Dual-Conditioning of Sludge using Chitosan and Metal Cations


* Department of Chemical Engineering, Faculty of Engineering and Science, Curtin University Sarawak Malaysia, CDT 250, 98009 Miri, Sarawak, Malaysia
(E-mail: lau.shiew.wei@curtin.edu.my; dabbie90@hotmail.com; chua.han.bing@curtin.edu.my)
** Department of Chemical Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
(E-mail: M.Ang@exchange.curtin.edu.au; T.Sen@curtin.edu.au)

Abstract
Sludge dewatering is important in sludge management and disposal. In practice, chemical conditioners are often introduced to aid sludge dewatering. This study investigated the simultaneous application of chitosan and metal cations as dual-conditioners to improve sludge dewaterability. The dewatering performance of sludge was evaluated using three common measurements, i.e. capillary suction time (CST), specific resistance to filtration (SRF), and moisture content of the filtered sludge cake. The effectiveness of metal cations in sludge conditioning and dewatering was found, in ascending order, to be Na⁺ < K⁺ ≈ Mg²⁺ < Ca²⁺ < Al³⁺ < Fe³⁺. Dual-conditioning using chitosan and metal cations further enhanced dewaterability. Cations may have significant effects on sludge conditioning by neutralization of negative surface charges, bridging of floc components, and the salt out effect, leading to improved dewaterability when used in conjunction with chitosan.

Keywords
Chitosan; metal cation; dual-conditioning; sludge dewatering

INTRODUCTION
Sewage sludge is known to be difficult to dewater, due to its high compressibility and gel-like water retention capacity. The presence of surface charges due to its biological nature and the presence of weakly charged extra-cellular polymeric substances (EPS) are often said to contribute to the deterioration of sludge dewaterability (Curvers et al. 2009). Sludge dewatering has become a critical issue in the reduction of transport and further treatment costs, and is still a treatment bottleneck. Ferric chloride and alum were commonly used for solids conditioning in the past, but the current practice is to use cationic polymers (polyelectrolytes) alone. Despite their higher unit cost, organic polymers have largely displaced inorganic chemicals in conditioning and dewatering processes (Chitikela and Dentel 1998).

Recently there has been considerable interest in using alternative substances such as soy and wheat proteins, surfactants, enzymes, natural or modified biopolymers, microbial flocculants, seawater and brine, to replace or supplement synthetic polymers in sludge conditioning, due to the high polymer costs, the high moisture content in the resulting sludge cake, and concern over the biodegradation and toxicity of polymers (Banerjee 2014; Liu et al. 2011, 2012; Prado et al. 2011a,b; Fu et al. 2010, Zhang et al. 2010; Ayol 2005; Huang et al. 2002; Chen et al. 2001). Dual-chemical conditioning and dewatering has been proposed as an alternative to either lower the cost using a less expensive inorganic conditioner, at least in part, or improve dewaterability through the combination of chemicals (Lau et al. 2013; Kuglarz et al. 2008; Ozkan and Yekeler 2004; Lee and Liu 2001, 2000; Chitikela and Dentel 1998).

This study further investigates the potential of dual-conditioning of sludge using the nontoxic and biodegradable biopolymer chitosan to replace synthetic polymers, together with some cheaper metal cations as an economical and eco-friendly dewatering alternative. The concept of dual-conditioning is based on the hypothesis that destabilization can be accomplished by eliminating the charge barrier through cation addition. This allows small flocs to form, while the polymer’s bridging action serves to link these into substantially larger units. The addition of cations could supplement the more expensive polymer and neutralize a portion of the negative charge, and/or introduce additional
binding (for multivalent cations) in the sludge system.

Although there are many data on the dewatering behavior of sludge conditioned with either chitosan or cations, there have not, as far as we know, been any detailed studies apart from the authors’ previous work (Lau et al., 2013) on the effect of cation addition on sludge dewatering when used in conjunction with chitosan. The mechanisms governing the different dewatering performances of cations are not well understood, although they should be related strongly to the physicochemical properties of sludge, and the simultaneous interactions between sludge and the dual-conditioners. Therefore, this work was intended to determine those characteristics experimentally and addressed the lack of data in the area of interest.

