. TFT will settle and within two or three years a layer of mature fine tailings (MFT) develops which is a mixture of fine clay particles (under 44 microns in size) and water, with approximately 30%-60% solids and has a consistency similar to yogurt. Complete settling of MFT is very slow (Mamer 2007; Masliyah 2007; WWF 2010) (almost a century). Figure 2 shows the segregation of tailings within a tailings pond and Figure 3 shows the typical depth for each layer in the tailing pond.

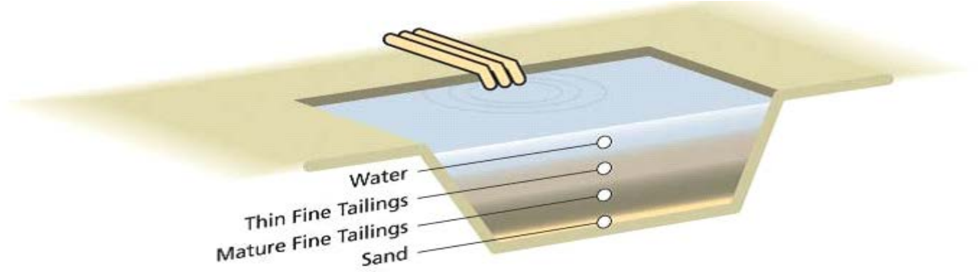

Figure 2: The segregation of tailings within a tailings pond (Mamer 2007)

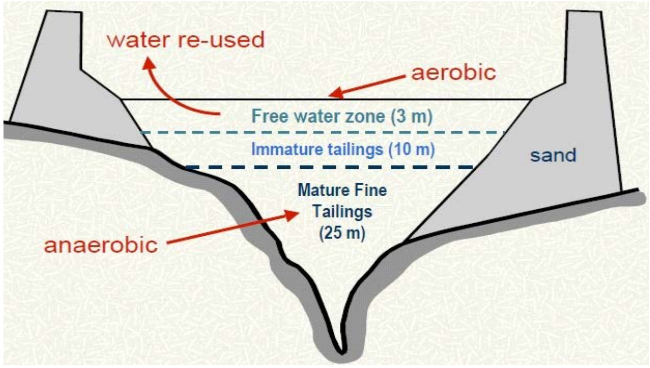

Figure 3. The different depth of tailing layers within a tailings pond (adapted from (MacKinnon 1989))

Now more than 170 km^2 of tailings ponds exist in Alberta. Toxic impacts of tailing ponds can affect ecosystem and human health (Timoney and Lee 2009). It means that management and increase the sedimentation of oil sand tailings is an important environmental and economical issue. An increase in tailings settlement rate can increase the efficiency of water recycling and reduce the volume of tailings ponds.

There are many methods in order to treat tailings ponds and increase sedimentation. These methods can be natural, physical or chemical/biological. In chemical/biological methods densification can be achieved by addition of agents such as calcium sulfate (gypsum), sodium silicate, organic flocculants, inorganic coagulants, oxidizing and reducing agents and most recently carbon dioxide and some microbial activity such as methanogenesis (Bordenave et al. 2010; Masliyah 2007). Currently most of the industrial methods for oil sand tailings densification are based on clay particle flocculation (BGC-Engineering-Inc. 2010). Flocculation process refers to the macroscopic aggregation of suspended particles into loosely packed flocs by addition of polymeric flocculants (Crittenden 2005; Hunter 2001). Microbial densification is a low cost method for increasing sedimentation (Quagraine et al. 2005; Siddique et al. 2007). Methane formation (methanogenesis) by anaerobic microbes can improve tailings densification.

The performance of the flocculants is an important issue in flocculation based methods. However the recycle water quality, startup and operational costs, experienced operators and careful operational control, in some cases should be considered (BGC-Engineering-Inc. 2010). In the microbial activity and methanogenesis method, methane and carbon dioxide emissions (up to 104 m^3 day^{-1} for methane) from tailing ponds should be controlled as they are greenhouse gases (Fedorak et al. 2003; Voordouw 2013).
It has been reported that surface active agents (surfactants) can be applied for increasing sedimentation and dewatering. Surfactants can reduce surface and interface tension by forming molecular film at the interface of air and water or two liquid phases (i.e. oil/water). There are some surfactants which are produced by living natural sources (i.e., from a plant, animal or microorganism) and known as biosurfactants (Chhatre et al. 1996; Mulligan 2005).

