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Reduction of COD and Highly Coloured Mature Landfill Leachate by Tin Tetrachloride with Rubber Seed and Polyacrylamide

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Abstract: Tin tetrachloride ($SnCl_4$) as a coagulant and rubber seed (*Hevea brasiliensis*) (RS), and polyacrylamide (PAM) as the coagulant aid were investigated in this work to treat matured and stabilised landfill leachate rich in COD and colour. A standard jar test was conducted at different pH values and dosages of coagulant/coagulant aid. When $SnCl_4$ acted as the primary coagulant, the optimum conditions occurred at pH 8 and 10,000 mg/L dosages, with 97.3% and 81% reductions of colour and COD, respectively. Both RS and PAM were not effective when used alone. When RS was used as the coagulant aid, the dosage of $SnCl_4$ was reduced to 8000 mg/L. The colour reduction was maintained at 97.6%, but the COD removal dropped to 43.1%. In comparison, when PAM was supplemented into 6000 mg/L $SnCl_4$, the reduction in colour was maintained at 97.6%, and the COD removal was almost at par when $SnCl_4$ was used alone. The addition of polymers as the coagulant aid helped in improving the sludge properties with a better settling rate (SSR) and larger flocs size. The decline of the SVI value indicates that less amount of sludge will be disposed of after the treatment. In addition, the rise of settling velocity (SSR) will reduce the size of the settling tank used in coagulation-flocculation treatment. Based on the results, it can be concluded that incorporation of coagulant aid into the treatment reduced the primary coagulant dosage without affecting the removal performances of pollutants.

Keywords: coagulation; flocculation; coagulant aid; colour; chemical oxygen demand; solid waste

1. Introduction

Throughout the years, landfills have remained the primary means of disposing of solid waste in most developing countries. One of the most serious challenges in the operation of sanitary landfills is the contaminated landfill leachate produced by the breakdown of organic wastes and rainwater percolation through the waste material. It is a complex and high strength wastewater with huge amounts of organic matter, ammonia, heavy metals, and toxic chemicals. Even after being covered, landfills continue to discharge considerable amounts of leachate. Several factors, including the age of waste, climatic conditions, waste composition, landfill design and its operation, influence the characteristics of leachate. The relative treatability of leachates is determined by their composition, which is determined by the age of the landfill. As the solid waste in a landfill settles over time, the characteristics of the leachate change considerably. Older landfill releases stabilised leachate with low biochemical oxygen demand/chemical oxygen demand (BOD_5/COD) ratio, which is difficult to be further biologically degraded. Mature leachate has increased alkalinity, salinity, ammonia nitrogen concentration, and biorefractory compounds such as humic and fulvic acids and is considered stable since it has a low COD (5000 mg/L), a low BOD_5/COD ratio (0.1), and a high pH (>7.5). In comparison, young leachate contains a significant amount of biodegradable organic matter, particularly volatile fatty acids (VFA), as well as a high chemical oxygen demand (>10,000 mg/L), a high BOD_5/COD ratio (>0.3), and a low pH. (6.5). The relative treatability of leachates is determined by their composition, which is determined by the age of the landfill and/or the BOD_5/COD ratio [1–3].

A lower level of VFAs is partially responsible for the characterisation of the old/mature leachate in the methanogenic phase. This is because, during the second fermentation cycle, they are converted to methane (CH_4) and carbon dioxide (CO_2) as gaseous end products. When the amount of VFAs and other rapidly biodegradable organic compounds in the leachate decreases, refractory molecules (such as humic substances) begin to dominate the organic matter in the leachate. Due to the presence of high organic materials (measured as COD) that are associated with suspended particles and turbidity, the leachate is highly coloured and turbid. The breakdown of the organic matter (humic substance) caused the water sample to have yellow, brown, or black colour [4,5].

Humic compounds are polymers of phenol and quinine with hydroxyl and carboxyl functional groups that have an average molecular weight of 300–3000 kDa and can be made from a variety of biological components. Humic substances are classified into three categories based on their acid and basic solubility: humic acid, fulvic acid, and humin acid. Humic acid is exclusively soluble in alkaline solutions, whereas fulvic acid is soluble in both acid and alkaline solutions, and humin acid is not soluble in either. Fulvic acid has a lower molecular weight and more hydrophilic functional groups than humic and humin acid among the three humic substance elements [6].

Among various treatment methods, generally, biological treatment (anaerobic/aerobic) is the first choice for landfill leachate treatment. This is due to their simple operation and less expensive. However, these methods of remediation are only appropriate for leachate that is young or intermediate in age. The biological treatment is not suitable for mature leachate since it has a low biodegradability ratio (BOD_5/COD). Therefore, the most suitable method for mature leachate is physical and chemical treatment like coagulation and flocculation [7].

They are many other chemical methods to treat landfill leachate, including chemical oxidation, advanced oxidation processes (AOP), precipitation, neutralisation, and others. We have published quite a number of papers on these in recent years [8–14]. However, the current work focuses on the coagulation and flocculation method as one of the promising techniques.

Because of its great selectivity for colloidal species and established effluent treatment efficacy, coagulation-flocculation is regarded as a trustworthy and cost-effective approach among these processes. Coagulation-flocculation allows for the neutralisation or decrease of electrical charges, allowing colloidal particles to approach each other closer and aggregate form flocs. It is a simple and inexpensive method for treating landfill leachates that have proven to be effective. However, choosing the right coagulant, determining the best-operating conditions, assessing the pH effect, and looking for the best reagent doses are all critical steps in improving the treatment's efficiency. Coagulation-flocculation is a common method for treating fresh leachates and is usually used as a pretreatment before biological treatment. Heavy metals and non-biodegradable organic molecules are removed from landfill leachates using this method [15].

Compared to the other method, which requires more techniques and is more expensive, the coagulation and flocculation process is preferable due to its simple process, [16]. Coagulants can be divided into three types of groups, namely inorganic coagulants, organic synthetic flocculants, and natural coagulants. The inorganic coagulant or chemical coagulant is produced from chemical products or material and are available commercially. Meanwhile, the natural coagulant is produced from natural sources, and the main components are usually contained polysaccharides and protein [16]. Example of inorganic coagulants includes ferric chloride, alum, polyaluminum chloride and poly ferric sulfate. Meanwhile, polyacrylamide derivatives and polyethyleneimine are organic synthetic flocculants. Example of naturally occurring flocculants is chitosan, bioflocculant and sodium alginate (SA) [17].

