Treatment of leachate by coagulation-flocculation process using polyaluminum chloride (PAC) and tapioca starch (TS)

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Abstract. Coagulation-flocculation is commonly used in the leachate treatment. The objectives of this study were to determine the optimum conditions (dosage and pH) and to compare the performances between single coagulants (polyaluminium chloride (PAC) and tapioca starch (TS)) and dual coagulant (PAC+TS) through a series of jar test. The highest percentage removal by PAC at the optimum conditions as a single coagulant (dose 2.5 g/L at pH 7) in terms of suspended solids (SS), turbidity, colour, chemical oxygen demand (COD), and ammonia was 92 %, 77 %, 94 %, 37% and 32 %, respectively. While for TS coagulant, at the optimum conditions (dose 2.5 g/L at pH 8), the percentage removal of SS, turbidity, colour and ammonia at pH 8 was 35%, 13%, 30% and 38% removals respectively. Thus, PAC performed better than TS as a single coagulant. While in dual coagulant, the percentage removal of SS, turbidity, colour, COD and ammonia of dual coagulant at optimum condition (dose PAC 1.5 g/L and dose TS 0.2 g/L at pH 5) was 90%, 74%, 87%, 40%, and 17%, while the percentage removal of single PAC (dose 1.5 g/L at pH 5) was 69%, 31%, 85%, 28%, and 13%, respectively. The addition of TS at a dose of 0.2 g/L into 1.5 g/L of PAC at pH 5 was able to achieve more percentage removal than single PAC and TS. This showed that the dosage of chemical coagulant could be reduced by 40% (2.5 g/L to 1.5 g/L) and indirectly reduced the drawbacks without affecting its efficiency.

1. Introduction

Leachate is a water contaminant originated from municipal solid waste that produces blackish liquid, which can enter the landfill through precipitation [1]. If the generated leachate is not properly treated and does not comply the standard of discharge requirements, the movement of leachate into the groundwater will pollute the clean water resources and increase the toxic level in the soil. Leachate affects the natural environment because of its hazardous compositions (heavy metal, ammonia, and bacteria) [2]. Normally, leachate enters the groundwater where it is mixed with clean water through several processes such as chemical precipitation, microbial degradation, and sorption [3].

Leachate is a toxic liquid, it must be treated properly and discharged safely or it could be a potential threat to soil, groundwater, and surface water [4], [5]. Furthermore, the low concentration of ammonia is destructive to aquatic life [6]. Therefore, the appropriate leachate treatment is important. Usually, the treatment of leachate needs a various combination of methods to achieve the highest removal of impurities. Example of the current methods is aerobic and anaerobic biological processes,
chemical oxidation and precipitation, photo-oxidation and membrane process, activated carbon and absorption, and coagulation and flocculation processes [7]. One simple technique and most widely used in physical and chemical treatment for leachate treatment is a coagulation-flocculation process. It works as a separation process of the impurities especially suspended and dissolved solids. The main removal mechanism in this process is charge neutralization of stable colloidal particles (negatively charged) by chemical coagulant (positively charged), and then the stable colloids are precipitated through flocculation [8].

The chemical coagulants are widely used as primary coagulant due to its availability that shows good efficiency. The common chemical coagulant used as a primary coagulant is such as alum and ferric chloride due to its cheaper price and easily available at local market [9]. However, many researchers found that the chemical coagulant caused secondary pollution and produced toxic sludge [10], [11]. Due to negative drawbacks of chemical coagulants, the natural coagulants are widely explored and used as next-potential coagulants [12]. Thus, in order to reduce the dosages and drawbacks of chemical coagulants, the application of dual coagulant by using natural coagulant is suggested. Natural coagulants normally originated from the animal-based, plant-based, microorganisms, and bacteria. It is widely used in the flocculation process to enhance the formation of micro flocs to macro flocs [13]. However, the effectiveness of natural coagulant as a primary coagulant is moderate and has a short shelf life. Thus, in order to combine the best properties of both chemical and natural coagulants, the application of dual coagulant is suggested. PAC is selected as a primary coagulant since it has better efficiency at a lower dosage and applicable at wider pH values compared to the conventional coagulant. While TS is available in abundance, cheaper, and environmentally friendly, is used as coagulant aids. The utilization of natural coagulants as coagulant aids in dual coagulant method able to improve the efficiency of coagulation process, reduce the dosage of chemical coagulants, and indirectly reduce the pollution and cost to treat the sludge [14]. Therefore, the scope of this works was to study the effectiveness of PAC and TS as a single and dual coagulants in removing SS, turbidity, colour, COD and ammonia of leachate by the coagulation-flocculation process under the influences of leachate pH and coagulants’ dosages.