METHODS
Materials
The septic sludge samples used in this study were supplied by Kiara Bumimas Sdn. Bhd., a local desludging contractor in Miri, Sarawak. They were stored at 4°C and brought to room temperature before use. The conditioning biopolymers used were low molecular weight chitosan (50,000-190,000 Da, Aldrich) and medium molecular weight chitosan (600,000-800,000 Da, Acros Organics) according to the polymer classification by Dentel (2010). They were prepared as 0.5% stock solutions by dissolving 0.5 g chitosan in 100 mL of 1% acetic acid solution. The inorganic conditioners used were laboratory grade chloride salts of sodium, potassium, magnesium, calcium, aluminum and ferric (trivalent) iron. They were prepared as 1.0% stock solutions.

Characterization of sludge
The sludge characteristics were determined using Standard Methods 2540 for total solids, as well as Standard Methods 2710 (APHA 2005) for capillary suction time (CST). The CST test was conducted using apparatus from Triton Electronics Ltd., UK, with a 1.8-cm diameter funnel. The measurement is done by determining the time taken to draw filtrate from a suspension by the capillary suction pressure generated from a standard CST filter paper (Triton 1998). Total dissolved solids (TDS), pH and temperature were measured using bench meters. The specific resistance to filtration (SRF) test was conducted using a simple laboratory filtration system as described by Novak (2001). Moisture content was determined by taking the weight of the filtered sludge cake before and after drying in an oven at 103 to 105°C over night. The sludge characteristics can be summarized as: pH 7.55; TS 23.2 g/L; TDS 0.6 g/L; CST 93.9 s; SRF 1.52 × 10¹⁴ m/kg; and moisture content of the filtered sludge cake 89.7%.

Conditioning and dewatering experiments
The conditioner was added to 100 mL of sludge at the predetermined dosage, expressed as the weight of conditioner over the weight of total solids in the sludge (g/kg), to study the “single conditioning” effect. The mixture was stirred at 500 rpm for 2 minutes and then 200 rpm for 5 minutes. To study “dual-conditioning”, the sludge was conditioned with simultaneous addition of chitosan and a metal salt under similar mixing conditions. All experiments were conducted at room temperature, 24±1°C, and neutral pH. The dewatering performance of the conditioned sludge was assessed immediately after mixing for the CST and SRF. The wet sludge cake after filtration dewatering was dried over night for moisture content determination. A decrease in these values indicates improvement in sludge dewaterability. Examination using these three parameters in combination could be a better gauge of sludge dewatering performance as the conditioned sludge could be easily filterable (with low CST and SRF), but still contain a high amount of residual water (indicated by high moisture content) as noted by Chen et al. (2001).

RESULTS AND DISCUSSION
Effect of molecular weight of chitosan and dosage
The relationship between the molecular weight (MW) and dosage of chitosan is presented in Figure 1. It can be seen that the medium MW chitosan shows greater reduction in CST at dosages between 2.5 and 10 g/kg than the low MW material. At dosages between 15 and 20 g/kg, there is no significant difference in CST reduction as both chitosans reach plateaus at an average CST
of 27.7 s. The SRF results match those for CST, showing a decreasing trend until they level off at a dosage of 20 g/kg.

Dentel (2001) suggests that the higher MW polymer consists of longer chains with more cationic sites which may bind to more than one particle, thus bridging the system of sludge solid particles. Thus a lower dosage of the medium MW chitosan can achieve higher dewaterability than the low MW chitosan used in this study. In addition, chitosan may be envisioned as a single cationic polymer attaching to a localized “patch” of sites and neutralizing the charge in this region. Two particles with such regions may mutually orient so that each patch is attracted to an unoccupied region on the opposing surface (Dentel 2010). Once all patches are occupied and polymer bridging has occurred, leading to the formation of a tightly bound floc matrix, increasing polymer dosage yields no further improvement in sludge dewaterability, as seen in this study. The excess polymer remains in solution due to the lack of charge attraction between it and the surfaces. This study suggests that restabilization did not occur when chitosan was added beyond the optimum dosage at 15 g/kg, as there was no deterioration in dewaterability. These findings are consistent with the authors’ previous work using anaerobic digested sludge (Lau et al. 2013).

