Potential use of Titanium Tetrachloride as Coagulant to Treat Semi Aerobic Leachate Treatment

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ARTICLE INFO
Article history:
Received 11 October 2014
Received in revised form 21 November 2014
Accepted 25 December 2014
Available online 16 January 2015

Keywords:
Titanium tetrachloride, Coagulation, Removal, Stabilized leachate.

ABSTRACT
Background: Coagulation is a relatively simple physical–chemical technique in the treatment of an old and stabilized landfill leachate. A variety of conventional coagulants has been widely used. Objective: This research aimed to investigate the capability of Titanium tetrachloride (TiCl4) in the treatment of stabilized leachate. Results: The leachate was first characterized. The leachate was high in colour 4253 PtCo., suspended solids 330 mg/L, ammonia 4.4 mg/L and UV254 0.017 cm-1. Standard jar test was conducted to determine the optimum pH and coagulant dosage. At the optimum pH 6, the optimum dosage was 600 mg/L which corresponds to 81.4%, 86.7%, 58.4% and 76.5% removals for colour, suspended solid, ammonia and UV254 respectively. Conclusion: Titanium tetrachloride is potential to be used as coagulant in semi aerobic landfill leachate treatment.

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INTRODUCTION

Leachate can lead to serious environmental problems if not handled properly. Leachate disposal is one the most persistent and expensive long-term challenges affecting the solid waste industry. There are a lot of methods in treating landfill leachate. (Renou et al, 2008). Coagulation is one of the common methods used. The coagulant that was generally used are Aluminium Sulphate (Al2(SO4)3) and Ferric Chloride (FeCl3). However, these two coagulants are normally used to treat surface water. The new coagulant Titanium Tetrachloride, TiCl4 has been chosen in this study to treat leachate. It is because TiCl4 has some significant advantages such as the possibility of recovering the sludge to produce a valuable product, namely titanium dioxide (TiO2) (Shon et al, 2009). The Malaysian government has introduced recycling campaign to reduce the solid waste generation due to the population growth in the country. However the recycling program not able to balance the increased solid waste generation due to the rapid population growth. As a result, more sanitary landfills need for solid waste disposal. In conjunction with the increasing number of landfills, leachate treatment has become an important issue. Previous studies have been conducted for leachate treatment in wastewater treatment using constructed wetlands (Rash and Liehr, 1999). Nevertheless, this technology is not utilised in Malaysia. Thus study is required to develop leachate treatment facilities using constructed wetlands by incorporating local components and expertise. The leachate treatment and disposal can represent one of the largest operational costs incurred by a landfill. Even though leachate treatment costs per gallon are often measure in fractions of a cent, the potentially large quantities of leachate generated at even a moderately sized landfill can tally up to a significant monthly fee (Mott et al., 1987).

Leachate production by its very nature is unpredictable and is dependent on such multiple variables as climate, season, type of cover, or thickness of waste. Therefore, leachate production cannot be projected or estimated but it has to be directly measured on a continuous basis (Tatsi and Zouboulis, 2002). Hazardous and non-hazardous landfills may produce leachate that has elevated concentrations of contaminants, such as ammoniacal nitrogen, heavy metals and organic compounds (Lu et al 1985). These could, if not contained and managed, affect both surface and groundwater resources if it is not managed properly.

Various coagulants had been used for leachate treatment. Alum, FeCland PACL are among the 3 valence metal salts (Morari and Ghanbari, 2014; Ghafari et al, 2009). Application of 4 valence state of metal salts has...
not been widely reported. Hence, this research aimed to investigate the potential use of TiCl$_4$ as a coagulant to treating landfill leachate sample from PBLS which was taken as the case study site. The objective of this research is to effectiveness of Titanium tetrachloride coagulation process in treating stabilized landfill leachate under optimum operational conditions.

MATERIALS AND METHODS

2.1 Leachate sampling and characteristics:

Leachate samples were collected from a leachate aeration pond of a semi-aerobic stabilized landfill leachate at the Pulau Burung Landfill Site (PBLS), Byram Forest Reserve, Penang, Malaysia. The PBLS has an area of 62.4 ha, of which 33 ha are currently operational, receiving approximately 2200 t of municipal solid waste daily. The site is equipped with a natural marine clay liner and three leachate collection ponds (Bashir et al., 2011). Approximately 20 L of leachate was manually collected and placed in plastic containers. The samples were immediately transported to the laboratory, characterized, and cooled at 4 °C to minimize the biological and chemical reactions. The average characteristics of the leachate used in the experiments are summarized in Table 1. Sample collection and preservation were performed in accordance with the Standard Methods for the Examination of Water and Wastewater (American Public Health Association (APHA), 2005).

