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Progressive Freeze Concentration for Leachate Treatment using Vertical Finned Crystallizer

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Landfill leachate brings serious threats to public health and the environment due to its complex composition and difficult degradation. With the growing landfill leachate produced, potential pollution would be a big cause for concern. The effects of circulation flow rate and coolant temperature in progressive freeze concentration (PFC) of leachate as a treatment process were investigated in this study. The parameters effecting efficiency such as; biological oxygen demand (BOD), chemical oxygen demand (COD) and turbidity in ice crystals produced were measured. The results showed that the circulation flow rate of 3,400 mL/min and coolant temperature of -11 ºC were optimum for their respective lower values. -Factor affecting this parameter is the ice crystal growth rate. For circulation flow rate of 3,400 mL/min, BOD5, COD and turbidity obtained were 18 mg/L, 96 mg/L and 62 NTU. While for coolant temperature of -11 °C, BOD5, COD and turbidity obtained were 47 mg/L, 124 mg/L and 63 NTU. This new alternative approach in treating leachate using freeze concentration (FC) will be able to offer a solution towards the environmental damages.

1. Introduction

Landfill leachate or high-strength wastewater is a liquid extracted from the solid waste decomposition that contains a complex mixture of harmful inorganic and organic compounds. It can leak into groundwater and surface water (i.e. rivers), which significantly threatens the aquatic organisms, human health and environment (Abobaker et al., 2022). The leachate may contain heavy metals, mineral salts, organic contaminants and nitrogen composites; which can be characterized by high values of chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH range (acidic), total dissolved solids (TDS), and heavy metals (Alabiad et al., 2017). Leachate characteristics also vary according to its volume, composition and condition of biodegradable matter, which are affected by factors of landfill climates, ages, waste types, rapid urbanization, lifestyle modification and increasing industrial activities. Leachate generation is uncontrolled and extremely difficult to treat due to which it becomes a significant concern for municipal solid waste (MSW) landfills and one of the most serious social problems in many developing nations (Alabiad et al., 2017).

For this reason, the concentrated leachate discharge must be effectively treated and safely disposed to avoid ecotoxicity and environmental damages. Generally, leachate treatment methods prior to disposal (e.g. precipitation-coagulation, biochemical processes etc.) is implemented to remove large amounts of organic matter and ammoniacal nitrogen, which include physical, physico-chemical and biological processes (Wang et al., 2018). The final in-depth treatments of leachate include electrochemical, advanced oxidation, activated carbon adsorption, and membrane treatment processes (e.g., evaporation, reverse osmosis, nanofiltration, membrane bioreactors or MBR) (Alabiad et al., 2017). However, some of the existing techniques remain complicated, costly and commonly necessitate certain adaptation during the process. Additionally, there is a growing need for advanced treatment technologies that concentrate on resource recovery with little impact on the environment (Samsuri et al., 2015).

Evaporation techniques for leachate treatment can be divided into (i) forced evaporation (i.e., through heating) and (ii) natural evaporation (i.e. with panels). Evaporation is a process of vaporization, where clean water can

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be recovered and concentrated wastewater containing solutes can be disposed (for contaminants) or recycled for further use (for useful chemicals). Commonly, the forced evaporation uses thermal energy from the landfill gas (LFG) produced, while the natural evaporation functions according to local climatic conditions (e.g., wind speed, solar radiation, air temperature) and the contact area enhancement between air and liquid. Forced evaporation is the most extensively used option that can reduce the leachate volume up to 95 % (i.e. removal of COD, ammonia and heavy metals), but still needs a longer operation time. Although it is easy to carry out, evaporation process could lead to emission of polluted gases, low efficiency and high energy cost (Lippi et al., 2018). Meanwhile, reverse osmosis (RO) is amongst the available technology in treating landfill leachate for surface discharge with an overall removal efficiency of over 90 % (for BOD, COD, TDS) (Fatima et al., 2017). It is a process where solvent is separated from the solution by the aid of concentration gradient through a semi-permeable membrane (Liu, 2014). RO provides an absolute separation barrier for all contaminants (including removal of heavy metals and salts), more compact footprint and superior automation over other options. However, RO also has disadvantages for leachate treatment, namely membrane fouling and high disposal cost for a large volume of RO leachate brine.