In the most of the work which has done on increasing sedimentation and dewatering the effect of synthetic surfactants on flocculation and dewatering of different clay particles were investigated (Besra et al. 2003; Nasim and Bandyopadhyay 2012; Singh et al. 1998; Ucbeyiay Sahinkaya and Ozkan 2011). They showed great ability for dewatering of slurries when they are combined with polymers as flocculants. They can change surface wetting characterization of particles and lead to an increase in flocculation and dewatering.

Biosurfactants have more advantages over synthetic surfactants such as low or non-toxicity and biodegradability. They are also more economic than the other surface active agents in some cases due to efficiency. In addition to these advantages which make them attractive for many environmental applications and protection, they have potential to decrease the environmental impacts of oil sands (Banat et al. 2000; Mulligan 2005; Rahman et al. 2002; Rodrigues et al. 2006; Urum and Pekdemir 2004; Xu et al. 2011). Rhamnolipids (RLs) are the most intensively studied biosurfactants. Many studies show their potential for remediation of oil contaminated soil and water (Mulligan 2014).

In this work the main objective is to evaluate the use of biosurfactants (rhamnolipid) as flocculating agents to enhance the sedimentation in tailing ponds which could reduce the need for fresh water and tailings ponds volume. In this approach sedimentation at different concentrations of rhamnolipid were measured and the mechanism was investigated.

Using microorganisms (inoculation or naturally present) together with rhamnolipid biosurfactant in order to enhance the sedimentation of oil sand tailings was also evaluated. Sedimentation measurements together with clay particle characterization and zeta potential measurements can determine the relation between biosurfactant/microbial flocculation and clay portion. In this approach, sedimentation will increase through flocculation and microbial activity without producing large amounts of CH_4 while taking advantage of the biosurfactants for remaining water and sediment bioremediation. Understanding the mechanism of sedimentation within this approach would lead to developing a more environmentally friendly densification method for oil sands tailings without having the limitations of other methods.

2 MATERIALS AND METHODS

2.1 Origin of the Oil Sand Tailings

The tailings pond sample was provided by Maria Demeter (Lab Manager / Environmental Engineering Technologist), Civil & Environmental Engineering Department, University of Alberta. Tailings samples were provided in 20 L plastic pail and stored at room temperature. It is comprised of bitumen (1-2 wt%), naphtha (<0.1 wt%), clay (30-60 wt%), and water with the pH in the range of 7.3-7.8. The clay content of 30-60wt% shows that the samples are taken from mature fine tailing layer from the depth below 10m of the tailing pond (Foght and Dunfield 2013).

2.2 Rhamnolipid

Rhamnolipid biosurfactant (JBR 425 from Jeneil Biosurfactant Co., USA) is used to investigate its effect on oil sands tailings. It is a mixture of two forms of rhamnolipid, at 25 wt% in water, with the CMC value of

30 mg/l at the lowest surface tension of 28 mN/m (Abbasi-Garravand 2012; Clifford et al. 2007; Wang and Mulligan 2009).

2.3 Microbial Cultures

Cultures of two microbial strains isolated (by growing on R2A nutrient agar medium (Sigma-Aldrich, for microbiology) and Bushnell Hass medium by one of my colleagues in the lab for her own research) from weathered oil (including light crude oil, diesel and biodiesel/B 100) were used for this study. The microbial cultures were grown aerobically in 25 ml of medium containing mineral salts of nitrogen (sodium nitrate) and phosphorous (monobasic and dibasic potassium phosphates) at C:N:P ratio of 100:10:1 (Cookson 1995), at 37ºC for 24 hours without shaking (Youssef 2006).