Tin tetrachloride ($SnCl_4$) is a four valence coagulant that can remove or attract the negatively surface charged particle better than the lower valence coagulants resulted in a lower dose required for coagulation [18]. Additionally, an increase in the counter-ion valency will decrease the stability of the particles [19]. According to most of the published literature, tin salts have been used in a variety of ways. For example, in a study by Mathews et al. (2015) [20] using tin (II) chloride ($SnCl_2$) and through the air stripping method, mercury (Hg), the content in-stream water could be removed by more than 90%. In addition, tin oxide (SnO_2) made from $SnCl_4$ was also successful in removing nickel (Ni^{2+}) and copper (Cu^{2+}) ions from an aqueous solution [21]. However, despite all these findings, the use of a tetravalent coagulant, such as $SnCl_4$ or stannic chloride, has not been extensively recorded. Generally, ions with a higher valency will have a bigger impact on the coagulation process compared to the lower one. When compared to divalent and trivalent coagulants, $SnCl_4$ with four valences is projected to contribute more positive ion/charge during destabilisation. It is expected that they will have a greater colloidal particle attraction force to remove the contaminant from the leachate. This is because the charge neutralisation mechanism, in which negatively charged colloids are attracted to positively charged metal coagulant by electrostatic forces, is primarily engaged in the destabilisation of particles in suspension. As a result of the attraction, the particles will come closer and clump together in a suspension [22]. According to the Hardy Schulze law, the efficiency of each coagulant in the coagulation and flocculation system is determined by its valency, which implies that the higher the valency of the coagulant, the better the coagulation process performs [23]. Therefore, this study was conducted to investigate the ability of $SnCl_4$ as the tetravalent coagulant in treating pollutants in the high strength leachate.

Application of coagulant aids would increase the effectiveness of the coagulation-flocculation process and improve the flocs produced. The coagulant aid is able to minimise the floc breakage during the stirring as it can make the flocs become stronger and increase the floc density. Additionally, it helps in reducing the amount or dosage of the metal coagulant as well as producing less chemical residues content in the sludge after the treatment [24,25].

Because of their benefits over natural polyelectrolytes, synthetic polyelectrolytes are now extensively employed in the treatment of industrial wastewaters. The benefits are its greater purity, higher quality, stability, and greater efficiency. They also do not add insoluble substances to the sludge and do not change the water's physical or chemical qualities [26]. The phrase "polyacrylamide" is defined for any polymer containing acrylamide as one of the monomers. Its IUPAC nomenclature is poly (prop-2-enamide), which describes it as a water-soluble polymer generated by polymerising either acrylamide monomers or *N*,*N′*-methylenebis (acrylamide). Because of its exceptional water solubility and high molecular state, the polyacrylamide (PAM) family of polymers and copolymers is the most widely used and universal coagulant [27]. Commercial PAM has a molecular weight (MW) of 105 to >107 Da. Due to its high viscosity, drag reduction capabilities, and water retention qualities, high MW PAM (>106 Da) offers a broader range of applications [28]. Polyacrylamide and its derivatives are often more effective than other inorganic flocculants because they have advantages such as a low dose, simplicity of handling, little pH interference, and higher floc-forming capabilities [29].

Tin tetrachloride was chosen as the metal coagulant mainly because it offers a high cation charge which is expected to be good in charge neutralisation mechanism. Generally, the selection was to investigate the effectiveness of high valence coagulant, which suggested by the Schulze–Hardy that the critical coagulation concentration (CCC) is strongly influenced by ionic valence [30].

According to the Association of Natural Rubber Producing Countries, Malaysia's rubber plantation land was estimated to be 1,229,940 hectares in 2007. Thailand (3,172,394 tonnes), Indonesia (5,367,980 tonnes), and Malaysia are the top rubber seed producers (1,735,522 tons). Based on an estimated average of 1000 kg seeds per hectare per year, Malaysia's annual rubber seed production is expected to be 1.2 million metric tonnes, and the rubber seed production keeps on increasing every year until it can reach 2060 kg ha/year in 2014. Despite the massive production of the rubber, the rubber seed will be wasted without alternative use, and we try to value add its usage in the current work. In addition, rubber seeds contain a non-edible vegetable oil content of 40–50% and crude protein content of 19–23%. Its high protein content and amino acids composition also become one of the reasons for the selection, as the protein content in natural coagulants is one of the factors that affect the efficiency or functionality of the natural coagulant [31–33].

PAM is one of the most used flocculants in the treatment of drinking water. It has been used widely in the water treatment industry. PAM could generate micron-sized aggregates with good settling qualities by establishing bridges between destabilised particles. The flocculation properties of cationic, non-ionic, and anionic PAM have been widely investigated. Because there are more binding sites, the flocculation and adsorption capacity increase as the MW increases. Therefore, the choice of PAM as the flocculants in wastewater treatment is practical as it offers good flocculants characteristics and has been used in various waters and wastewater treatment processes [28].

Hence, this study was undertaken to evaluate the effectiveness of $SnCl_4$ as the chemical coagulant and rubber seed (RS), as well as PAM as the potential coagulant aids in treating concentrated colour and chemical oxygen demand (COD) from the old local landfills (Ampang Jajar Landfill Site, Alor Pongsu, Perak), chosen as a case study site which may also represent similar old landfills in other countries. Both contaminants are commonly present at high intensity in old and matured leachate and are hard to comply with the standard discharge limit of effluent. A series of coagulation-flocculation experiments were conducted to determine the optimum conditions of pH and dosage for coagulation. The sludge properties were also evaluated and compared between the use of $SnCl_4$ alone and with combinations of RS and PAM.

2. Materials and Methods

2.1. Preparation of Coagulants Stock Solution

Tin tetrachloride ($SnCl_4$) and polyacrylamide, PAM (-$CH_2CHCONH_2$-) were purchased from BG OilChem Sdn.Bhd., Permatang Pauh, Malaysia. Rubber seed (RS) was collected from one of the local rubber plantations in Kedah, Malaysia. A 40 g/L stock solution of $SnCl_4$ was made by dissolving 40 g of $SnCl_4$ in 100 mL of distilled water. RS was prepared by removing and drying the seed at 105 °C for 30–60 min to remove the moisture content. Then, the dried seed was ground into fine powder by using a heavy-duty grinder. The powder was then mixed with distilled water and stirred for 30 min. After the stirring, the mixture was filtered using a filter cloth. The required stock solution for RS and PAM was prepared by following the dilution principle [32,34].

2.2. Leachate Sampling and Characteristics

The case study leachate sample was collected monthly for 12 months (November 2018 to October 2019) from one of the local landfills, Alor Pongsu Landfill Site (APLS), which is located at 5°4′ N, 100°35′ E in Alor Pongsu, Perak, Malaysia. APLS is a stabilised anaerobic landfill that began operation in 2000 (20 years old) and deposited about 200 metric tons of domestic solid waste a day, with more than 60 tons of them being organics. The sample was kept in 10 L of HDPE containers. The onsite parameters, namely pH, dissolved oxygen and temperature, were measured directly by dipping the multi-sample system YSI 556 into the landfill leachate collection pond. The samples were immediately transferred to the laboratory and put in a cool chamber at 4 °C to minimise chemical and biological interactions. Following that, tests for biochemical oxygen demand (BOD) (Standard Method 5120 B), suspended solids, chemical oxygen demand (COD) (HACH Method 8000), turbidity (HACH Method 8006), true colour (HACH Method 8025), and ammonia were performed using a DR 2800 Spectrophotometer and the procedures in Standard Method of the Examination of Water and Wastewater were followed [26].

