



Treatment of Kulim and Kuala Sepetang Landfills Leachates in Malaysia using Poly-Aluminium Chloride (PACl)

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Abstract

The main concern in sanitary landfill management is leachate generation that is known to be highly polluted wastewater. Migrations of untreated leachates are potential sources of hazardous contaminants in soil, groundwater and surface water. This paper is focused on landfill leachate treatment by coagulation-flocculation process using poly-aluminum chloride (PACl) as coagulant. The performance of PACl was evaluated by removal of suspended solid (SS), turbidity, colour, chemical oxygen demand (COD) and ammonia nitrogen ($\text{NH}_3\text{-N}$) by jar-test experiments. Samples used in this study were collected from Kulim Landfill Site (KLS) and Kuala Sepetang Landfill Site (KSLs) in Malaysia. The results show that, pH optimum for KLS was obtained at pH 7 while KSLs at pH 6. In this study, optimum dosage of PACl for KLS and KSLs leachates was concluded at 500 mg/L and 1000 mg/L respectively. At optimum dosage, PACl successfully removed 98% SS, 92% turbidity, 100% colour, and 70% COD in KLS leachates while the removal percentage of SS, turbidity, colour and COD in KSLs leachate were 94%, 96%, 95%, and 70% respectively. These results showed a good performance of PACl as coagulants in landfill leachates treatment. However, PACl was less effective in treating $\text{NH}_3\text{-N}$. Low removal efficiency may be due to $\text{NH}_3\text{-N}$ and PACl cationic nature, it is suggested that additional of coagulant aids with anionic characteristic may improve the performance of coagulation-flocculation process in removing contaminants like $\text{NH}_3\text{-N}$ in landfill leachates.

Keywords: Landfill, leachate, PACl, coagulation-flocculation.

Introduction

Landfilling is the main method used for municipal solid waste disposal in Malaysia. However, the main problem associated with this method is leachate generation. Landfill leachates were produced from combination of water percolation and biodegradation activities (decomposition of biodegradable materials) in landfill and known to be highly polluted wastewater. Generally, leachate contains four types of pollutants such as dissolved organic matter, in-organic macro-components (chloride, sulphate, $\text{NH}_3\text{-N}$, phosphate, and sodium), xenobiotic organic components (benzene, toluene, ethylbenzene and xylene) and heavy metals (zinc, iron, plumbum, nickel and manganese)¹⁻³. Thus, improper management of landfill leachate may cause surface and groundwater contamination which is threatened to human health as well as natural environment⁴.

Basically, the characteristics of landfill leachate range widely depending on the waste composition, climate condition, age of landfill, site hydrology, bacterial activities and landfill design⁵⁻⁷. Chemical composition and concentration of leachate were mainly affected by landfill age; therefore, leachate constituents gradually changed as leachate getting older. According to several studies^{5,9-11} of landfill leachate, young leachates have lower pH (<6.5), heavy metals (> 2 mg/L) and high biological oxygen demand (BOD_5) and chemical oxygen demand (COD) (>15, 000 mg/L). Meanwhile, old leachate tends to produce low COD (< 3000 mg/L), slightly alkaline pH (>7.5), heavy metals

(< 2 mg/L) and high humic substances. So leachate treatment is very important to ensure that effluent is safe to be discharged into the natural environment.

An appropriate method for leachate treatment is determined by the characteristics of the leachate itself. Changes in the leachate constituents with time need to be considered in choosing leachate treatments so that contaminating components is effectively removed¹². Young leachates which contain high biodegradable components such as volatile fatty acids are suitable to be treated by biological treatment while physical-chemical method is more suitable for old or stabilized leachates^{11,13}. The coagulation – flocculation process is a physical-chemical method known to be effective for water and wastewater treatments. These processes involve charge neutralization or destabilization of contaminants (coagulation), using chemical substances (coagulant), and conversion of unstable particle into bulky flocules (flocculation) to increase particle size¹². There are four coagulation mechanisms that occur according to the types of coagulant use, namely double layer compression (destabilize the particles), sweep flocculation (encapsulates the particles), adsorption and charge neutralization (bridging between opposite charge ions), and adsorption and interparticle bridging¹⁴. Therefore, the use of right coagulant will enhance the removal of pollutants.