2.4 Experimental Approach

2.4.1 Sedimentation Experiments

The effect of rhamnolipids and microbial cultures on sedimentation was evaluated through sedimentation experiments. The tailings densification process includes consolidation and sedimentation processes near the bottom and top of a tailings column, respectively (Eckert et al. 1996). The sedimentation process can be easily monitored as the downward movement of the boundary between clear liquid and suspended tailings. Its rate of movement, the ‘‘hindered settling velocity” (Eckert et al. 1996), is orders of magnitude smaller than the Stokes’ single particle settling velocity (35 cm/day for a 2 micron diameter particle with a density of 2.65 g/cm^3 (Bordenave et al. 2010); tailings sedimentation rates in our experiments (about 0.1 cm/day) were much smaller than this). In this way, the sedimentation (S) was determined according to the following equation (Bordenave et al. 2010):

$$S(\%)=1-h/H$$

where h is the position of the boundary and H is the total height of the liquid column (Bordenave et al. 2010). All the sedimentation experiments were performed with 13-15 g of tailings diluted in 5 mL of deionized water in 20 mL glass tubes (15 cm) closed with a paper towel in order to prevent liquid evaporation. Sedimentation experiments were performed at room temperature (23 ºC± 2°C) (It has been reported that the in situ temperature of MFT was ~12–20°C) (Foght and Dunfield 2013; Siddique et al. 2014). Each test was repeated three times (triplicate) and the average data are reported.

2.4.1.1 Sedimentation experiments using rhamnolipid

Five ml of rhamnolipid at different concentrations (0.5%, 1%, and 2%) were added into the glass tubes containing a diluted tailing sample. 5 ml of deionized water were added to 20 mL glass diluted tailing sample tube as control. Sedimentation tubes were homogenized by 10 repeated inversions and were left without agitation at room temperature. Sedimentation (S) was measured every 5 days in unshaken tubes over a period of 25 days. In order to unify the condition in all experiments pH was adjusted by NaOH (0.1N) to 8.

2.4.1.2 Sedimentation experiments by rhamnolipid and microbial cultures

The sedimentation of tailings ponds samples was evaluated in the presence of microbial cultures and rhamnolipid. 1 mL of mixed culture of two microbial strains isolated from weathered oil and 5 mL rhamnolipid biosurfactant at different concentrations (0.5%, 1%) were added to the diluted tailing pond samples. Sedimentation tubes with diluted tailings samples and 6 mL of deionized water served as the control. pH of the samples were adjusted to 8 by adding NaOH (0.1N). Homogenized sedimentation tubes were incubated at room temperature (23 ºC± 2°C) and measurement of the sedimentation in unshaken tubes was performed every 10 days over a period of 50 days.

2.5 Analysis

Settled tailings and tailing process water in each set of experiments were separated using a pipette in order to perform analysis on them.

2.5.1 Settled Tailings

2.5.1.1 Particle size distribution

The size distribution of tailings was measured using a Horiba model LA-950V2 laser scattering particle size analyzer which uses Mie Scattering (laser diffraction). Dried tailings samples from all parts of the sediment column (Rock crystal with Refractive Index (R): 1.540) were dispersed in deionized water (Water with Refractive Index (R): 1.333) before introducing into the particle size analyzer.

2.5.1.2 Zeta potential measurement

The zeta potential (or electrophoresis mobility) of the oil sands tailings particles in their diluted suspension (after using rhamnolipid and/or microbial cultures, and before it) was measured by Zeta-Meter System 3.0+ (USA). Fifteen measurements were done for each sample.

3 RESULTS AND DISCUSSION

3.1 Results of Sedimentation Experiments

3.1.1 Role of rhamnolipid, and mixture of rhamnolipid and microbial cultures in tailings sedimentation

The potential of rhamnolipid to increase sedimentation was analyzed by comparing sedimentation of diluted tailing pond samples amended with different concentrations of rhamnolipids (0.5%, 1%, and 2%). The presence of rhamnolipid increased the sedimentation compared to the control under the experimental conditions (Figure 4). Increasing the rhamnolipid concentrations can increase sedimentation. However after a longer time, 1% rhamnolipid concentrations have shown approximately the same amount of sedimentation compared with 2%.