2.3. Jar Test

The current study used a conventional jar test apparatus with six agitators (VELP-Scientifica, Model: JLT6, Usmate Velate, Italy). Six beakers were filled with 500 mL of leachate with pH adjusted to desirable level with 3M hydrochloric acid (HCl) or 3M sodium hydroxide. The pH values were varied from pH 3 to pH 12 to evaluate the effect of pH, and the dosage of $SnCl_4$ was maintained at a predetermined concentration of 10 g/L. The optimum dosage of 10,000 mg/L was predetermined before with the concentration varied from 0.5 g/L to 20 g/L. The highest percentage removal was found to be at 10 g/L; therefore, this optimum dosage was used as the standard in the testing. The samples were agitated at 220 rpm for quick mixing for 5 min, followed by 30 min of slow mixing at 60 rpm. Then, the stirred samples were let to settle for 40 min (predetermined in the batch studies). The supernatants were collected with a syringe at 2 cm below the surface immediately after settling. Following that, the samples were checked for zeta potential, colour, and suspended solids. The performances were determined using Equation (1).

$$\text{Removal (\%)} = (\text{Raw Leachate} - \text{Treated Leachate})/(\text{Raw leachate}) \times 100 \quad (1)$$

2.4. Analytical Method

All analytical measurements in this work were performed using the Standard Methods for the Analysis of Water and Wastewater [35]. True colour and SS were measured according to Method no. 2120C and HACH Method 8006, Photometric Method, respectively. The colour sample was pre-filtered using 0.45 µm filter paper. The DR2800 HACH spectrophotometer was used to measure both colour and SS. All analysis was performed in triplicates.

2.5. Sludge Settling Characteristic

After the completion of jar testing, the mixture was immediately transferred to 1-L graduated cylinder for settlement. The settleability test involved three types of measurement based on APHA (2017) [35], those are Sludge Settling Velocity (Vs), Sludge Volume Index (SVI) and Total Suspended Solids (TSS).

2.5.1. Sludge Volume Index (SVI)

The Sludge Volume Index (SVI) was determined based on Standard Method 2710 D. Coagulation-flocculation jar studies with three types of coagulants, $SnCl_4$, Rs and PAM were carried out using a standard jar tester. The optimum dose of each coagulant was administered to 6 beakers containing 500 mL each, and the mixture was homogenised immediately. Coagulation-rapid mixing was done for 5 min at 220 rpm, followed by flocculation-slow mixing for 30 min at 60 rpm. According to Jairo Feria-Díaz et al. (2017) [36], the sediment sludge volume was measured after the mixture was put in 5 Imhoff cones and allowed to settle for 30 min. The glass filter disc was inserted into the crucible, washed with distilled/deionized water, and the crucible was taken to the furnace (103–105 °C) for two hours to test the suspended particles. The filter paper was then weighed on the analytical scale after cooling in the desiccator. The drying and cooling process was repeated until the weight remained constant. The homogenised samples were filtered and baked for a second time for two hours, then chilled for half an hour in the desiccator before the filter paper was weighed on the analytical balance. Finally, the sludge volume index was determined using the volume of sludge compacted in the cone Imhoff for 30 min and the beginning total suspended solids concentration in each sample, utilising the following Equation (2).

$$\text{SVI} = \frac{V_{30} \times 1000}{V_0 \text{TSS}} \times 1000 \quad (2)$$

where,

V_{30} = volume below the supernatant–suspension interface after 30 min of settling (mL)

V_0 = initial wastewater volume expressed in mg/L, and

TSS = total suspended solid content of the wastewater in mg/L.

Total Suspended Solids (TSS) (mg/L) was determined in accordance with Standard Method 2540 D (Equation (3))

$$\text{TSS} = \frac{(P_2 - P_1) \times 1000}{\text{Vm}} \times 1000 \quad (3)$$

where,

P_1 = mass of the capsule plus filter paper before the filtration (g)

P_2 = mass of the capsule plus filter paper (g) after filtering a volume *Vm* (mL) of wastewater and drying at 105 °C for 12 h.

2.5.2. Settling Sludge Rate (SSR)

A 1-L graduated cylinder is filled with a sludge sample, and a timer is started to maintain track of the length of the experiment to measure a batch settling curve. After allowing the sludge to settle, the position of the suspension-liquid interface is monitored at various time intervals. The Sludge Settling Velocity (Vs) was recorded every 1 min for 15 min settling time and expressed in cm/min (Standard Method 2710 E). Because the sludge settles quickly at the start of the test, the suspension-liquid interface is normally monitored more often. Because the interface moves more slowly later in the test, the measurement frequency is reduced [37]. Then, the settling velocity is computed using Equation (4).

$$\text{Vs} = \frac{\text{m}h_0}{V_0} \quad (4)$$

where,

h_0 = height (cm) of the initial column of wastewater,

V_0 = initial volume of wastewater (mL), and

m = slope obtained from a plot of the data volume beneath the interface (mL) versus time (min).

2.6. Particle Size

The particle size of leachate sludge was determined by using Malvern Mastersizer 2000. The process involves passing a laser beam through a suspension of particles. A suitable amount of sludge sample was slowly transferred into a stirring vessel that contained ultra-pure water using a hand pipette. Then, the suspension constantly flowed through the instrument during the measurement cycle.

3. Results and Discussion

3.1. Characterisation of Leachate

Table 1 shows the minimum, maximum and average levels of leachate compositions sampled from the site. A high concentration of colour (9480–22,970 Pt.Co.) and COD (1390–5078 mg/L) were observed, far exceeded the discharge limit of effluent (400 mg/L for COD and 100 ADMI for colour). The high concentration of both COD and colour is mostly due to the high content of organic matter. Mature leachate usually has a low biodegradability ratio (BOD_5/COD), which is <0.1. Hence, this leachate is highly non-biodegradable and recalcitrant with a BOD_5/COD ratio of 0.03. Further biological biodegradation is very difficult; hence, physical and chemical treatment such as coagulation-flocculation is a good option for this type of leachate.

Table 1. Raw characteristics of APLS landfill leachate (based on 12 data, sampled between November 2018 until October 2019).

Parameter	Min	Max	Average	Discharge Limit [1]
pH			8.12	6.0–9.0
BOD_5 (mg/L)	45	112	85	20
COD (mg/L)	1390	5078	2937	400
BOD_5/COD	0.02	0.07	0.03	-
Suspended Solids (mg/L)	258	547	411	50
Colour (Pt.Co.)	9480	22,970	15,062	100 *
Turbidity (NTU)	9.68	44.59	22.0	
Zeta Potential	−18.6	−22.4	−20.5	

[1] Discharge limit from the Malaysian Environmental Quality Act-MEQA (Control of Pollution from Solid Waste Transfer Station and landfill) Regulation 2009. * Assumed to be equivalent with ADMI unit.

3.2. The Effect of pH on COD and Colour Reduction from Landfill Leachate

All the data presented in all figures were obtained from an average of triplicate testing carried out during the experiments. Figures 1 and 2 show the influence of pH on the removal of colour and COD using $SnCl_4$, RS, and PAM as a coagulant, respectively.