Investigation of the moisture content of the filtered sludge cake reveals that varying the chitosan dose seems to have little effect on final water retention capacity, once it reaches an average of about 74%. The moisture content of the raw sludge was 97.7%, which indicates poor sludge dewaterability. After filtration dewatering, the moisture content of unconditioned sludge had fallen to 89.7%. With chitosan addition, the moisture content reduced significantly further to between about 73.5 and 75.7% for low MW and 71.4 and 75.0% for the medium MW material. The difference in moisture content was less than 4%, with slight variation at different doses. It is therefore concluded that increasing the chitosan dosage increases the dewatering rate (or the filterability of sludge), as indicated by the CST and SRF, results but does not further reduce the moisture content of the filtered sludge cake.
Figure 1. Effect of chitosan dosage on sludge dewaterability expressed in terms of (a) CST, (b) SRF, and (c) moisture content of filtered sludge cake
**Effect of dual-conditioning using chitosan and metal cations**

A fixed dose of 5 g/kg chitosan was selected for studying the dual-conditioning effect with different species of metal cation. It represents approximately one third of the optimum chitosan dose, based on the CST results in Figure 1(a). The aim was to assess the possibility of using the less expensive metal cation to supplement chitosan in sludge conditioning, to achieve a similar level of dewaterability.

Table 1 shows the changes in sludge dewaterability produced by different types and combinations of conditioners. Dual-conditioning of sludge using chitosan and metal cations contributed significantly to CST and SRF reductions in comparison with the use of either chitosan or metal cation(s) alone. The enhanced dual-conditioning effect was more noticeable for monovalent and divalent cations compared to trivalent cations. The effect of MW became less when chitosan was used in conjunction with cations. Nevertheless, dual-conditioning using a combination with the higher MW chitosan, generally showed marginally better dewatering performance.
### Table 1. Sludge dewaterability with single and dual-conditioners

<table>
<thead>
<tr>
<th>Type of conditioner</th>
<th>CST (s)</th>
<th>SRF × 10&lt;sup&gt;13&lt;/sup&gt; (m/kg)</th>
<th>Moisture content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unconditioned sludge</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>93.9</td>
<td>15.20</td>
<td>89.7</td>
</tr>
<tr>
<td>Low MW chitosan</td>
<td>35.0</td>
<td>1.71</td>
<td>73.5</td>
</tr>
<tr>
<td>Medium MW chitosan</td>
<td>29.4</td>
<td>1.06</td>
<td>74.3</td>
</tr>
<tr>
<td>NaCl</td>
<td>68.6</td>
<td>3.72</td>
<td>87.2</td>
</tr>
<tr>
<td>KCl</td>
<td>59.2</td>
<td>3.48</td>
<td>87.4</td>
</tr>
<tr>
<td>MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>54.7</td>
<td>3.26</td>
<td>87.0</td>
</tr>
<tr>
<td>CaCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>39.5</td>
<td>3.49</td>
<td>86.7</td>
</tr>
<tr>
<td>AlCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>16.4</td>
<td>1.95</td>
<td>82.7</td>
</tr>
<tr>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>12.0</td>
<td>1.86</td>
<td>83.5</td>
</tr>
<tr>
<td>Single conditioning (10 g/kg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low MW chitosan (control)</td>
<td>60.5</td>
<td>2.27</td>
<td>73.7</td>
</tr>
<tr>
<td>Dual-conditioning (5 g/kg chitosan + 10 g/kg metal cation)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>15.5</td>
<td>1.69</td>
<td>86.3</td>
</tr>
<tr>
<td>KCl</td>
<td>13.1</td>
<td>1.16</td>
<td>84.5</td>
</tr>
<tr>
<td>MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>12.0</td>
<td>0.70</td>
<td>82.3</td>
</tr>
<tr>
<td>CaCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>12.8</td>
<td>0.76</td>
<td>81.5</td>
</tr>
<tr>
<td>AlCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>9.3</td>
<td>0.57</td>
<td>79.4</td>
</tr>
<tr>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>9.3</td>
<td>0.42</td>
<td>81.2</td>
</tr>
<tr>
<td>Single conditioning (5 g/kg chitosan)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium MW chitosan (control)</td>
<td>44.5</td>
<td>1.40</td>
<td>71.4</td>
</tr>
<tr>
<td>Dual-conditioning (5 g/kg chitosan + 10 g/kg metal cation)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>12.5</td>
<td>1.32</td>
<td>80.4</td>
</tr>
<tr>
<td>KCl</td>
<td>12.9</td>
<td>0.74</td>
<td>80.3</td>
</tr>
<tr>
<td>MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>11.3</td>
<td>0.46</td>
<td>85.2</td>
</tr>
<tr>
<td>CaCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>11.5</td>
<td>0.56</td>
<td>80.1</td>
</tr>
<tr>
<td>AlCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>9.5</td>
<td>0.24</td>
<td>80.3</td>
</tr>
<tr>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>9.1</td>
<td>0.19</td>
<td>80.0</td>
</tr>
</tbody>
</table>