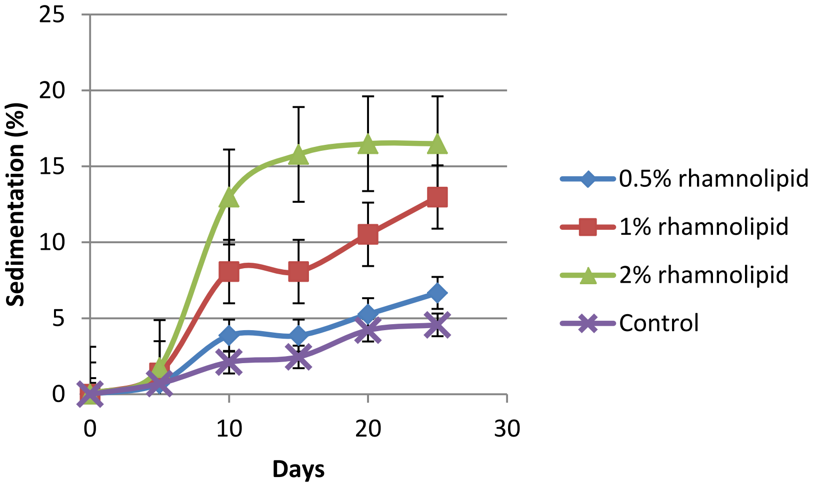

Figure 4: Sedimentation of oil sand tailings at different concentrations of rhamnolipid over time

Sedimentation of tailings amended with the different concentrations of rhamnolipid (0.5% and 1%) and two microbial strains isolated from weathered oil were compared in order to evaluate the role of adding microbial cultures in sedimentation of tailing pond samples (Figure 5). All of these show an increase in sedimentation compared to the control. Microbial cultures together with rhamnolipid can significantly increase the sedimentation of tailings compared to the amount of sedimentation of tailings amended only with rhamnolipid. Adding microbial cultures results in more sedimentation at a lower concentration of rhamnolipid (0.5% compared to 1%).

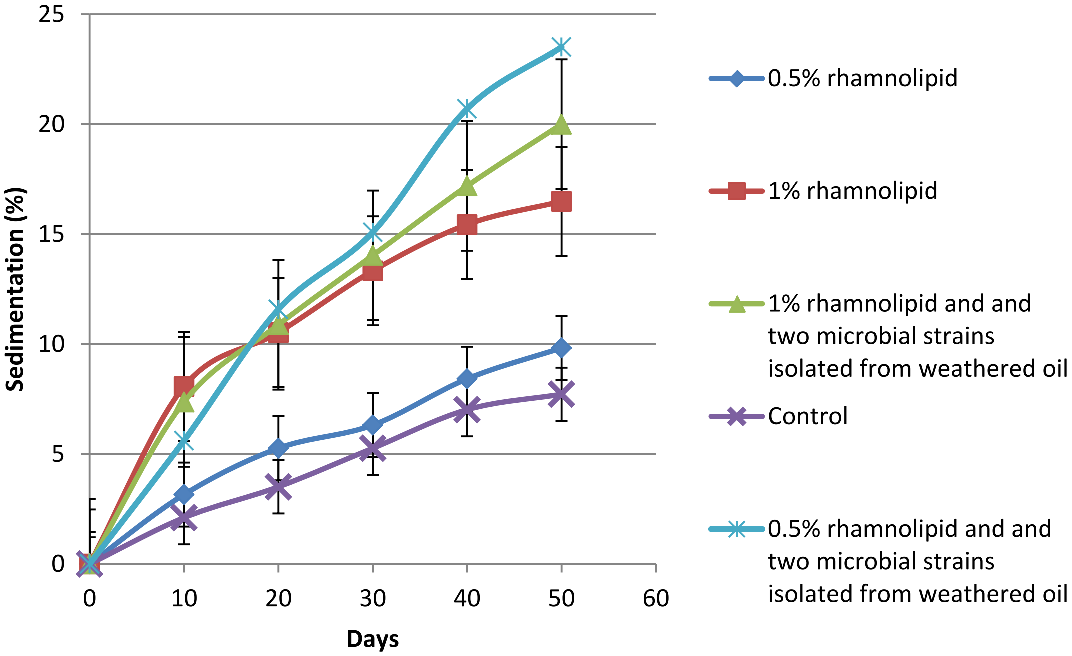

Figure 5: Sedimentation of oil sand tailings at different concentrations of rhamnolipid (0.5% and 1%) and two microbial strains isolated from weathered oil over time

3.1.2 Particle size distribution

Using the particle size analyzer, the particle aggregation and flocculation were evaluated. Dried settling tailings samples from sedimentation experiments using microbial cultures and different concentrations of rhamnolipid were dispersed in deionized water. Figure 6 shows the particle size distribution and table 1 shows the summery of the measurement results, using four different sedimentation agents: 1% rhamnolipid, 0.5% rhamnolipid, 1% rhamnolipid and microbial cultures, and 0.5% rhamnolipid and microbial cultures. The measured particle diameter based on cumulative% (90%) and the mean diameter are respectively 5.83, 4.85, 7.20, 8.30μm and 1.31, 1.16, 1.81, 2.32 μm in four different sedimentation agents. These values are actually the diameters of the flocculation of tailings particles.