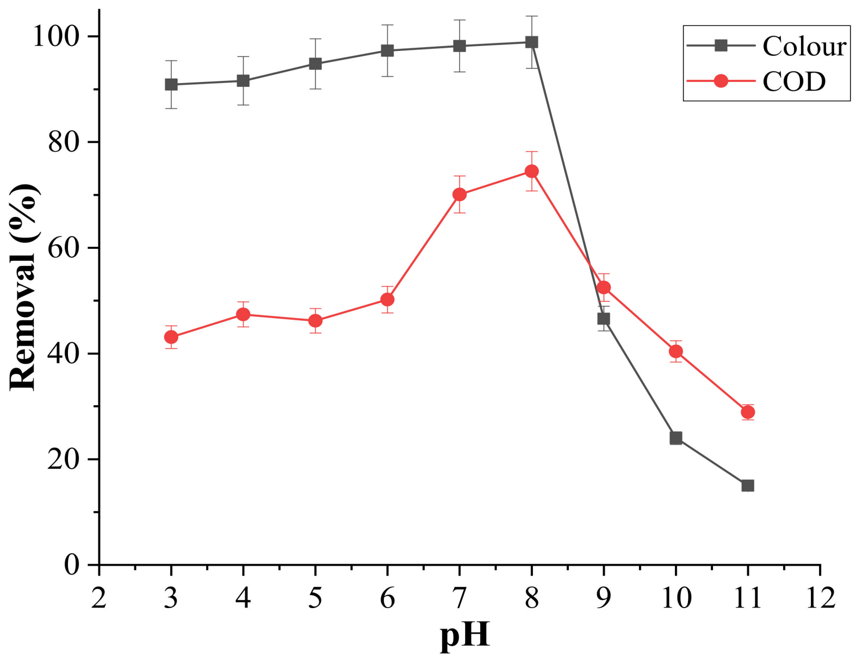

Figure 1. Influence of pH on the removal of colour and COD using $SnCl_4$ (10,000 mg/L).

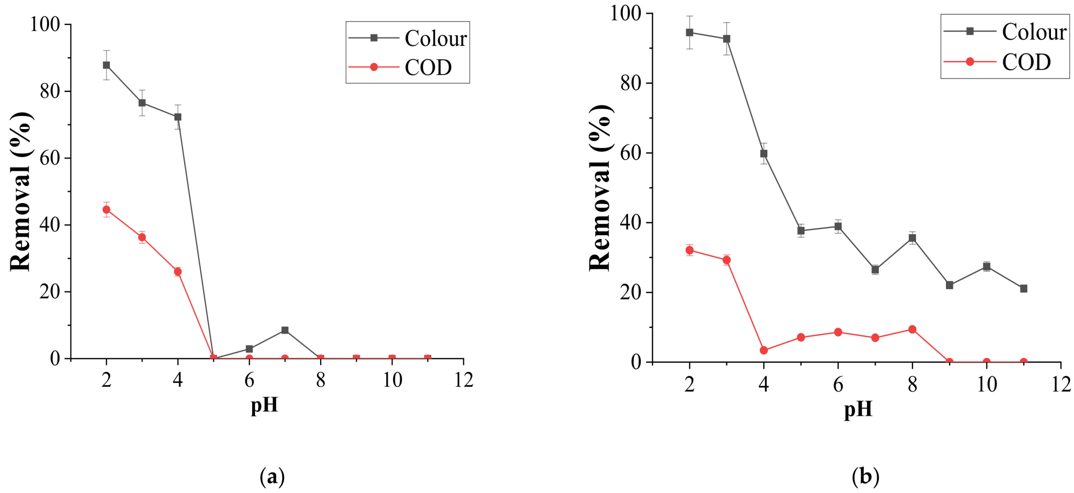

Figure 2. Influence of pH on the removal of colour and COD using (**a**) Rubber Seed (RS), (**b**) Polyacrylamide (PAM).

It can be noted from Figure 1 that as the pH climbed from acidic to basic, the elimination of colour and COD increased until it reached the optimum pH level at pH 8. The highest COD and colour reductions at this pH was 74.5% and 98.9%, respectively. However, after pH 8, the removal of both pollutants started to decrease with the increased pH. Once a metal or chemical coagulant is added to the solution, the soluble hydrolysis species will be formed. Depending on the pH of the solution, the species might be negatively or positively charged. The agglomeration of the particles (which also contribute to COD and colour) will only occur when the positively charged species attract the negatively surface charged particle in the solution. The destabilisation of the articles leads to agglomeration, which then forms large flocs. The formation of flocs can only happen due to the attraction of the differently charged particles to each other. This is known as the charge neutralisation mechanism. Therefore, the removal of pollutants from the leachate using the chemical coagulant is mainly due to the difference of surface charge between two particles [38].

3.3. Effect of Dose on COD and Colour Reduction from Landfill Leachate

The effect of $SnCl_4$ dosages (6000–18,000 mg/L), RS (1000–10,000 mg/L) and PAM (100–6000 mg/L) is displayed in Figures 3 and 4.

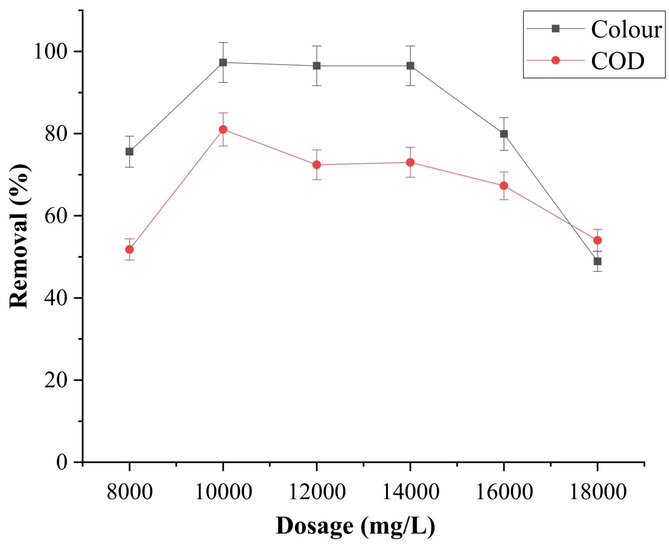

Figure 3. Influence of $SnCl_4$ dosage (6000–18,000 mg/L) on the removal of colour and COD at optimum pH 8.