The comparison of cation effect on sludge dewatering performance is shown in Figure 2. Addition of Na<sup>+</sup> alone reduced the CST of raw sludge by 26.9% while dual-conditioning using chitosan and Na<sup>+</sup> reduced it by 83.5% and 86.7%, for the low and medium MW chitosans respectively. A similar trend was observed for K<sup>+</sup>. For the divalent cations, although Ca<sup>2+</sup> lowered the CST more than Mg<sup>2+</sup> in single conditioning, that effect diminished when it was used in conjunction with chitosan. Al<sup>3+</sup> and Fe<sup>3+</sup> generally yielded better dewaterability than the other cations. When used with chitosan, the improvement was less noticeable than for the other cations as the “sole” use of these trivalent species had demonstrated remarkable dewatering performance. Considering the equivalent concentrations and the respective dewaterability values from Table 1, the effectiveness of metal cation(s) in sludge conditioning and dewatering may be presented in
ascending order as: Na\(^+\) < K\(^+\) < Mg\(^{2+}\) < Ca\(^{2+}\) < Al\(^{3+}\) < Fe\(^{3+}\). Consequently dual-conditioning using chitosan and metal cations increased sludge dewaterability in a similar sequence. The improvement in sludge dewaterability observed was more significant than in the authors' previous work (Lau et al. 2013).

![Figure 2](image)

**Figure 2.** Effect of dual-conditioners on CST values, compared with raw sludge

A notable downside of dual-conditioning is that it cannot improve the moisture content of dewatered sludge to the extent achieved by single conditioning using chitosan. As shown in Table 1, conditioning with low MW chitosan reduced the moisture content from 89.7% (for dewatered sludge without conditioning) to 73.7% at a dose of 5 g/kg, while additional conditioning with metal cations yielded a moisture content range of 79.4 to 86.3%, depending on the cationic species. This study has revealed that dual-conditioning may enhance the rate of dewatering as indicated by the CST and SRF results, but the resulting sludge cake may contain more trapped water compared to single conditioning using chitosan.

**Mechanism of dual-conditioning**

The improvement in sludge dewatering properties due to cation addition could be explained by many things. In most cases, the addition of cations is expected to improve sludge dewaterability. The classical Double Layer or Derjaguin-Landau-Verwey-Overbeek (DLVO) theory describes charged particles as having a double layer of counter-ions surrounding them (Sobek and Higgins 2002). This double layer or cloud repels adjacent particles and inhibits aggregation. It is therefore anticipated that the addition of cations will increase the solution’s ionic strength and compress the double layer, thereby improving bio-flocculation, settling and dewatering properties. Several researchers have performed experiments that support the DLVO theory for the role of cations in bio-flocculation (Lau et al. 2013; Liu et al. 2012; Sobek and Higgins 2002; Lo et al. 2001; Cousin and Ganczarczyk 1998; Zita and Hermansson 1994).
on the other hand, there are different opinions on the effect of cation valency on the binding properties of negatively charged sludge particle surface, which in turn affects sludge dewaterability. Although monovalent cations such as Na⁺ and K⁺ lack a binding role within the sludge floc, Lo et al. (2001) believe that their presence in the sludge might cause a salting out effect, which in turn helps release bound water from the flocs to the bulk solution. Erdi clin and Vesilind (2000) also suggest that the biological sludge cells could be disrupted by Na⁺, so that water flows out and the cell tends to shrink due to the osmotic effect. Because of this, better dewaterability (decreases in CST and SRF) was observed with the addition of Na⁺ and K⁺. However, the moisture content of the filtered sludge cake did not show significant improvement, probably due to extra water-binding surfaces created by cell disruption, leading to a net increase in the vicinal water content of sludge samples.