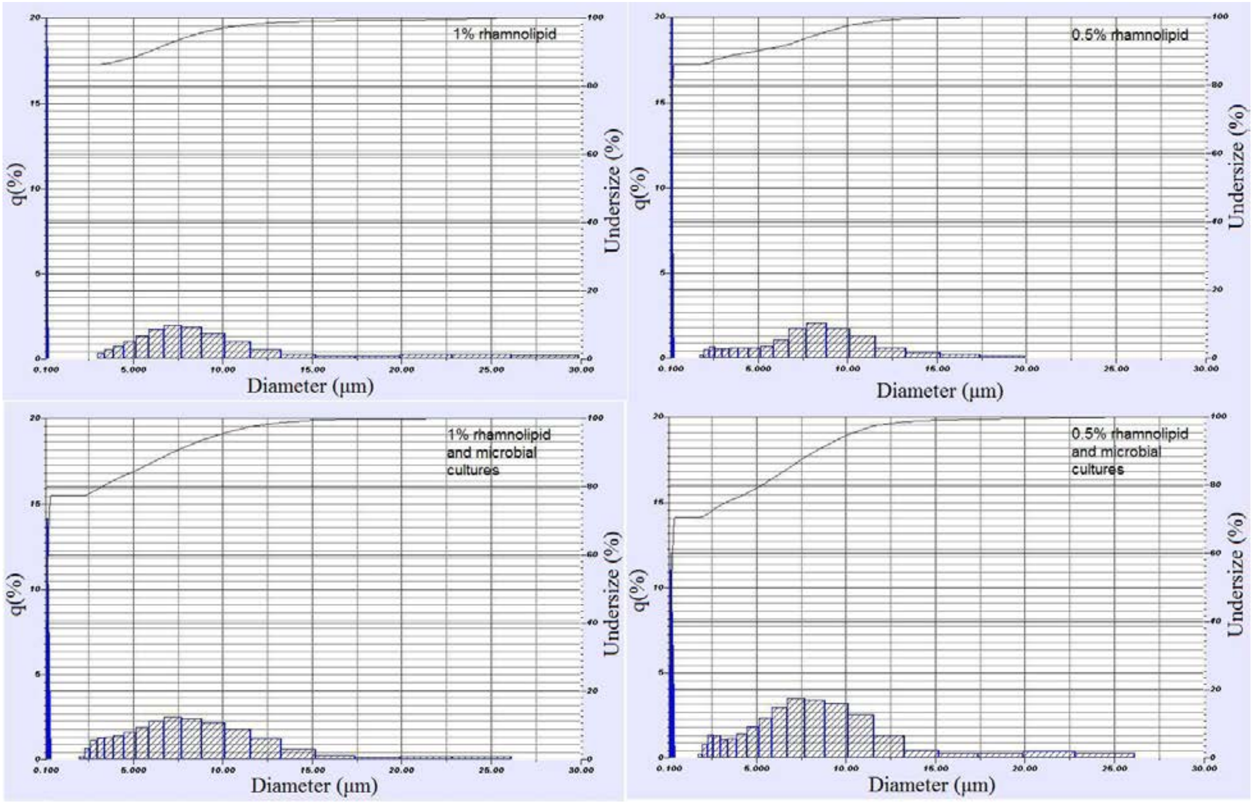

Figure 5: Particles size distribution of the settled oil sand tailings from sedimentation experiments using microbial cultures and different concentration of rhamnolipid dispersed in deionized water

Table 1: Measured particle diameter based on cumulative% (90%) and particle mean diameter of sedimentation experiments

Rh conc.	1%	0.5%	1%	0.5%	Control
Microbial culture	-	-	*	*	
Diameter based on cumulative% (90%)	5.83µm	4.85µm	7.20µm	8.30µm	4.36 µm
Mean diameter	1.31µm	1.16µm	1.81µm	2.32µm	1.10 µm