2. Materials and methodology

2.1. Leachate sampling and characterization

Simpang Renggam landfill is located at Kluang district. The latitude of the landfill site is 10°53’41.64” North and longitude 103°22’34.68” East. The characterization of leachate sample was analysed as shown in table 1. Since the leachate could be categorized as old leachate, the suitable and selected treatment method for this study was coagulation-flocculation, which categorized as physical-chemical treatment [15]. All analytical procedures were performed according to the Standard Method of Water and Wastewater APHA (2012) [16].

| Parameter       | Experiment value |
|-----------------|------------------|
| Age (years)     | 12               |
| pH              | 7.6 – 8.3        |
| COD (mg/L)      | 1836-2150        |
| BOD5/COD        | 0.085            |
| Ammonia (mg/L)  | 692- 1272        |
| SS (mg/L)       | 78-268           |
| Turbidity (NTU) | 84-244           |
| Colour (Pt.Co)  | 4700-6100        |

* sampling duration (January – April 2017), number of samples (12)
2.2. Experimental procedure
The jar test experiment was carried out for different pH values of leachate and different doses of chemical coagulant (PAC) and natural coagulant (TS). Firstly, the jar test was run for a single coagulant to find the optimum dose of PAC and pH of the leachate sample. The sodium chloride and sulphuric acid were used to adjust the pH of the leachate. The pH value, colour, suspended solids, turbidity, COD, and ammonia of the leachate were measured before and after treatment. The 500 ml of leachate sample was filled into six different beakers. The prescribed dose of coagulant was added to each jar except for the control sample. If a coagulant aid was required, it was added to each jar at beginning of slow mixing. The used constant factors in the jar test were shown in table 2. While the percentage removal was determined by using equation 1.

Table 2. Constant jar test factor [17].

| Factors                | Value |
|------------------------|-------|
| Rapid mixing (rpm)     | 200   |
| Rapid mixing duration (minutes) | 4     |
| Slow mixing (rpm)      | 30    |
| Slow mixing duration (minutes) | 15    |
| Settling time (minutes) | 30    |

Percentage removal = \( \frac{\text{Initial concentration} - \text{Final concentration}}{\text{Initial concentration}} \times 100\% \)

3. Results and discussion

3.1. Optimum pH and dose for PAC as a single coagulant
The initial step of the experiments was carried out with the optimization doses of PAC as a single coagulant. Doses of PAC with a range of 0.5 g/L – 5.0 g/L and pH 7 were used as shown in figure 1. From the graph, the highest percentage removal for SS, turbidity, colour, COD, and ammonia was recorded at the dose of PAC 2.5 g/L with 92 %, 77 %, 94 %, 37%, and 20 % removal, respectively. Thus, the dose of PAC at 2.5 g/L was selected as the optimum dose for single PAC due to the higher percentage removals recorded. Experiment on different pH values of the sample was carried out between 3 to 9. Results of the experiment were shown in figure 2. From the graph, the results of percentage removal at pH 6 and 7 showed the highest removal. The percentage removal of SS, turbidity, colour, COD, and ammonia for PAC at pH 6 was 90%, 55%, 79%, 31%, and 18%, while for PAC at pH 7 was 89%, 74%, 89%, 33%, and 19%. Hence, the optimum pH of PAC as a single coagulant in this study was selected at pH 7 due to higher removal in term of turbidity, colour, COD, and ammonia.