Typically, coagulant can be categorized into three major groups which are metallic salts (e.g. aluminium sulphate and ferric chloride), polymeric metallic salts (e.g. poly-aluminium

chloride and poly-aluminium sulphate chloride), and polymer (zeolite, starch, chitosan, and polyamines)¹⁴. Aluminium and ferric salts are the most common coagulants used for water and wastewater treatment. However, in the past few years, poly aluminium chloride (PACl) has surged and gradually replaced these coagulants due to its reputation in high coagulation efficiency, rapid precipitation, less dosage, lower alkalinity consumption, lesser sludge production, low cost and wider availability^{13,15}.

This paper is focused on landfill leachate treatment using PACl in two sanitary landfill sites situated in Peninsular Malaysia which are Kulim Landfill Sites (KLS) and Kuala Sepetang Landfill Sites (KSLS). KLS was started to operate in 1996 as an open dumping site and upgraded into anaerobic sanitary landfill in 2006 while KSLS was classified as improved anaerobic landfill in 2007, equipped with HDPE pipe conveyer to leachate collection ponds and it has been operated for about 14 years¹. The effectiveness of PACl was evaluated on the removal of turbidity, colour, COD, ammonia nitrogen (NH₃-N), and suspended solid from KLS and KSLS landfill leachate.

Methodology

Leachate: All leachate samples used in this study were collected from KLS and KSLS landfill sites in 25 L plastic container and stored at 4°C in laboratory cold room to minimize biological and chemical reaction¹⁶. The samples were taken out from cold room and allowed to reach ambient temperature for about 2 hours before conducting a jar test. Then, the samples were thoroughly agitated for re-suspension of possibly settling solids prior to any tests. The characteristics of raw leachate collected are shown in table-1.

Coagulation-Flocculation: The tests were performed using conventional Italy VELD- Scientifica Jar test apparatus Model: JLT6, equipped with six unit multiple stirrers (2.5 cm x 7.5 cm) and 6 beakers of 1L volume each. Coagulant used in this study was hydrolysed solution of Poly-aluminium Chloride (PACl) with the formula Al(OH)_xCl_y (where x is between 1.35-1.65, and y = 3-x) and pH ranging from 2.3-2.9 (due to the hydrochloric acid presence) provided by Hasrat Bestari Sdn. Bhd. A stock solution of 18% PACl was prepared and used for the experiments in this study. Different dosage of PACl was added after all beakers were filled with 500 mL of agitated leachate samples. Before the samples were rapidly mixing, pH was adjusted to the required value using sulphuric acid and sodium hydroxide.

There are three important stages in conducting coagulation-flocculation by Jar test, including: i. Rapid mixing, ii. Slow mixing and iii. Settlement time. A primary Jar - test was conducted to select the best combination of these three stages. Jar-test for varying rapid mixing speed and duration showed that the combination of 200 rpm in 3 min gives the highest removal efficiency for all parameters tested. Meanwhile, the slow mixing test has the best condition at speed of 40 rpm with mixing

duration of 30 minutes. During the test, the most effective time for flocculants to settle was 30 minutes. More than 90% removal of SS, turbidity and colour was recorded under this condition. The operating conditions set up for this study are listed in table- 2.