Compared to the measured particle diameter based on cumulative% (90%) (4.36 µm) and particle mean diameter (1.10 µm) of control experiments which were simply composed of deionized water and tailings without any sedimentation agents, one can conclude that both rhamnolipid and microbial cultures mixed with oil sand tailings can improve effectively the aggregation and flocculation of tailings particles. The tailing comprises a high concentration of smaller and lower concentrations of larger particles before flocculation process and a relatively high concentration of large flocculates after the flocculation process. Comparing the size distribution and mean diameter of particles obtained from tailings samples and rhamnolipid inoculated with microbial cultures and tailing samples with non-inoculated rhamnolipid, shows that microbial culture can improve particle aggregation and flocculation and relatively increase the concentration of larger particles when mixed with rhamnolipid. It seems that microbial cultures can work better in the lower rhamnolipid concentration as mixing tailings with microbial cultures and 0.5% rhamnolipid was more effective for particle flocculation and aggregation than those of 1% rhamnolipid probably due to antimicrobial effect of rhamnolipid which inhibit the microbial growth and EPS production. EPS (extracellular polymeric substances) are compounds secreted by microorganisms into their environment. These compounds are important in biofilm formation and cells attachment to surfaces (Li et al. 2007).

3.1.3 Zeta potential measurement

The results of zeta potential measurement of dried settling tailings samples (gained from sedimentation experiments using microbial cultures and different concentrations of rhamnolipid) resuspended in deionized water are presented in Figure 6. The zeta potential remained negative and decreased after adding rhamnolipid and decreased more by increasing the concentrations of anionic rhamnolipid. However adding microbial culture and rhamnolipid together slightly increased the zeta potential but still remained negative.

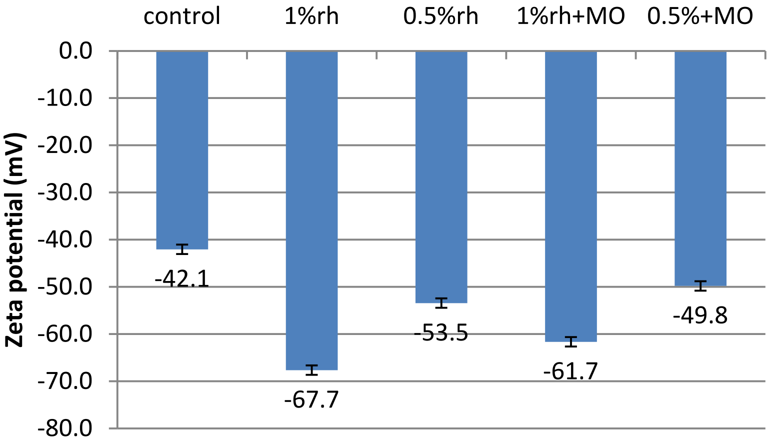

Figure 6: Zeta potential of different dried settling tailings samples resuspended in deionized water

The results of zeta potential and particle size distribution supported the idea that rhamnolipid has potential as flocculating agents for oil sand tailings sedimentation. It is well known that the particle hydrophobicity has a significant effect on flocculation (Song et al. 2000; Song et al. 2001; Ucbeyiay Sahinkaya and Ozkan 2011; Warren 1992). Increased surface hydrophobicity, which is dependent on increasing the concentration of surfactant could increase flocculation of clay particles (Ucbeyiay Sahinkaya and Ozkan 2011). The rhamnolipid anions which remained in solid phase adsorb on the oil sand tailings surfaces and rendering the surfaces hydrophobic and resulting in the flocculation of oil sand clay particles due to the hydrocarbon chain association (Ucbeyiay Sahinkaya and Ozkan 2011) when the rhamnolipid adsorption layers on particles contact each other. The increase in negative zeta potential should give rise to the increase of the energy barrier, preventing the particle aggregation. However, the increase in the surface charge by the rhamnolipid adsorption on the particle surfaces did not lead to decrease in the flocculation of tailing particles and even lead to improve their flocculation which means that the rhamnolipid adsorption onto the tailing particle surfaces improved the hydrophobic interaction between the particles much more strongly than the electrical double layer repulsion. These results also show that the rhamnolipid together with microbial culture had a stronger activity than rhamnolipid by itself. Rhamnolipid (which is a biosurfactant produced by *Pseudomonas aeruginosa*) mixed with microbial culture showed strong flocculating activity, while zeta potential still remained negative. It means that the mechanism of flocculation is not charge neutralization. Microbial activity can increase MFT by microbial cells and/or EPS secreted by microbial cells (Bordenave et al. 2010) and or biogenic gas production (Bressler et al. 2010; Fedorak et al. 2003). Macromolecules (such as EPS) could be viewed as naturally produced flocculants (Tenney and Stumm 1965).