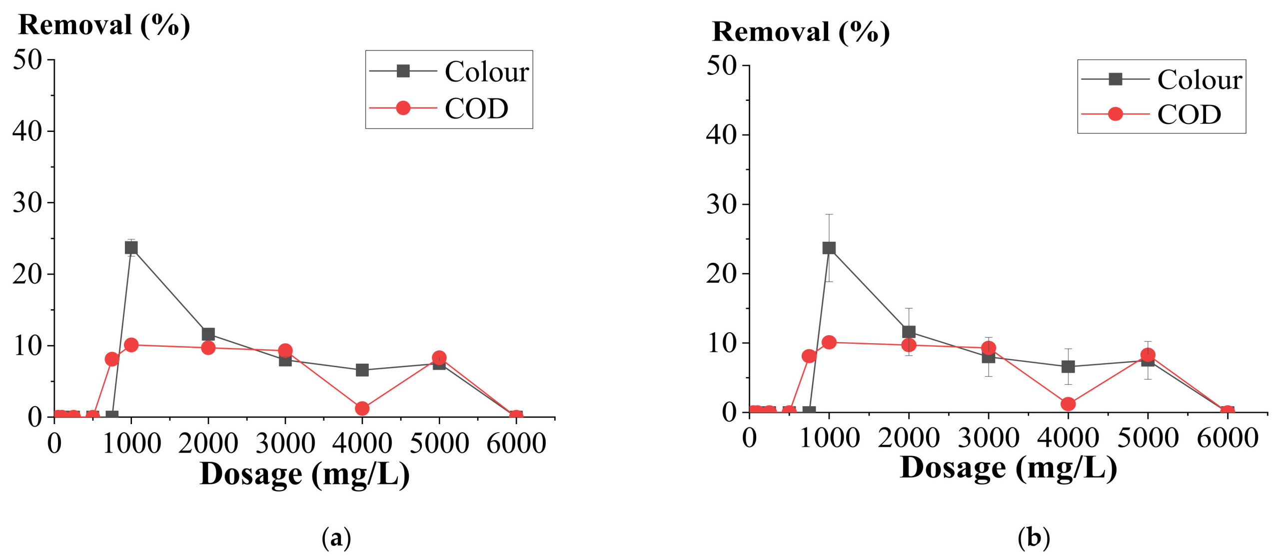

Figure 4. Influence of dosage on the removal of colour and COD using (**a**) Rubber Seed (RS) (1000–10,000 mg/L), (**b**) Polyacrylamide (PAM) (100–6000 mg/L) at pH 4.

The reductions in colour and COD increase with the increase in coagulant dosages. The highest removal occurred at 10,000 mg/L of $SnCl_4$, where 81% and 97.3% of COD and colour was removed. The removals were almost constant until the dose reached 14,000 mg/L and dropped beyond this point. These reductions were mainly due to the overdosing of the coagulant. Overdosing lead to the re-stabilisation of the particles, which will prevent the agglomeration of the particle from forming large flocs.

RS and PAM were not effective when used as a primary coagulant (Figures 2 and 4). The pH effect on the removal of colour and COD was only effective in the acidic pH range.

The leachate particles are negatively charged in acidic conditions, enabling greater performance with the cationic coagulant. When the pH level is high for polymer hydrolysis products, there may be a conflict between OH^- and negatively charged impurities. This indicated that hydrolysis products might neutralise the negative charges on the leachate molecules, but that when the pH drops, the charge density drops, causing the anionic leachate molecules to self-aggregate [39]

In acidic pH, the amine groups in PAM coagulant are protonated, resulting in an increase in positive charges at low pH. Coagulation becomes more effective as positive charges increase. The charge concentration in the coagulant reduced as the pH increased, resulting in little or no colour removal. As a result, the coagulant should be used at acidic pH [40]

The use of RS and PAM alone as the main coagulant (Figure 4) tends to increase the organic matter content in the leachate itself. This is because RS and PAM are both natural coagulants. The high content of organic matter will increase the value of colour and COD. Due to this reason, RS and PAM as natural coagulants are not suitable to be used alone in treating the high contaminant wastewater like leachate.

3.4. Rubber Seed (RS) and Polyacrylamide (PAM) as the Coagulant Aid

A series of jar tests were conducted to determine the potential of RS and PAM as the natural coagulant aid. Figure 5 shows the removal of COD and colour and COD using 8000 mg/L of $SnCl_4$ with various dosages of RS as the coagulant aid (50 to 10,000 mg/L).

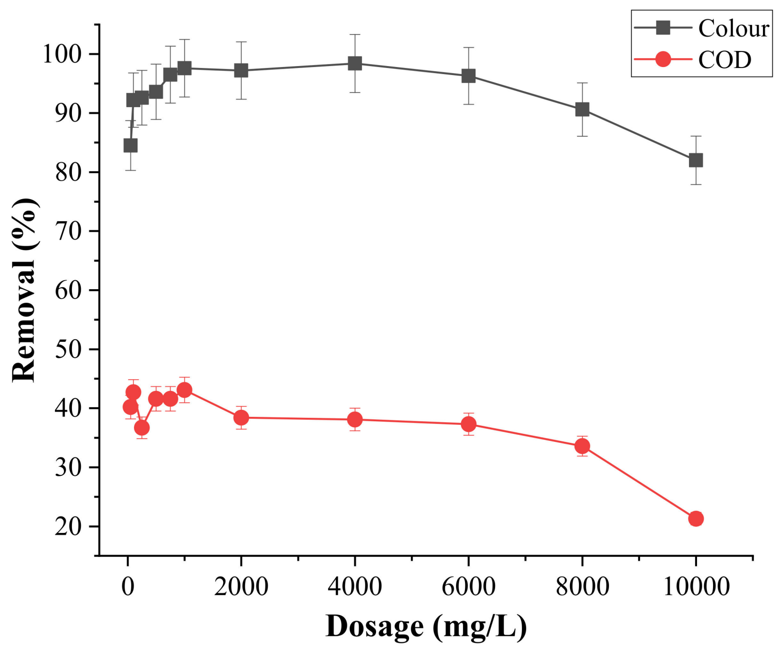

Figure 5. Colour and COD reductions at pH 8 and 8000 mg/L $SnCl_4$ in the presence of RS as the coagulant aid.

The removal of COD was fairly identical with and without the presence of a coagulant aid up to 8000 mg/L RS. For colour, a great improvement was noted when RS was present with over 98% reduction at 1000 mg/L of RS (compared with only 84% reduction when $SnCl_4$ was used alone). The colour reduction was maintained above 90% within the next RS dosages (until 8000 mg/L). The COD and colour reductions dropped beyond this point because of the overdose of RS added into the solution, which resulted in an increase of organic content in the solution. This shows that the addition of RS helps in removing almost similar removal with less chemical coagulant needed.

The molecular mass or chain length of the polymer, the charge density on the molecule; the dose employed; the biomass concentration; the ionic strength and pH of the broth; and its mixing in the fluid all influence the efficiency of polyelectrolyte flocculants. The size and polarity of a polyelectrolyte flocculant determine its efficiency. They are classified as cationic, anionic, or non-ionic based on their polarity. The quantity of charged monomers attached to the polymer chain determines their charge, which can range from insignificant to 100 percent. Because surface charges are negative in nature, research has shown that cationic polymers are 90 percent more successful in flocculating biomass than anionic or non-ionic polymers, which have efficacies ranging from 0 to 40% under the same conditions. In marine media, natural polysaccharides like chitosan and cationic starch have been proven to perform poorly. Higher salinity media reduce flocculation efficiency because the polymer molecule folds in on itself, requiring a higher dosage. In comparison to the dosage required by freshwater microalgae, which may be effective in the range of 1–10 mg/L, a 100 percent flocculation efficiency of marine microalgae required a chitosan flocculant dosage above 40 mg/L. The pH has a significant impact on the flocculation effectiveness of cationic polymers. In low salinity media, chitosan with a pH of 7 is ideal for flocculation [41]. Polyelectrolytes with a high molecular weight, such as natural coagulants (i.e., longer chain polymers), are better bridging agents. The molecular weight (MW) of RS in this study was 103 kDa which was measured using Zetasizer. The MW in this study is almost similar to the MW obtained by Cherian et al. (2019) [42], which was 131 kDa. Generally, the MW of natural coagulant is usually not too higher. Studies done by several researchers have illustrated that the MW of coagulant extracted from plant-based coagulants might vary from as low as 6 kDa to 800 kDa. Obiora-Okafo and Onukwuli (2016) [43] and Kanneganti and Talasila (2014) [44] obtained about 6 kDa of MW when *Vigna-unguiculata* seed proteins were used as the coagulant for the treatment of dye. Meanwhile, studies conducted by Kagithoju et al. (2015) [45] and Chen (2018) [46] were able to remove about 96% turbidity from surface water when used Nirmali seeds extracts with 62 kDa MW. In addition, higher MW natural coagulants such as *Tamarindus-indica* seed gums, with 700–800 kDa of MW, only needed 15 mg/L dosages to remove turbidity from the river water. According to Muylaert et al. (2017) [47], natural coagulants of a lower molecular weight frequently flocculate via the charge patch process. Meanwhile, the natural coagulant's high molecular weight is frequently dominant in bridging mechanisms. The ability of the polymer molecule to neutralise the surface charge on cells and its bridging capability improves when the charge density is high.