Analytical Determination: Withdrawal of supernatant samples took place at a point located 2 cm below the liquid level using plastic syringe. The performance of PACl in removing contaminants in leachate samples was determined through leachate characteristics such as pH, COD, NH₃-N, turbidity, and colour. pH meter model Cyberscan 20 was used to measure pH value while turbidity was read by 2100N HACH laboratory turbidimeter. Concentration of COD was determined in accordance with closed reflux and Calorimetric Method (5220-D). Meanwhile, NH₃-N was analysed using the Nesslerization method (4500-NH₃). Colour was measured as true colour by DR2800 HACH spectrophotometer after filtered through GC-50 filter papers with 0.45 µm pore size from Advantec Toyo Kaisha Ltd., Japan and the values obtained were reported in Platinum-cobalt (PtCo) as mentioned in the Method No.21210C. The removal efficiency of each parameter was calculated using the following formula.

$$\text{Removal (\%)} = [(C_i - C_f)/C_i] * 100 \quad (1)$$

where C_i and C_f are the initial and final concentrations of leachate sample in mg/L, respectively.

Results and Discussion

Raw leachates characteristics: Raw leachates analysis for both landfill sites have alkaline pH with an average of 8.05 (KSLS) and 7.59 (KLS) respectively (table-1). The obtained pH agrees with the other studies conducted for stabilized leachates characteristics in Malaysia^{1,17}. However, according to BOD₅/COD ratio in table-1, KLS and KSLS leachates showed higher biodegradability (0.19 and 0.24) than expected. The values obtained indicating that both leachates are partially stabilized leachates (0.1 < BOD₅/COD < 0.3) rather than stabilized leachate (BOD₅ < 0.1), even though the age of both landfills are already more than 10 years¹. This probably happened because both landfill are still operating and producing young leachates which are mixed together with old leachates and increased its biodegradability. Thus, biological degradation is still occurring in both landfills¹⁷.

Optimum coagulants dose: In this study, PACl doses of 0 – 1000 mg/L were tested at pH 7 for KLS leachates while doses of 0 – 6000 mg/L were tested at pH 6 for KSLS leachates. Optimal dosage of PACl was optimized according to its performance in removing SS, turbidity, colour, COD, and NH₃-N in leachates samples. Figure-1 and figure-2 illustrated the removal percentage of parameters versus different PACl doses. Based on the results obtained, optimum dosage of PACl for KLS and KSLS leachates were concluded at 500 mg/L and 1000 mg/L respectively. At 500 mg/L, PACl was successfully removing 98% SS, 92% turbidity, 100% colour, and 70% COD in KLS

leachate. Meanwhile, percentage removal of SS, turbidity, colour and COD in KSLs leachate at 1000 mg/L PACl were 94%, 96%, 95%, and 70% respectively.

These results displayed high removal efficiency of contaminants by PACl, this is conforming that stabilized leachates are rich with organic matter¹¹ such as humic substance (measured as COD intensity) and fulvic like fraction^{1,18} which weak against hydrolysing coagulants such as PACl¹⁹, hence these substances were successfully removed. The removal of substance can be explained by the charge neutralization mechanism in coagulation-flocculation process whereas negative charges of particles in leachates are neutralized by addition of cationic coagulant (PACl) and form larger particles during flocculation²⁰. As the landfill getting older, more organic matter with negatively charged particles exist in the leachates. Naturally, the amount of coagulant required to neutralize this

charge is also increased. Basically, the amount of coagulant added depends on the magnitude of electrical charge surrounding the colloidal particles (zeta potential) in samples. In this study, KSLs samples required larger amount of PACl to obtain the optimum coagulant dosage compared to KLS samples which show that there are more organic particles with negative charge in KSLs leachate compared to KLS leachate. Therefore, larger amount of coagulant is required as more negative charges exist in the samples²⁰. Besides, PACl showed good performance in colour removal. According to Aziz et al.,²¹ colour in landfill leachates was mainly contributed by organic matters with some insoluble forms that were determined in turbidity and SS form. Thus, colour removal exhibits a similar pattern to these parameters. The removal efficiency of colour by PACl in this study is also comparable to the best conventional coagulant, Ferric chloride (97%) reported by Aziz et al.²¹.