Figure 1. Effect of PAC dose at pH 7.
As comparison for single PAC as shown in table 3, a study by Ghafari et al., [18], found that the PAC at a dose of 1.9 g/L and pH 7 was able to remove 99% of SS, 97% of colour, 99% of turbidity, and 57% of COD. A study by Zainol et al., [19], found that the dose of PAC at 7.2 g/L and pH 7.5 was able to remove 95% of SS, 80% colour, and 50% of COD. An investigation by Rusdiza et al., [20], showed the chemical coagulant PAC at a dose of 1.5 g/L and pH 6 was able to remove 95% of SS, 99% of turbidity, 96% of colour, 63% of COD, and 46% of ammonia. While this study found the optimum dose and pH of PAC at 2.5 g/L and pH 7 respectively. The percentage removal recorded for SS, turbidity, colour, COD, and ammonia was 92%, 77%, 94%, 37% and 20% respectively as showed in table 3. When compared the results from this research with the study by Ghafari et al.,[18] and Rusdiza et al.,[20] the removal recorded for this study were slightly lower in term of all removals probably due to different concentration of leachate. However, when compared with the study by Zainol et al., [19], the percentage of removal did not have much different but the dose required in this study was much lower. The difference of percentage removal probably due to the composition of the leachate sample, different mixing energy and settling time used. Thus, the result of coagulation by single PAC was in line with other studies in term of percentage removals, range dose and pH.

3.2. Determination of optimum pH and dose for TS as a single coagulant
In case of optimum dose of TS as a single coagulant, the dose of TS at the range of 0.1 g/L – 3.2 g/L and pH value 7 were tested as shown in figure 3. The highest percentage removal of SS, turbidity, colour, COD, and ammonia was detected at dose 2.5 g/L with 36%, 4%, 24%, 0%, and 18% respectively. The highest removal was recorded at pH 3 with the same dose of PAC at 2.5 g/L where the percentage removal for SS, turbidity, colour, COD, and ammonia was 88%, 78%, 79%, 28%, and 38% respectively as shown in figure 4. However, for real application on site, pH 3 is not applicable due to the high volume of reagent used in adjusting the pH. Percentage removal by TS between pH 4 – pH 10 was analysed, then pH 8 has been selected as optimum pH for single TS. Moreover, pH 8 required less reagent used in adjusting pH from the raw leachate (pH 7.6 – 8.79). The percentage removal of SS, turbidity, colour, and ammonia at pH 8 was 35%, 13%, 30% and 38%, respectively.
The usage of TS in leachate treatment is not yet widely explored and has limited information to be used as the comparison as shown in table 3. A study by Zin et al., [21], the dose of TS at 2.5 g/L and pH 4 removed 12% of SS, 55% of colour, and 13% of ammonia [22]. Another study by Mohd-Faiz-Muaz et al., [22], by using starch from durian seed at a dose of 4.0 g/L and pH 4, the removal recorded for turbidity and colour was 37% and 34% respectively. While, this study found that removal of SS, turbidity, colour, COD, and ammonia at optimum dose and pH (2.5 g/L and pH 8) of tapioca starch (TS) was 35%, 13%, 30%, 0%, and 38% respectively. While in terms of percentage removal, this study showed the highest removal of SS and ammonia. A comparison with [22] showed that TS was more effective at a lower dosage and had recorded higher removal than durian starch. Both studies recorded optimum pH at 4 and this study also found the highest removal at the acidic condition which is pH 3. However, the pH 3 is not acceptable to the real application. The removal at pH 4 in this study was not much different from pH 8. Thus, due to pH of raw leachate is between 7.6 – 8.79, the pH 8 had been selected as the optimum pH of TS. The obtained results of percentage removal at optimum dose and pH were consistent with the previous studies.

3.3. Optimum pH and dose for PAC and TS as a dual coagulant
The experiment was carried out with a range doses of TS at 0 – 3.6 g/L and fixed dose of PAC at 2.5 g/L (optimum dose from single coagulant) as shown in figure 5. From figure 5, the highest percentage removal for SS, turbidity, colour, COD, and ammonia was recorded at dose of TS 0.2 g/L and PAC 2.5 g/L at pH 7 where the percentage removal was found at 92%, 53, %, 92%, 40%, and 21% respectively. Fewer removals in term of turbidity and colour were recorded when compared with single PAC. The
removal recorded for single PAC (dose of 2.5 g/L at pH 7) was 77% and 94%, while for dual coagulant, the percentage removal was 53% and 92% respectively. On the other hand, COD and ammonia removals were increased from 37% to 40% and 19% to 21% respectively. Percentage removal in term of SS remained the same at 92% for both coagulants. The addition of TS at 0.2 g/L as coagulant aid into PAC at the optimum dose of 2.5 g/L increased the removal of COD but reduced the removals of turbidity and colour. Probably, application of TS induced the unsettled microparticles of TS causing an increment of turbidity and colour. Compelling this into consideration, the experiment was continued by varied pH of the samples and fixed dosage of PAC at 2.5 g/L and TS at 0.2 g/L.