The bridging phenomenon happens in a fluid containing biopolymers with long chains that can be absorbed simultaneously on many particles, connecting them together through the development of "bridges." Polymers having long chains are required to bond to molecules suspended in an aqueous solution. During the creation of loops and chains, the polymer can adsorb on colloidal particles. Binding occurs when another molecule (with free absorption sites) comes into contact with these structures, and aggregates develop [48].

Figure 6 shows the removal of COD and colour using 6000 mg/L of $SnCl_4$ with the presence of various dosages of PAM (50 to 1500 mg/L) as a coagulant aid.

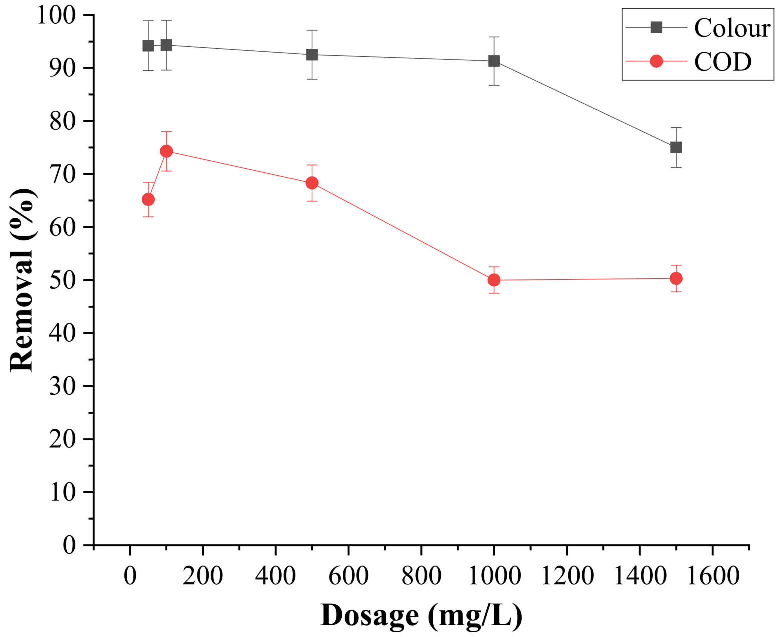

Figure 6. Removal of colour and COD pH 8 and 6000 mg/L $SnCl_4$ with the presence of PAM as the coagulant aid.

The presence of PAM (from100 to 500 mg/L) improved the COD reduction from 63% (without PAM) to 70–75% in the presence of PAM. However, the performance on colour in the presence of PAM was not significant at all ranges of PAM dosages (50–1000 mg/L). The formation of bridges between flocs increases at dosage levels of 100–500 mg/L due to more sites available on particle surfaces for the formation of interparticle bridges, whereas the formation of bridges between flocs decreases at dosage levels of 500–1500 mg/L due to no sites available on particle surfaces for the formation of interparticle bridges due to excess polymer (coagulant) being adsorbed [49].

3.5. Particle Size

The particle size distribution of $SnCl_4$ as the major coagulant and RS as the coagulant aid are summarised in Table 2.

Table 2. Particles size distribution of 10,000 mg/L $SnCl_4$, 8000 mg/L $SnCl_4$ with 1000 mg/L RS as coagulant aid.

Floc Condition	Floc Equivalent Volumetric Diameter (µm)		
	d_{10}	d_{50}	d_{90}
$SnCl_4$ 10,000 mg/L	20.33	65	178.1
$SnCl_4$ 8000 mg/L + RS 1000 mg/L	43.7	183.4	741.2
$SnCl_4$ 6000 mg/L + PAM 100 mg/L	55.9	216.5	540.2

Based on Table 2, the size of the floc when $SnCl_4$ was used alone were smaller in size compared to when RS was added in the treatment as the coagulant aid. The increase in the floc size can be seen in every percentile. At d_{10} the size of the floc increased from 20.3 µm to 43.7 µm (RS) and 55.9 µm (PAM). The size also shows an increase of d_{50} when the size of floc increased from 65 µm when 10,000 mg/L $SnCl_4$ was applied as the primary coagulant to 183.4 µm when 1000 mg/L dosage of RS and to 216.5 µm when PAM was added as a coagulant aid, respectively. This indicated that the addition of RS and PAM as coagulant aids helped in increasing the size of the flocs during the agglomeration process. Generally, the natural-based coagulants have a higher molecular weight which helps in producing the larger flocs. In addition, the natural polymer coagulant as the coagulant aid also supposedly helps in producing stronger flocs through its bridging mechanism [50]. The combination of charge neutralisation from the application of $SnCl_4$ coagulant (primary coagulant) and bridging effect from the RS (as coagulant aid) will produce bigger, stronger, and faster settling flocs.

3.6. Sludge Settling Velocity (Vs)

The height of the sludge as a function of time is measured as sludge settling velocity. Figure 7 showed the sludge settling rate when $SnCl_4$ was employed alone as the principal coagulant (a) and RS (b), and PAM (c) were added as coagulant aids.

When $SnCl_4$ was employed alone, the sludge settling rate increased with an increase in the coagulant dosages. The settling rate is at a maximum (0.4 cm/min) at 10,000 mg/L of coagulant. The settling rate of the sludge is influenced by the adequacy of the coagulant and the size of the floc. Insufficient coagulant doses may not create adequate flocs to improve the settling. Too much coagulant, on the other hand, may cause sludge bulking which hinders settlement.

The settling rate trend of RS and PAM as coagulant aids showed a similar trend line as the settling rate increased with an increase of coagulant aid dosages until it achieved its best condition at 1000 mg/L of RS (0.5 cm/min). The sludge settling rate of RS is higher than when $SnCl_4$ was used alone (0.4 cm/min).

For PAM, the highest sludge settling rate (0.55 cm/min) was highest when 100 mg/L of PAM was used as the coagulant aid. The introduction of both coagulant aids improved the settling rate of sludge as more flocs were formed.

The charge neutralisation of the tetravalent ions caused $SnCl_4$ coagulant to precipitate, resulting in smaller and less compact flocs. In comparison, the polymers involving bridging required a combination of bridging and sweep flocculation. When utilised as a coagulant aid, the polymers resulted in a larger sludge size. This is due to its high molecular weight, which allows for longer bridges and larger structures. Polymers with a high molecular weight form huge flocs in general. When compared to $SnCl_4$, the action of the bridging mechanism by RS/PAM as polymers resulted in a bigger size of flocs as well as a higher settling rate. This is due to the polymers' capacity to adsorb particles at different places throughout the long and extended polymer chain [51].