Table – 1
Characteristics of KLS and KSLs raw leachate

Parameter	KSLs			KLS		
	Minimum	Maximum	Average	Minimum	Maximum	Average
pH	7.86	8.31	8.05	7.27	7.92	7.59
Turbidity (NTU)	40.3	178	88.9	12.7	67	26
Colour (Pt Co)	1120	3100	2220	192	440	326
SS (mg/L)	151	278	233	11	99	47
BOD ₅ (mg/L)	97	184	158	7	69	29
COD (mg/L)	680	950	855	105	131	117
BOD ₅ /COD	0.11	0.26	0.19	0.06	0.52	0.24
Ammonia-N (mg/L)	410	1185	857	174	280	210

Table- 2
Condition employed for Jar-test experiment in this study

Critical parameter	Unit	Value
Speed of Rapid Mixing	rpm	200
Duration of Rapid Mixing	min	3
Speed of Slow Mixing	rpm	40
Duration of Slow Mixing	min	30
Settling Time	min	30

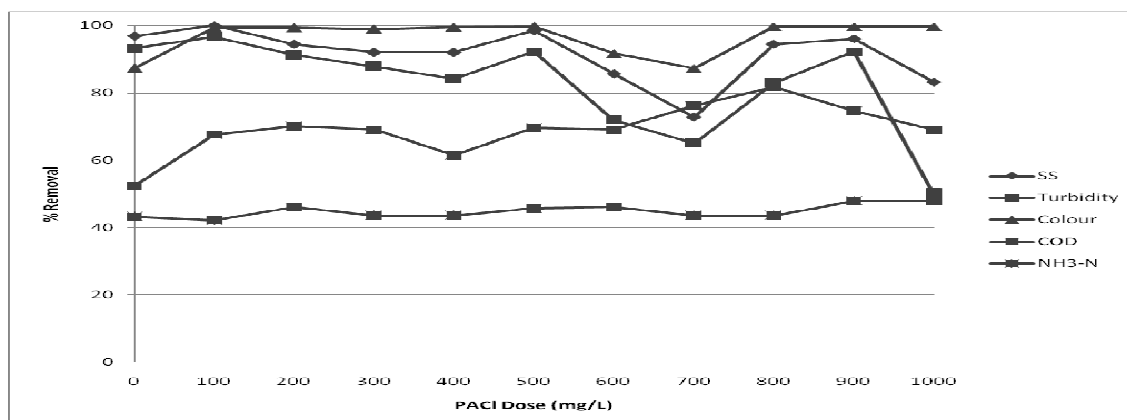


Figure-1
Percentage removals of SS, Turbidity, Colour, COD and NH₃-N vs PACl Dose for KLS leachates