Figure 6 shows the percentage removal for dual coagulant at a fixed dose of PAC at 2.5 g/L and fixed dose of TS at 0.2 g/L with varied pH values. Not much different removal of SS, turbidity, colour, COD, and ammonia was recorded between pH 5 (90%, 73%, 77%, 31%, and 19%), pH 6 (89%, 64%, 84%, 33%, and 18%) and pH 7 (87%, 52%, 86%, 32%, and 15%). However, pH 5 showed the highest percentage removal in term of SS, turbidity, and ammonia. Thus, pH 5 had been selected as the optimum pH for dual coagulant. The experiment was continued with fixed pH at 5, fixed dose of TF at 0.2 g/L, and the varied dose of PAC at 1.5 – 3.5 g/L as shown in figure 7. The removal of SS, turbidity, colour, COD, and ammonia for dual coagulant at dose of PAC at 1.5 g/L (90%, 74%, 87%, 40%, and 17%) and 2.0 g/L (93%, 77%, 64%, 36%, and 13%) was slightly close.

The application of dual coagulant (PAC 1.5 g/L + TS 0.2 g/L, SS:90%, turbidity:74%, colour:87%, COD:40%, and ammonia:17%) required lower dosage compared with the optimum dosage of single PAC at 2.5 g/L and pH 7 (92%, 77%, 94%, 37%, and 22%) and single TS at dose of 2.5 g/L and pH 8 (35%, 13%, 30%, 0%, and 38%) respectively. However, the percentage removal of optimum dual coagulants was lower than the optimum single PAC, but the percentage difference of removal was less than 5% and due to the dual coagulant that required a lower dosage. Application of dual coagulant made from PAC and TS was able to reduce the dose of chemical coagulant by 40% (2.5 g/L of single PAC and 1.5 g/L of dual coagulant of PAC and TS). Thus, the dose of TS at 0.2 g/L and the dose of PAC at 1.5 g/L and pH 5 had been selected as the optimum dose and pH for dual coagulant (PAC + TS).

Figure 5. Percentage removal by dual coagulant - PAC (2.5 g/L), TF (0-3.6 g/L) at pH 7.
As for the dual coagulant method, it was compared with a study by Rui & Latif [3] that used dual coagulant (PAC + cationic/anionic polymer) (Table 3). It showed that the addition of small amount of coagulant aids (cationic/anionic polymer) was able to improve the coagulation efficiency of single coagulant PAC [3]. The removal of single coagulant PAC (2.0 g/L at pH 7, COD: 49% and ammonia: 29%) increased after the addition of small amount of cationic polymer (2.0 g/L + 0.01 g/L at pH 7, SS: 99%, colour: 89%, COD: 59%, and ammonia: 49%) and anionic polymer (2.0 g/L + 0.01 g/L at pH 7, COD: 59%, and ammonia: 49%). While in this study, the removal of single PAC (2.5 g/L at pH 7, SS: 92%, turbidity: 77%, colour: 94%, COD: 37%, and 20%) was slightly decreased after dual coagulant (PAC 1.5 g/L + TS 0.2 g/L at pH 5, SS: 90%, turbidity: 74, colour: 80%, COD: 40% and ammonia: 17%). However, the decrement of removal was not much different and in term of coagulant dose, dual coagulant required a lower dosage. This showed, with the addition of small coagulant aids could improve or reduce the percentage removal of several parameters and decreased the dose of chemical coagulant. While in this study, it showed the decrement of PAC dose over 40% (2.5 g/L to 1.5 g/L). The decrement of PAC dose as chemical coagulant was due to the addition of natural coagulant aid that managed to increase the removal of several parameters. Besides, it managed to reduce the optimum pH condition of leachate closer to the acidic state that caused by the addition of TS. This also showed that TS worked effectively at the acidic rather than in alkaline state. TS as natural aid is
known to have higher molecular weight, which might help in the faster settlement of sludge and flocs in this study that could also become the reason for the improvement of the results [23].