A new alternative approach in treating leachate which is freeze concentration (FC) seems to be able to offer a solution towards the shortcomings of biological treatment due to the co-existence of heavy metals and microbes. FC is a non-thermal process that turns the solution's water content into ice crystals (Samsuri et al., 2015). According to Jusoh et al., (2018) FC process is a phenomenon in which an ice crystal develops from an aqueous solution and expels the impurities to produce pure ice crystals. Suspension freeze concentration (SFC) and progressive freeze concentration (PFC) are two FC approaches Yahya et al. (2019). The major difference between SFC and PFC is the development of ice crystals. SFC is usually a scraped surface heat exchanger (SSHE) assisted technique which initiates the ice growth from seed ice and eventually produces small ice crystals which are found as a suspension in the mother liquor (Samsuri et al., 2015). Whereas PFC is a technique in which a single large ice block is produced layer by layer on a cooled surface, which makes the separation between the ice crystals and mother liquor easier. This study's objective was to investigate the possibility of PFC application using Vertical Finned Crystallizer (VFC) to treat landfill leachate and subsequently recover the high-quality water either for direct discharge or reuse. Thus, the effects of circulation flow rate and coolant temperature towards BOD, COD, turbidity and yield of ice formed were determined.

2. Materials and method

2.1 Materials

In this experiment, leachate was collected from Pekan Nenas landfill (Pontian, Johor). Ethylene glycol mixed with distilled water (50/50 v/v) was used as a coolant liquid in the water bath to maintain the sample temperature.

2.2 Analytical method

The leachate sample is decomposed by present microorganisms, the oxygen consumed for the decomposition process is known as BOD. The BOD5 value (refers to 5-days amount of oxygen consumed) was measured using Dissolved Oxygen instrument (YSI Model 58, USA) with accuracy up to 0.01 mg/L. Meanwhile, COD is the measurement of the oxygen equivalent consumed by organic matter in a sample during strong chemical oxidation condition. The COD reactor (HI 839800, HANNA Instrument) was used to heat up chemical vials containing samples at temperature ranging from 105 to 150 °C. The COD value was measured by COD meter (HI 83099, Hanna Instrument). Both BOD and COD were analysed using APHA Standard Method (APHA, 2005). Turbidimeter (HACH) with ability to measure up to 2,000 NTU was also used for sample analyses. Turbidity was monitored as an indicator of potential pollution in the PFC water recovery.

2.3 Experimental procedure

A PFC system called Vertical Finned Crystallizer (VFC) was used in this work as shown in Figure 1a and 1b. It is a cylindrical ice crystallizer made of stainless steel with wall thickness of 1 mm and diameter of 8 cm. VFC is equipped with four vertical rectangular fins with 30 cm height, 2 cm length and 1.5 cm width on the inner wall of it, which leads to an increase in heat transfer area by 63.7 % (Amran and Jusoh, 2016). The experimental setup is shown in Figure 1d, consisting of a VFC, a refrigerated water bath, a peristaltic pump (Masterflex, USA), silicone tubes and a shaker. Prior to treatment process, leachate sample was kept in a freezer at a temperature close to the freezing point of water. The temperature of coolant in both jacket and refrigerated water bath were kept at the desired temperature before initiating the PFC experiment.