Mixing microbial culture with rhamnolipid slightly increased the zeta potential but still remained negative and shows a stronger activity than rhamnolipid by itself. It means that the mechanism of flocculation is not charge neutralization and probably it is due to the interaction of the biosurfactant and high molecular weight microbial organics through a bridging mechanism with clay particles in the way that the macromolecules bridge the individual clay particles into an aggregate (Yu et al. 2009). Another possible reason for strong flocculating activity of rhamnolipid mixed with microbial culture could be due to the change in chemistry of pore water as a result of microbial metabolism which could lead to slightly decrease in pH (~7.5 for 1% rhamnolipid and microbial culture, and ~7.6 for 0.5% rhamnolipid and microbial culture), possibly due to the dissolution of MFT carbonate minerals, increase the ionic strength (I) of the pore water, reduce the thickness of the DDL of clay particles and increase the flocculation as a result of double layer compression or by cation (such as (Ca^{2+})) bridging. Further analysis is needed to better understand the microbial role.

4 CONCLUSIONS

The results obtained from sedimentation tests and particle size distribution analysis indicate that presence of rhamnolipid at different concentration (0.5%, 1% and 2%) could increase the sedimentation and the sedimentation would be increased by increasing the rhamnolipid concentrations. Different concentrations of rhamnolipid (0.5% and 1%) together with the two microbial strains isolated from weathered oil could lead to significant increases in sedimentation, the concentration of larger particles, particle mean diameter and flocculation in the tailings samples amended with them compare to the control. Microbial cultures can work better in the lower rhamnolipid concentration (0.5%) probably due to antimicrobial effect of rhamnolipid which inhibit the microbial growth and EPS production. However it is not proven yet.

The results of zeta potential and particle size distribution supported the idea that rhamnolipid have potential to be used as flocculating agents for oil sand tailings sedimentation. Rhamnolipid adsorption on the particle surfaces improved the hydrophobic interaction between the particles much more strongly than the electrical double layer repulsion. Mixing microbial culture with rhamnolipid has significant effect on sedimentation that rhamnolipid by itself. This effect is probably due to the interaction of the biosurfactant and high molecular weight microbial organics through a bridging mechanism with clay particles or due to the change in chemistry and the ionic strength (I) of pore water as a result of microbial metabolism (reduce the thickness of the DDL of clay particles and increase the flocculation as a result of double layer compression or by cation (such as (Ca^{2+})) bridging), or due to increasing the hydrophobicity of the particles. These results show the potential of using rhamnolipid and microbial culture in order to increase the oil sand sedimentation through flocculation and microbial activity without producing large amounts of CH_4 while taking possible advantages of the biosurfactants for remaining water and sediment bioremediation. Investigation on biosurfactant fate in the recycled water and understanding the mechanism of sedimentation would lead to developing a more environmentally friendly and economically oil sands tailings densification method without having the limitations of other methods.

5 FUTURE WORK

Future work needs to focus on water quality determination and rhamnolipid's fate after sedimentation as rhamnolipid have the ability to bring some heavy metals such as copper from sediment into the water. It has been reported that rhamnolipid as the biosurfactant could remove more than 99% of heavy metals such as zinc, nickel, and cadmium (El Zeftawy and Mulligan 2011), 100% of copper (Ridha 2010) and 96% of chromium (Abbasi-Garravand and Mulligan 2014) from water through the micellar enhanced ultrafiltration (MEUF) process.

Determination of Ca^{2+}, Mg^{2+} and HCO_3^- concentrations in pore water at the presence of rhamnolipid and microbial culture could explain the role of microbial metabolism (i.e. producing biogenic CO_2) in changing the chemistry of pore water which lead to dissolution of MFT carbonate minerals and consequently changing the pH, changing the ionic strength (I) of pore water and thickness of DDL of clay particles.

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