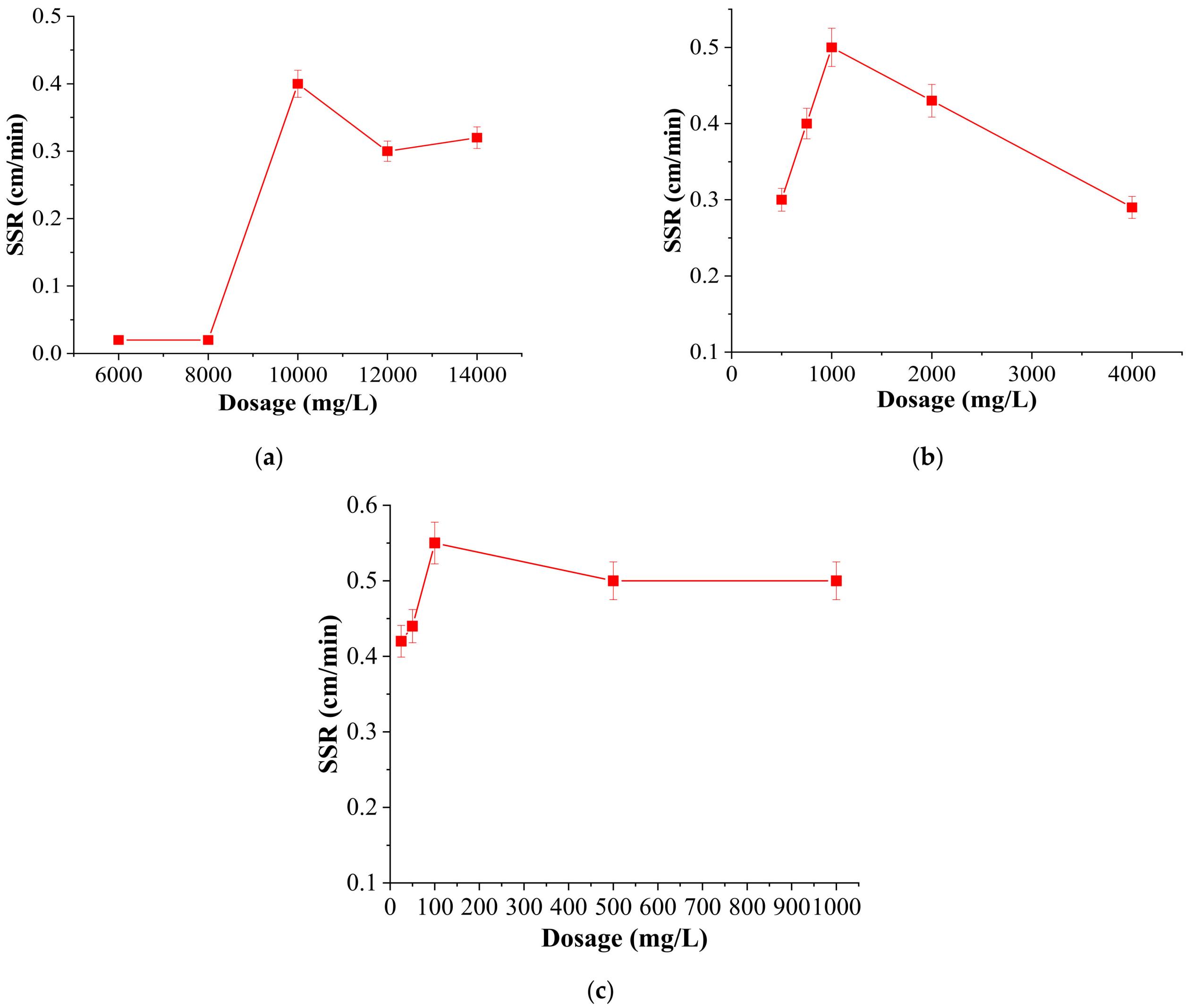

Figure 7. Sludge settling rate (SSR) of (**a**) 10,000 mg/L $SnCl_4$; (**b**) $SnCl_4$ 8000 mg/L + RS 1000 mg/L; (**c**) $SnCl_4$ 6000 mg/L + PAM 100 mg/L, at pH 8.

3.7. Sludge Volume Index (SVI)

SVI is considered as the widely used parameter used in determining the sludge settling ability, and normally, SVI is related to the size and the structure of the floc [52]. Figure 8 illustrates the sludge volume index of (a) $SnCl_4$ as the sole coagulant (b) $SnCl_4$ in combination with RS, and (c) $SnCl_4$ in combination with PAM.

When $SnCl_4$ was used alone as the main coagulant, the SVI showed an increase from 49.1 mL/g to 84.2 mL/g at 6000 mg/L and 10,000 mg/L $SnCl_4$, respectively. The size of particles at the higher SVI was 65 µm. As stated by Grady et al. [53], sludge with an SVI value less than 80 mL/g is deemed to have good settling and compaction characteristics, while Grandi, 2002 [39] stated that the SVI value in the range of 80–120 mL/g is considered to have a good settling ability. According to Patel and Vashi (2012) [18], a very good sludge has an SVI value of around 50 mL/g.

At 8000 mg/L $SnCl_4$, the introduction of 1000 mg/L RS into the process as the coagulant aid improved the SVI values to 41.6 mL/g, close to the range of 50 mL/g [10]. The particle size of flocs was also bigger (183.4 µm), which enhances settling. When the concentration of $SnCl_4$ (6000 mg/L) was mixed with 100 mg/L PAM as coagulant aid, the SVI was almost identical (43.1 mL/g) as the case of PAM; however, a bigger flocs size was observed (216.5 µm). The amount of sludge produced by the three coagulants was also different. It was observed that, after the addition of polymer as the coagulant aid, less amount of sludge was produced. 190 mL of sludge was produced when $SnCl_4$ was used as the sole coagulant. With the introduction of RS and PAM as the coagulant aid, the amount of sludge produced was reduced to 130 mL and 140 mL, respectively. The addition of these polymers as the coagulant aid help in reducing the sludge volume after the treatment. Lower SVI was observed at other concentrations due to the precipitation of metal coagulant. This was mostly due to the charge neutralisation of trivalent ions, which resulted in smaller and less compact flocs. In contrast, when polymers (RS and PAM) are used, a combination of bridging and sweep flocculation mechanisms occur. High molecular weight and a long chain polymer in RS and PAM exhibited larger particles size as it provided longer bridges that will enhance the particle size.