2.3 Composition of Leachate:

Table 1: Characteristics of raw leachate of Pulau Burung Landfill Site (PBLS).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>25–31</td>
<td>2.7</td>
</tr>
<tr>
<td>pH</td>
<td>8.2–8.5</td>
<td>8.4</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>1794–2094</td>
<td>1925</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>38–96</td>
<td>80</td>
</tr>
<tr>
<td>NH$_4$-N (mg/L)</td>
<td>1070–1300</td>
<td>1184</td>
</tr>
<tr>
<td>Color (Pt. Co.)</td>
<td>3640–4100</td>
<td>3869</td>
</tr>
<tr>
<td>Turbidity (FAU)</td>
<td>268–502</td>
<td>347</td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO$_3$)</td>
<td>4260–5510</td>
<td>5093</td>
</tr>
</tbody>
</table>

2.2 Experimental procedures:

In this experiment, coagulant is needed to mix with the samples. The coagulant used is TiCl$_4$. Before the jar test proceeds, the concentration of TiCl$_4$ dosage is determined. It is important because it will give the benchmark to pick the optimum pH value and dosage value. The concentration of TiCl$_4$ ranged between 10 mg/L and 5000 mg/L. TiCl$_4$ is a high purity chemical in liquid form at standard temperature and pressure. TiCl$_4$ has a melting point of -24.1°C. TiCl$_4$ is not an explosive, not oxidizing and not self-ignitable. (Dupont. Titanium Tetrachloride, 2011). Concentration of TiCl$_4$ must be determined at the early stage before conducting the coagulation treatment. During this treatment, the dose of TiCl$_4$ chosen was 1728 mg/L. This concentration of TiCl$_4$ is dissolved in acidic solution. It is because the TiCl$_4$ is extremely volatile when exposed to the air and water. Hence Hydrochloric Acid, HCl was used to dissolve the TiCl$_4$. The optimum pH value is determined by using the same dosage of coagulant. Six beakers are filled with the leachate for 500 ml. The pH value must be set each of the beaker which are pH4, pH5, pH6, pH7, pH8 and pH9. The pH was adjusted using Hydrochloric acid (HCl) and Natrium Hidroxide (NaOH). The concentration of HCl and NaOH are 3 molar. The samples are placed into jar test floc tester (VELP- Scientifica, Model J LT6, Italy). Samples is mixed with high speed (250 rpm) for 5 minutes. The speed is reduced to 60 rpm and the mixing is continued for 30 minutes. Later flocs are allowed settle for 20 minutes. (Ghafari et al., 2009). The jar test floc tester can be seen in Figure 1.

Figure 1: Jar test floc tester. (J LT6).

2.3 Analytical methods:

Color, NH$_4$–N, Suspended solid (SS) and pH were immediately tested before and after each run of the experiments in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA, 2005). The NH$_4$–N concentration was measured by the Nessler Method using a HACH DR 2500
spectrophotometer. The pH was measured by a portable digital pH/MV meter. COD concentration was determined by the closed reflux colorimetric method using a DR2500 HACH spectrophotometer. Color concentration was measured using a DR 2600 HACH spectrophotometer. Suspended solid was measured by using the same DR2800 HACH spectrophotometer. Some of the samples need to be diluted with a dilution factor from 100 to 200. Suspended solids was measured in unit of mg/L according to the Method No. 2540D. The removal efficiency of COD, color, and ammonia were obtained using the following equation:

\[
\text{Removal} \, (\%) = \left(\frac{C_i - C_f}{C_i}\right) \times 100
\]

where \(C_i\) to \(C_f\) refer to the initial and final, color, ammonia and suspended solid (SS), respectively.

RESULTS AND DISCUSSIONS

This section discusses the performance of Titanium Tetrachloride (TiCl₄) as a coagulant for treating landfill leachate based on the laboratory test results. The removal efficiencies for leachate parameters include ammonia, colour, suspended solid (SS) and UV₂₅₄ were measured. The test results obtained are also compared with other works in order to assess the general performance of the coagulant tested.

3.1 Optimum pH:

The result of the influence of pH on colour concentrations is given in Figure 2. Based on the graph, the intensity of colour slightly decreases from pH 4 to pH 6 and increases thereafter. This happens to all the TiCl₄ concentrations examined. Detailed results are given in Appendix A. This indicates that the TiCl₄ reacts more effectively on colour. All of the colour concentration value was steadily decreasing until pH 6 and slightly increase after pH 6. Hence, pH6 was chosen as the optimum pH in the subsequent experiments. Figure 3 shows the influence of pH on suspended solid concentrations with three different TiCl₄ concentrations.

Figure 3: The influence of pH on suspended solid at different TiCl₄ dosage 10 mg/L, 100 mg/L and 200 mg/L.