Table 3. Result of percentage removal from the previous study.

| Sample                  | Coagulant (mg/L)          | Removal (%)                                      | Authors |
|-------------------------|---------------------------|-------------------------------------------------|---------|
| Leachate (pH 7)         | alum (9400)               | 85% COD, 92% colour, 95% SS, 95% turbidity     | [18]    |
|                         | PAC (1900)                | 57% COD, 97% colour, 99% SS, 99% turbidity     |         |
| Leachate (pH 6-7.5)     | PAC (7200)                | 55% COD, 80% colour, 95% SS                     | [19]    |
|                         | alum (11000)              | 58% COD, 79% colour, 78% SS                     |         |
|                         | dual - PAC (7200) + psyllium husk (400) | 64% COD, 90% colour, 96% SS                  |         |
| Leachate (pH 6)         | PAC (1500)                | 63% COD, 46% ammonia, 96% colour, 95% SS, 99% turbidity | [20]    |
| Leachate (pH 4)         | tapioca starch (2500)     | 13% ammonia, 55% colour, 12% SS                 | [21]    |
| Leachate (pH 6)         | durian seed starch (4000) | 34% colour, 37% turbidity                      | [22]    |
| Leachate (pH 7)         | PAC (2000)                | 49% COD, 29% ammonia                            | [3]     |
| Composite - PAC (2000)  | + cationic polymer (10)   | 59% COD, 49% ammonia                            |         |
| Composite - PAC (2000)  | + anionic polymer (10)    | 56% COD, 46% ammonia                            |         |
| Leachate (2500 - pH 7)  | PAC                       | 92% SS, 77% turbidity, 94% colour, 37% COD and 32% ammonia |         |
|                         | PAC (1500 - pH 7)         | 69% SS, 31% turbidity, 85% colour, 28% COD and 13% ammonia |         |
|                         | TS (2500 - pH 8)          | 35% SS, 13% turbidity, 30% colour, 0% COD and 38% ammonia |         |
|                         | PAC + TS (1500 + 200, pH 5) | 90% SS, 74% turbidity, 87% colour, 40% COD and 17% ammonia |         |
4. Conclusion
Leachate treatment had been done by using coagulation-flocculation process with PAC and TS as the primary and the coagulant aid, respectively. The results indicated that the removal of turbidity, colour, COD, and ammonia was increasing with the increases of coagulants dose until reaching the optimum dose. PAC provides the higher removal percentage of SS, turbidity, colour, COD, and ammonia at neutral pH value compared with TS with moderate percentage removal at the acidic condition. These showed that the PAC could act effectively as primary coagulant while TS acts as coagulant aids. Addition of small amount of TS at dose of 0.2 g/L into 1.5 g/L of PAC at pH 5 (90%, 74%, 87%, 40%, and 17%) increased the removal compared with single PAC at dose of 1.5 g/L and at pH 7 (69%, 31%, 85%, 28%, 13%). While in dual coagulant, the results indicated that the addition of small amount of TS as coagulant aids into PAC as primary coagulant increased the efficiency of coagulation and flocculation process with less dose of PAC. The application of dual coagulant can achieve same or better percentage removal than the optimum single PAC at 2.5 g/L and pH 7 (92%, 77%, 94%, 37%, and 32%), single TS at dose of 2.5 g/L and at pH 8 (35%, 13%, 30%, 0%, and 38%). Thus, the dose of TS at 0.2 g/L and the dose of PAC at 1.5 g/L and pH 5 have been selected as the optimum doses and pH for dual coagulant PAC and TS. Application of dual coagulant made from PAC and TF is able to increase the effectiveness of the coagulation-flocculation process and reduce the dose of chemical coagulant. It can be concluded that the application of dual coagulant is better than single coagulants in term of coagulant dose and percentage removal.

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