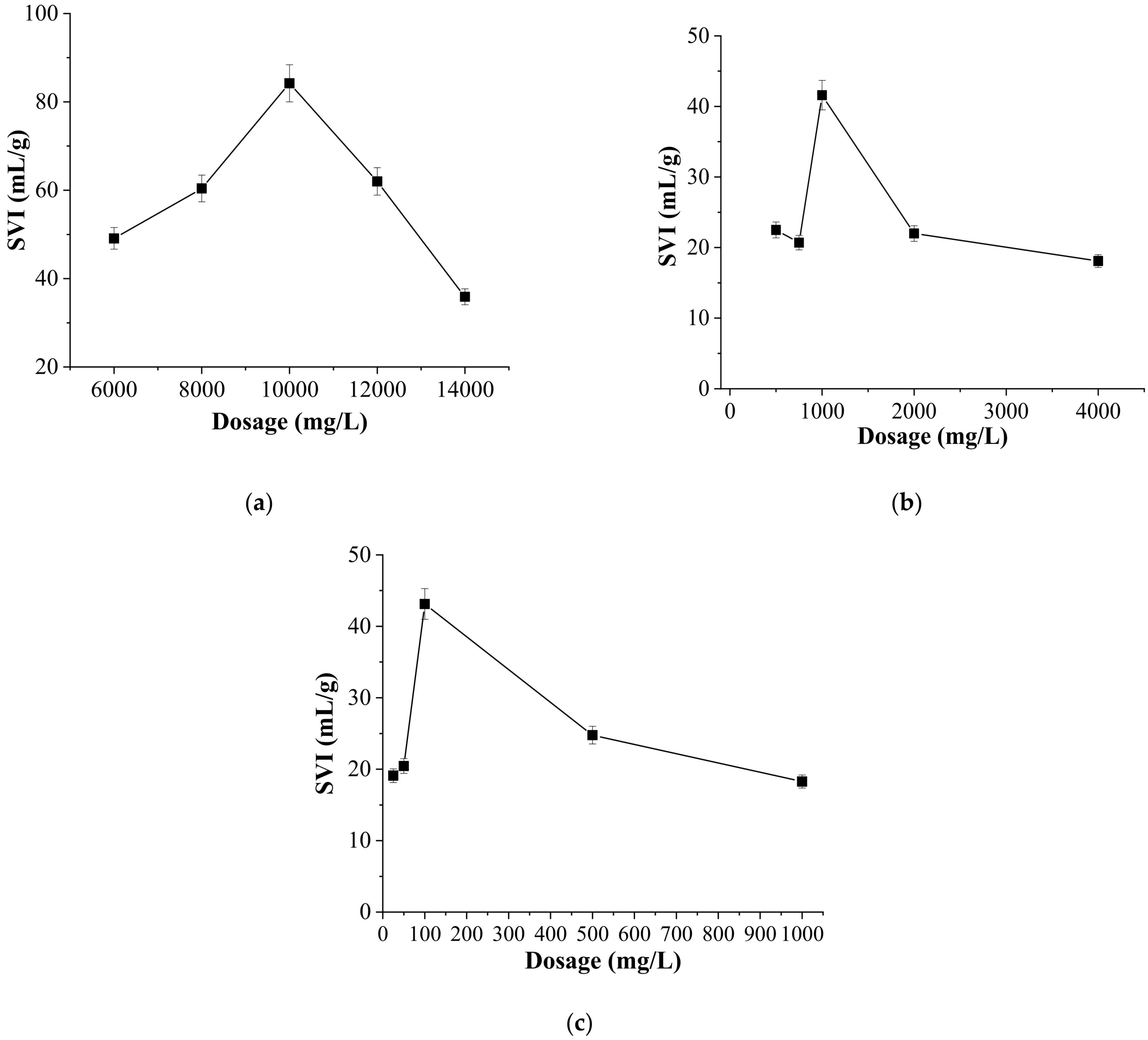

Figure 8. Sludge velocity index (SVI) at pH 8 for (**a**) 10,000 mg/L $SnCl_4$; (**b**) 8000 $SnCl_4$ mg/L + 1000 mg/L RS; (**c**) 8000 mg/L $SnCl_4$ + 100 mg/L PAM.

3.8. Cost Estimation of Coagulation Flocculation Process

Table 3 shows the cost estimation based on laboratory data which only include the chemical usage and energy expenditures. The total cost is only a rough estimate for a laboratory scale that compares the use of $SnCl_4$ as the main coagulant with the other most used metal coagulants.

Table 3. Cost estimation between $SnCl_4$ and other metal coagulants in coagulation-flocculation treatment.

Coagulant	Estimation Cost per 1 L (in USD)	Estimation Cost per 3 L (in USD)	References
$FeCl_3$	188	562	[40]
PAFCl	30	90	
$SnCl_4$	29	85	**This Study**

As the work only involves laboratory work, we could only estimate the cost based on the lab work. To evaluate the scale-up cost requires further study, which involves many other factors, including the performance of a pilot plant which was not done and beyond the scope of the current work. A feasibility study is also necessary before a recommendation on the cost factor could be proposed. Table 4 below show the cist estimation when $SnCl_4$ was used as the main coagulant and when RS and PAM were used as the coagulant aids.

Table 4. Cost estimation for $SnCl_4$ and the coagulant aids (RS and PAM).

Coagulant	Price of the Chemical (RM) *	Optimum Concentration Used	Amount of Chemical to Treat 1 m^3 of Leachate/Day	The Cost to Treat 1 m^3 of Leachate (RM) *	Total (RM) *
10,000 mg/L $SnCl_4$	193/100g	12.5 mL/500 mL	25 L	48,250	48,250
8000 mg/L $SnCl_4$	193/100 g	10 mL/500 mL	20 L	38, 600	38,616.50
1000 mg/L RS	2.50/kg	3.3 mL/500 mL	6.6 L	16.5	
6000 mg/L $SnCl_4$	193/100 g	7.5 mL/500 mL	15 L	28,950	29,900
100 mg/L PAM	95/kg	5.0 mL/500 mL	10 L	950	

* 1 USD = RM 4.15.

4. Conclusions

When $SnCl_4$ was used as a primary coagulant, a dosage of 10,000 mg/L was needed for the removal of 97.3% of colour and 81% of COD in leachate. On the other hand, the use of RS and PAM as the main coagulant was not as effective as $SnCl_4$. Low removal was observed. However, the use of RS and PAM as coagulant aid reduced the dosage of metal coagulant ($SnCl_4$) from 10,000 mg/L to 8000 mg/L and 6000 mg/L for RS and PAM, respectively. A combination of 8000 mg/L $SnCl_4$ and 1000 mg/L RS removed 97.6% of colour and 43.1% of COD in leachate. Low removal of COD by RS (as coagulant aid) mainly because RS imparted the organic matters content into the leachate, as it is originally a natural coagulant. On the other hand, 6000 mg/L of $SnCl_4$ in conjunction with 100 mg/L of PAM reduced 94.3% and 74.3% of colour and COD, respectively. The SVI and SSR of sludge also improved when polymers were introduced as the coagulant aid. The addition of 1000 mg/L with 8000 mg/L of $SnCl_4$ gave SVI and SSR values of 41.6 mL/g and 0.5 cm/min, respectively, with an average particle size of 183.4 µm. When 6000 mg/L $SnCl_4$ was used in combination with 100 mg/L PAM, the SVI and SSR values of sludge were improved to 43.1 mL/g and 0.55 cm/min. The decrease in the SVI value after the combination of polymers (coagulant aid) with $SnCl_4$ (main coagulant) implies that the volume of sludges to be disposed of will also be reduced. In addition, the increase in settling velocity in settling indicates the reduction in the size of the settling tank needed in the leachate treatment process. An average of 216.5 µm size of particle was obtained for PAM. Overall, the use of natural coagulant aid (RS and PAM) helps in reducing the amount of the main coagulant needed in the treatment of leachate.

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