Firstly, sample was filled in a feeding tank and then fed into the VFC with the help of a peristaltic pump and silicon tubes as connections. The circulation flow rate was manipulated by the pump in the range of 2,600 and 3,400 mL/min. There was a time delay occurred at the beginning of experiment for leachate to fully fill the crystallizer. The coolant temperature was varied between -5 to -13 °C. After the crystallizer and the silicone tube were fully filled with the sample, the valve was closed to stop the feeding process. The shaker speed was maintained at 40 ohms. Feed solution was circulated for 50 min in the crystallizer containing a silicon tube for the smooth crystallization process to take place (Amran and Jusoh, 2016). After the circulation and shaking was stopped, the concentrated leachate solution from the crystallizer was successfully recovered. The thickness of ice layer produced was observed from the top (close-up view) and measured with a caliper ruler. Then, the volume of concentrated leachate and ice layer were determined. Eventually, the thawed sample of ice was analyzed for its BOD5, COD and turbidity.

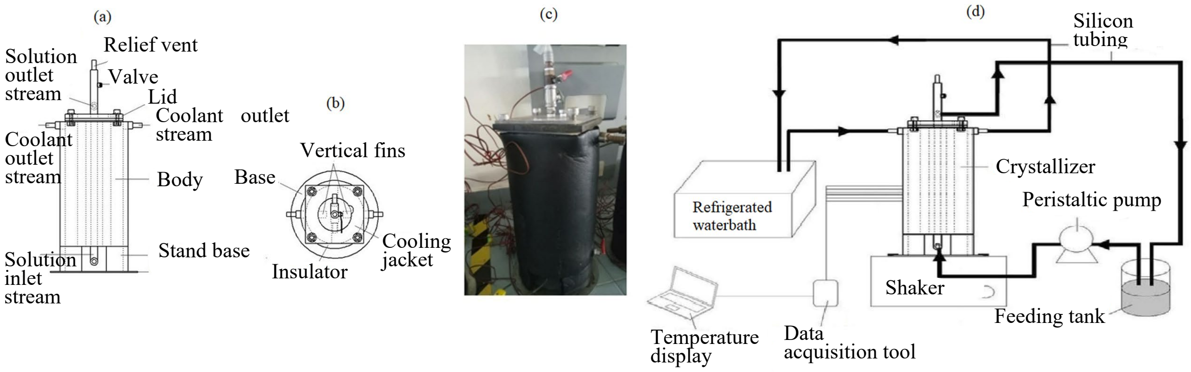

Figure 1: Schematic diagram of PFC (a) Side view of VFC (b), top view of VFC, (c) real image of VFC and (d) Experimental setup for VFC.

2.4 Experimental design

In order to determine the effects of circulation flow rate and coolant temperature on the dependent variables (Table 1), the tabulated designs were performed as follows. A fixed circulation time of 50 min was selected to run the experimental designs.

Table 1: Parameters at different circulation flow rate (coolant temperature constant at -9 °C)

	Circulation Flow Rate (mL/min)				
	2,600	2,800	3,000	3,200	3,400
Volume of feed (mL)	1,070	1,070	1,070	1,070	1,070
Volume of Ice formed (mL)	300	290	270	240	235
Volume of concentrate (mL)	770	780	800	830	835
Ice thickness (cm)	0.80	0.75	0.70	0.65	0.60
Initial BOD5 (mg/L)	325	325	325	325	325
Final BOD5 (mg/L)	147.0	81.0	52.2	49.0	18.0
Initial COD (mg/L)	1,940	1,940	1,940	1,940	1,940
Final COD (mg/L)	243	201	156	123	96
Initial turbidity (NTU)	375	375	375	375	375
Final turbidity (NTU)	78	71	69	64	62

Table 2: Parameters at different coolant temperature (circulation flow rate constant at -3,200 mL/min)

	Coolant Temperature (°C)				
	-5	-7	-9	-11	-13
Volume of feed (mL)	1,070	1,070	1,070	1,070	1,070
Volume of Ice formed (mL)	35	141	250	277	500
Volume of concentrate (mL)	1,035	929	820	793	570
Ice thickness (cm)	0.25	0.35	0.60	0.70	0.95
Initial BOD5 (mg/L)	325	325	325	325	325
Final BOD5 (mg/L)	290	247	51	47	166
Initial COD (mg/L)	1,940	1,940	1,940	1,940	1,940
Final COD (mg/L)	311	236	125	124	195
Initial turbidity (NTU)	375	375	375	375	375
Final turbidity (NTU)	124	94	65	63	82

3. Results and discussion

3.1 VFC product for leachate treatment

After treated using PFC system, the recovered water from the crystallizer was compared to raw leachate (before experiment) and concentrated leachate (separation from the thawed ice). Figure 2a clearly shows the VFC recovered product was much clearer, which yielded light brown in colour.