For divalent cations, greater improvement in sludge dewaterability due to Mg²⁺ and Ca²⁺ addition could be due to the bridging of negatively charged functional groups in the sludge creating a more tightly bound floc matrix, as suggested by the Divalent Cation Bridging (DCB) theory (Sobeck and Higgins 2002). This suggests that divalent, rather than monovalent, cations can bridge negatively charged functional groups within the exocellular biopolymers or polymeric substances (EPS) present in sludge. Sludge dewaterability is closely related to sludge floc-forming ability. The results of this study show that Mg²⁺ and Ca²⁺ improve dewaterability (or filterability) as indicated by the CST and SRF results, which is believed to happen due to the improved floc formation according to the DCB theory. Ca²⁺ ions seem to have a more significant effect on dewaterability than Mg²⁺ ions. This is in agreement with the findings of Sanin et al. (2006), who studied cationic effects on dewatering properties in an activated sludge reactor, rather than during conditioning and dewatering processes.

According to Sanin et al. (2006), monovalent cations incorporated into flocs are believed to be mostly inside the cells rather than being in the EPS matrix, due to its osmotic function. On the other hand, Ca²⁺ is believed to remain mostly outside the cells, in the EPS matrix, while Mg²⁺ is thought to act somewhere in between. This may explain the enhancing dewaterability sequence of Na⁺ < K⁺ < Mg²⁺ < Ca²⁺ as observed in this work. In addition, the alginate theory proposed by Bruus et al. (1992) suggests that alginate may be present in sludge, and, since alginate aggregation is specific for Ca²⁺, the researchers infer that the better dewaterability demonstrated by Ca²⁺ arises from the greater affinity of the sludge suspension for Ca²⁺ than Mg²⁺ (Sobeck and Higgins 2002). In fact, Ca²⁺, in the form of lime, is commonly used as a conditioner in dewatering units to improve dewaterability, indicating that the positive effect of calcium has been known for a long time (Sanin et al. 2006).

Apart from lime, the other chemicals normally used in conditioning sludge are ferric chloride, and, less commonly, ferrous sulfate, ferrous chloride and aluminum sulfate (USEPA 1987). The mechanism of action for ferric and aluminum salts is well established and is not discussed in this paper. As shown in Table 1, superior dewaterability was observed as expected for trivalent cations Al³⁺ and Fe³⁺, with moderate improvement when dual-conditioned using chitosan. As pointed out by Dentel (2010), conditioning using ferric or aluminum salts alone is inadequate due to the properties of the iron or aluminum hydroxides, which are hydrophilic, amorphous, and compressible, leading to a slurry that retains water and yields under shear. Our results show that the addition of Al³⁺ and Fe³⁺ with chitosan can substitute a portion of the polymer dosage while still attaining excellent dewaterability with reduced CST and SRF, but at the expense of moisture content.

We have also found that dual-conditioning using chitosan and metal cations is effective with other types of sludge – e.g., anaerobic digested sludge, activated sludge, and synthetic sludge, as well as the septic sludge used in this work. There are more aspects to be explored in terms of the relationship between dewaterability, and rheological and physicochemical properties, as well as floc size and strength. Although the effect of the polymer’s MW in dual-conditioning seems nominal in terms of filtration dewatering for this study, it should be noted that a lower MW polymer provides
efficient flocculation but much lower floc resilience than a higher MW polymer, which is important for high-shear separation processes (Dentel 2010). In addition, floc strength may suffer to some extent due to the partial substitution of polymer by metal cations in dual-conditioning. Further studies should also look into the dual-conditioning effect in high-shear dewatering operations – e.g., centrifugation.

CONCLUSIONS
This study affirms an encouraging improvement in sludge dewaterability when chitosan and metal cations are used in the dual-conditioning of sludge. The results indicate a higher rate of water removal at the expense of moisture content as compared to the use of chitosan alone. The improvement was more obvious for the combination of chitosan with monovalent and divalent cations. It is thought that neutralization of the sludge surface charge, bridging of the colloidal particles and salting out arising from the addition of cations, all contribute to the enhanced dewatering performance, along with polymer bridging induced by chitosan. Thus it is possible to improve sludge dewaterability by dual-conditioning using chitosan with metal cations, to reduce the polymer demand, as well as to address concerns about polymer toxicity.

REFERENCES
Design Manual: Dewatering Municipal Wastewater Sludges 1987, U.S. Environmental Protection Agency, USA.
Bioleaching Approach with Comparison to Other Physical and Chemical Conditioning Methods. *Journal of Environmental Sciences*, **24**(8), 1403-1410.