Based on Figure 3, the graph shows that the suspended solid value is decreasing after dosage is added into the leachate. Detailed results are given in Appendix B. The lowest suspended solid value was 122 mg/L at dosage 200 mg/L which at pH 6. All dosage produced the lowest value of the suspended solid value of pH 6. Hence, pH 6 was chosen as the optimum pH in the subsequent experiment. The result of pH influence on ammonia concentrations is given in Figure 4.

In Figure 4, there’s only two different concentrations used because the result of ammonia content is not stable like colour and suspended solid. The raw ammonia content has been diluted by 200 ml distilled water by 1 ml of raw ammonia. The result is high compared to the characterization of ammonia content in Appendix C. Based on the result of ammonia content, there’s no exact optimum pH can be selected because the curved of the plot not constant compared to the colour and suspended solid. The optimum pH has been selected using the color and suspended solid result which is pH 6.

Fig. 2: The influence of pH on colour at different concentration of TiCl₄ 10 mg/L, 100 mg/L and 200 mg/L.

3.2 Optimum Dosage:

The optimum dosage was examined at the optimum pH, which was determined previously. Trial and error method was conducted to find the optimum dosage, the range examined was 250mg/L, 300 mg/L, 400 mg/L, 450 mg/L, 500mg/L, 600mg/L, 700mg/L and 800mg/L. The result of the dosage influence of color is given in Figure 5. Based on Figure 5, the colour content is slightly decrease as the dosage was increased. As the intensity of the colour decreases, the colour of the leachate will become lighter compared to the colour of raw leachate. The lower value of colour content, the colour of leachate might be more lighter. However, the graph is slightly increased after 600 mg/L of TiCl₄. The colour value at dosage 600 mg/L was 802 Pt co. Detailed results are given in Appendix D. This shows that the optimum dosage is at 600 mg/L. The result of the dosage influence of suspended solid is given in Figure 6.

Fig. 5: The influence of pH on suspended solid at different of TiCl₄ dosage 10 mg/L, 100 mg/L and 200 mg/L.
Fig. 4: The influence of pH on ammonia at different dosage of TiCl$_4$ 10 mg/l and 100 mg/L.

Figure 4.5 shows that the optimum dosage was 600 mg/L which is 44 mg/L of suspended solid. Detailed results are given in Appendix D. It is shown that suspended solid had been removed from the raw leachate steadily until the dosage 600 mg/L. However, the suspended solid removal is increased after dosage 600 mg/L to 800 mg/L. It shows that the optimum dosage for suspended solid is 600 mg/L which has the lowest removal of suspended solid.

The result of dosage influence of on ammonia is given in Figure 6. In Figure 6, the ammonia removal did not show the required optimum dosage. The ammonia content is decreasing steadily from 3.25 to 1.83. Detailed results are given in Appendix D. In that case, the ammonia content is neglected from the optimum dosage because this parameter is a critical part to deal affected by the aging of leachate. It can be concluded from the plots from Figure 4.4, 4.5 and 4.6 the optimum dosage from this experiment is 600 mg/L.

After determining the optimum pH and optimum dosage, the removal efficiencies can then be determined. Figure 7 compares the removals for colour and suspended solid. The reduction of ammonia was negligible due to very low removal.

It can be seen from the plot that at concentration 200 mg/L, the colour removal efficiencies at pH 4 is 58.93% which is more than 50%. Detailed results are given in Appendix E. The removal efficiencies increases steadily from pH 5 to pH 6 with 62.19% to 68.00%. From the result, pH 6 produced the highest removal which is 68%. After pH 6, the removal efficiencies started to decrease until 7.4% at pH 9.

The removal pattern exactly follows the same pattern as the case of colour removal. The removal efficiencies started at pH 4 which is 62.61%. The removal is slightly higher than the color removal at pH 4. The removal also increased at pH 5 and pH 6 which 67.42% and 68.56%, respectively. The removal is starting to decrease after pH 6 and drop to 21.25% at pH 9. However, this experiment was only conducted to determine the desired optimum pH. Three different dosages have been examined to compare whether the optimum pH differs. As there was no difference after the experiment, pH 6 was taken as the optimum as it gave highest removal.

Figure 8 shows the removal efficiencies at optimum dosage and pH 6. The removals for colour, suspended solid and ammonia were compared. The removal of colour at 250 mg/L dosage of TiCl$_4$ produced 68.26%. This is lower than 90% reduction obtained by Ghafari, et al., 2009 who worked on PACI.