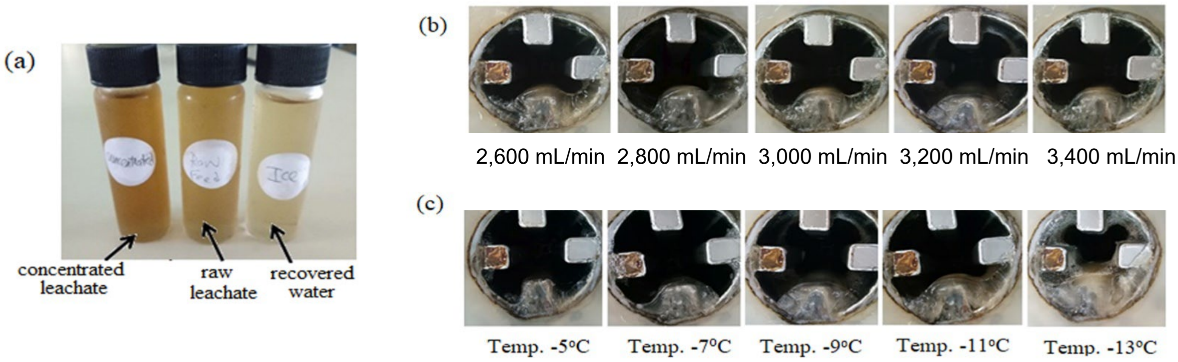

Figure 2: (a) Comparison among samples of raw leachate, concentrated leachate and PFC water recovery, (b) Close-up views from the top of VFC for ice thickness at different circulation flow rate. (c) Close-up views from the top of VFC for ice thickness at different coolant temperature.

Of further interest, the thickness of ice produced from different circulation flow rate were examined, as presented in Figure 2b. It was found that the ice thickness decreased with increasing circulation flow rate. However, the thinnest ice produced (i.e., 0.60 cm) was recorded at the circulation flow rate of 3,200 mL/min, followed by the circulation flow rate of 3,400 mL /min (i.e. 0.65 cm). Still, the ice thicknesses of both high circulation rate were considered the lowest. It was in agreement with the measured volume of the ice formed, where the ice volume decreased with increasing circulation flow rate as shown in Figure 3a. Hence, the lowest ice volume of 235 mL was obtained at the highest circulation rate of 3,400 mL/min. The results are in accordance to a similar study, in which this trend was due to the saturation of the solute in the concentrate when too high circulation rate was applied (Amran et al., 2018). In other words, the growth of ice layer could erode due to ice-liquid interface containing rejected solute, which in turn caused the solution less concentrated to be trapped in ice (Jusoh, 2018).

Meanwhile, the thickness of ice formed from different coolant temperature is depicted in Figure 2b and Figure 2c. It can be seen that the thickness of ice produced is merely 0.25 cm at the highest temperature, i.e., -5 °C. As temperature decreases, the thickness of ice was recorded to increase accordingly. At coolant temperature of -13 °C, the thickest ice was successfully produced with the ice thickness of 0.95 cm. From Figure 3b, it can also be seen that the volume of ice formed increased with decreasing coolant temperature. This was due to the fact that lower coolant temperature promotes higher crystallization rate, in which the temperature difference between the feed solution and coolant becomes greater. Therefore, the highest volume of ice obtained was 500 mL, i.e., at the lowest temperature of -13 °C.

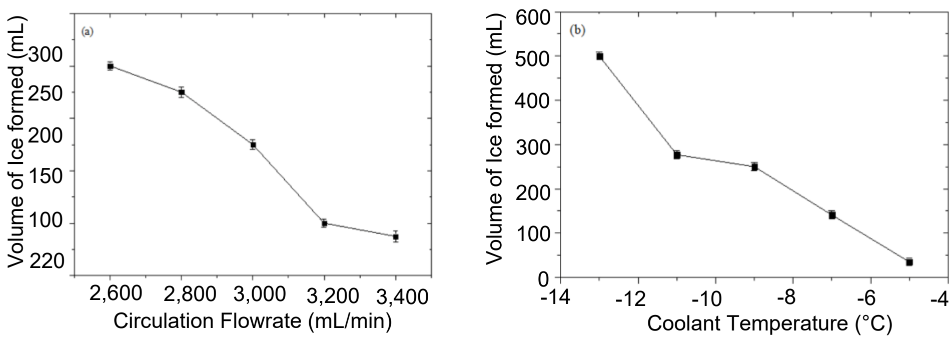

Figure 3: (a) Effect of circulation flow rate on volume of ice formed, (b) Effect of coolant temperature on volume of ice formed.

Figure 4 presents the effect of circulation flow rate and coolant temperature on the BOD5, COD and turbidity. Obviously, it could be seen that the values of BOD5, COD and turbidity reduced with an increase in circulation flow rate. In brief, the lower values indicated the higher purity of ice formed. The fluid flow structure of the solution regulates the heat and mass transfer in VFC. Thus, at higher flow rate, the shear force could carry away the trapped solute from the ice layer into the solution, resulting in more purified ice formation (Yin et al., 2017) . From the results, the BOD5 and COD values obtained were 18 mg/L and 96 mg/L at the highest circulation flow rate (i.e., 3,400 mL/min). These values met the specification limits by Malaysian Environmental Act (EQA, 1974) under Second Schedule of Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009, that is 20 mg/L and 400 mg/L for BOD5 and COD.