The removal seems to increase with an increase in the dosage of TiCl$_4$ is the highest removal of color is 81.43% occurred at 600 mg/L dosage. The removal starts beyond 700 mg/L to 800 mg/L, with 77.03% and 76.49% removal, respectively. The removal might be decreased because the coagulant has reached the optimum dosage needed for the leachate which is at 300 mg/L dosage. The result is slightly a little bit lower compared to previous research which has minimum 90% removal of colour. (Ghafari et al., 2009)

The suspended solid also produce exactly the same plot as colour removal based on Figure 4.8. The removal at the 250 mg/L dosage is 79.39%. Detailed results are given in Appendix F. The removal is slightly higher compared to colour removal at 250 mg/L dosage. The removal also increases with increase in the dosage. The highest removal of suspended solid is 86.67%. It can be seen in Figure 4.9 that the colour and suspended solid changed after completing the experiment.
Figure 8 also shows the removal of ammonia by using the same dosage as colour and suspended solid. Trial and error method has been made for the removal of ammonia because there was no removal recorded at the optimum pH. It should be noted that ammonia was not widely investigated in coagulation experiment of leachate to its high concentration which may be contributed by the aging factor. (Ghafari et al., 2009). The removal of ammonia at 250 mg/L dosage is much more lower (26.14%) compared to the removal of colour and suspended solid. The removal increases at higher coagulant dosages. For example, at 400 mg/L the removal is 37.8% and increased to 58.4% at 600 mg/L. It increases further thereafter. Detailed results are given in Appendix F.

The UV$_{254}$ test was only examined at optimum pH and optimum dosage. The UV$_{254}$ of raw leachate was 0.017 cm$^{-1}$. The value after treatment which accounts to 76.47% removal. This is higher than 65-71% reduction as obtained by Okour et al., 2007.

The summary of results is given in Table 2.

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**Fig. 5**: Colour intensity using different concentrations at TiCl$_4$ at pH6.

**Fig. 6**: Concentration of suspended solid using different concentrations of TiCl$_4$ at pH6.

**Fig. 6**: Ammonia concentration using different dosages of TiCl$_4$ of ammonia at pH6.
Fig. 7: Comparison removal efficiencies between colour and suspended solid for optimum pH at dosage 200 mg/L.

Fig. 8: Comparison removal efficiencies between colour, suspended solid and ammonia for optimum dosage at pH 6.

Table 2: Summary of coagulation experimental results.

<table>
<thead>
<tr>
<th>Optimum conditions</th>
<th>Concentration levels and removal</th>
<th>Suspended Solids (mg/L)</th>
<th>Ammonia (NH₃)</th>
<th>Colour (Pt. Co) UV-254 (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rapid mixing 250 rpm for 3 minutes, Slow mixing 60 rpm for 30 minutes, pH 6, Dose of TiCl₄ 600 mg/L</td>
<td>Maximum concentration before experiment</td>
<td>330</td>
<td>4.40(after Diluted with 200ml distilled water)</td>
<td>4253</td>
</tr>
<tr>
<td></td>
<td>Maximum concentration after experiment</td>
<td>44</td>
<td>1.83(after Diluted with 200ml distilled water)</td>
<td>802</td>
</tr>
<tr>
<td></td>
<td>Removal (%)</td>
<td>86.67</td>
<td>58.41</td>
<td>81.43</td>
</tr>
</tbody>
</table>

4. Conclusions:
Titanium Tetrachloride, TiCl₄ was investigated as potential coagulant to treat semi-aerobic leachate. It was found from the study that pH6 was the optimum pH that exhibited highest removals for suspended solid 86.67% and colour 81.43%. However, TiCl₄ did not work well for ammonia with the removal percentage of less than 60%. The removal efficiencies for the colour and suspended solid the optimum pH and 200 mg/L TiCl₄ were 68% and 68.56% respectively. The removal efficiencies, increased with an increase in the dosage of TiCl₄ up to 600 mg/L. The highest removal for colour and suspended solid were 81.43% and 86.67%, respectively at 600 mg/L. The removal of ammonia at the same pH and dosage was 58.41%.

It can be concluded from this study that TiCl₄ is potential to be used as coagulant in semi-aerobic leachate treatment.

ACKNOWLEDGMENT

The authors wish to acknowledge the School of Civil Engineering at university Sains Malaysia for facilitating and supporting the present work by Post-doctoral fellowship.

Authors’ Contribution:
Prof. Dr. Hamidi Abdul Aziz and Muhamad Yatim Bin Rosli developed the idea and had an important role in the result and material section. Dr. Salem S. Abu Amr performed the statistical analysis, the discussion and the abstract submission.

Financial Disclosure:
There is no conflict of interest.
Funding/Support:
This work is funded by Universiti Sains Malaysia under Iconic grant scheme (Grant no. 1001/CKT/870023) for research associated with the Solid Waste Management Cluster, Engineering Campus, Universiti Sains Malaysia.

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