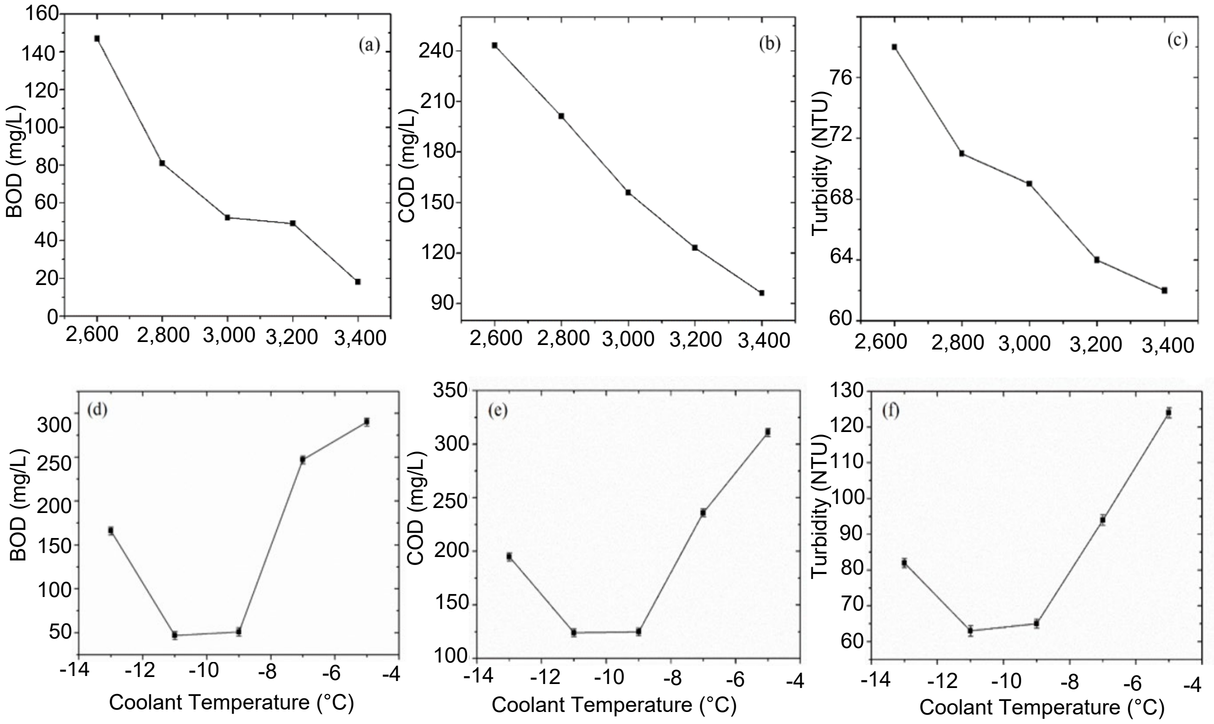

Figure 4: Effect of circulation flow rate and coolant temperature on (a) BOD5, (b) COD and (c) Turbidity; Effect of coolant temperature on (d) BOD5, (e) COD and (f) Turbidity

This study concluded that the water recovery from the VFC ice layer formed is allowable to be safely released into the environment. In the meantime, the lowest turbidity (i.e., 62 NTU) at the highest circulation rate proved that the turbid materials were effectively removed after the VFC treatment, which a decrease by 83.5 % from the raw leachate (i.e., 375 NTU).

3.2 Effect of coolant temperature on dependent variable

The coolant temperature range was selected below the freezing point of water, that is from -5 °C to -13 °C. Theoretically, the pure water in the leachate solution will form an ice layer during the PFC process while impurities (e.g. pollutants, organic matter) continue to circulate and leave a more concentrated leachate at freezing temperature supplied by the coolant (Yin et al., 2017). The results for the study of the effect of coolant temperature on (a) BOD5, (b) COD and (c) turbidity of the ice formed are illustrated in Figure 4b.

From the plotted graphs, it could be seen that the best coolant temperature was approximately -11 °C. At this temperature, the highest purity of ice was produced in VFC in terms of BOD5, COD and turbidity values. Obviously, the values of BOD5, COD and turbidity decreased with decreasing temperature from -5 °C to -9 °C, describing the higher purity of ice layer at lower temperature Yahya et al. (2017). In line with Miyawaki *et al.* (2016), the ice front growth is significantly dependent on the coolant temperature. At lower temperature, the temperature difference between the surfaces of crystallizer and solutes in leachate was larger thus resulted in greater heat transfer as well as better crystallization efficiency.

However, when too low temperature (i.e., -13 °C) was applied, the values of BOD5, COD and turbidity increased. This phenomenon is called solute inclusion where the impurities in ice layer started to increase caused by the higher rate of ice formation. As a result, employing too low temperature could trap more solutes in the ice layer

(Amran and Jusoh, 2016). It occurred when the rate of solutes moving towards the ice crystal layer was greater than the rate of outward movement from the ice crystal layer.

4. Conclusion

In short, PFC using VFC has promising potential to effectively treat the landfill leachate in addition to lower capital cost compared to conventional freeze concentration. VFC has a shorter operating time and lower energy requirement. Besides, the application of PFC can be an excellent system in removing the dissolved organic matter, heavy metals and microorganisms, which are currently very troublesome in most landfill treatment processes. In this study, it can be concluded that the best circulation flow rate for VFC to treat leachate is 3,400 mL/min. The high-quality of ice formed was found to be the highest at this condition, where the lowest values were obtained for BOD5, COD and turbidity, namely 18 mg/L, 96 mg/L and 62 NTU. Meanwhile, for the coolant temperature, the best temperature was at -11 °C, in which BOD5, COD and turbidity obtained were the lowest, i.e., 47 mg/L, 124 mg/L and 63 NTU. Conclusively, the outcome of this study provides fundamental information to further investigate for optimization of the landfill leachate treatment using PFC.

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