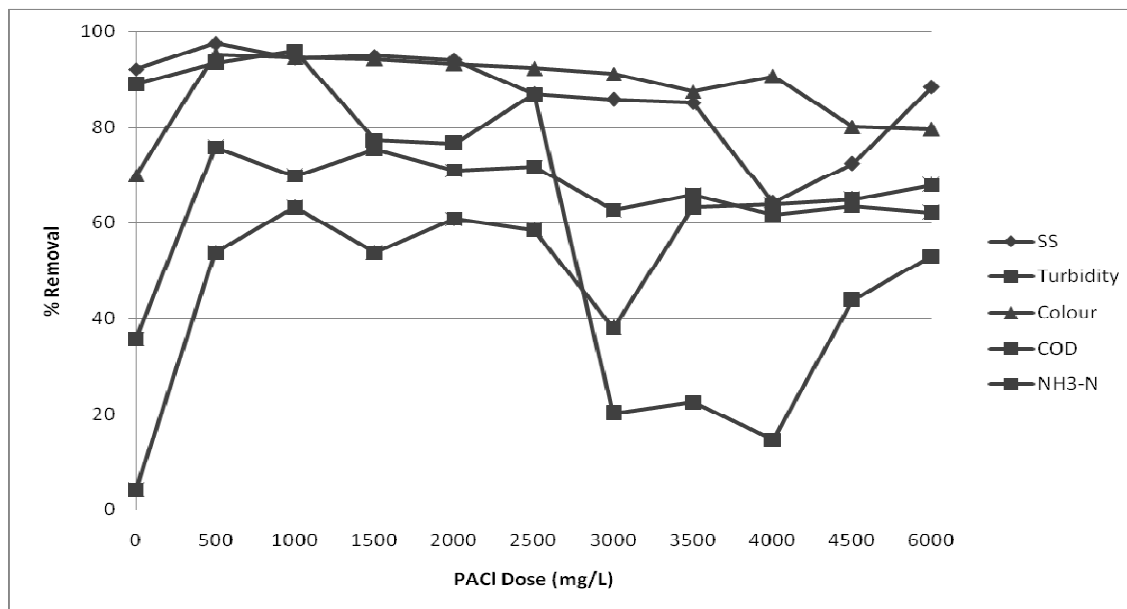


Figure -2
Percentage removals of SS, Turbidity, Colour, COD and NH₃-N vs PACl Dose for KSLs leachates

Moreover, higher removal efficiency was obtained in this study compared to the similar study by Ghafari et al.²² on Pulau Burung Landfill Site (PBLs) leachates where the removal percentage of SS, turbidity, colour and COD at the optimum dosage (1.9 g/L) were 71%, 82%, 87%, and 40% respectively. The difference in removal capacities by PACl between these landfill leachates are possibly related to the landfill age since the characteristics and constituents of leachates depend on this factor. Aziz et al.⁵ mentioned that leachates undergo four phases of changes according to the age of the landfill, including transition (0-5 years), acid formation (5-10 years), methanogenic phase (15-20 years), and final maturation (> than 20 years). As for the age of the landfills, PBLs is older than KSLs and KLS is younger than KSLs.

As for NH₃-N, the presence of elements was higher in KSLs (410-1185 mg/L) leachate compared to KLS (174-280 mg/L) leachate. These values verified Kulikowska and Klimiuk¹⁸ statement that older leachates are rich in NH₃-N as a result of methanogenics phase where biodegradable materials containing nitrogen substance was hydrolysed and fermented²⁰. The removal efficiency of NH₃-N by PACl in coagulation-flocculation process is lower, compared to other parameters. As shown in figure-1, NH₃-N in KLS leachate has low removal efficiency with merely 3% removal. Hamadani et al.²⁰ stated that low removal efficiency of NH₃-N is related to the positive surface charge of NH₃-N that prevents the attraction between PACl (positively charges) and NH₃-N in samples. However, a rare behaviour was shown in removal of NH₃-N in KSLs leachate sample (figure- 2). A significant removal percentage was detected where removal percentage reached up to 63% at optimum PACl dosage (1000 mg/L).

pH optimum: Effect of different pH was evaluated and the results obtained are presented in figure-3 and figure- 4. The range used to determine optimum pH is 2 to 12, and fixed percentage of PACl was added to all samples during this experiment. KLS leachate samples were added with 500 mg/L of PACl while KSLs leachate samples were added with 1000 mg/L PACl. Coagulation-flocculation process showed the best condition at pH 7 for KLS and pH 6 for KSLs. The values obtained are slightly lower compared to Ghafari et al.²² where the pH optimum was 7.5 with removal efficiencies of 96% SS, 96% turbidity, 92% colour, and 47% COD respectively. Meanwhile, figure-3 shows that SS and turbidity in samples were almost completely removed (99% and 96%) while colour was completely removed (100%). But, COD and NH₃-N only recorded about 71% and 59% removal efficiency. In figure- 4, the removal percentage of SS, turbidity and colour at optimum pH (pH 6) is slightly lower compared to the results from KLS leachates with obtained values of 96%, 91%, and 92% respectively. Nevertheless, COD showed a very low removal capacity with a difference of 40% from COD removal in KLS at optimum pH. Meanwhile, NH₃-N exhibits similar removal pattern and removal efficiency to KLS leachates.

Conclusion

Performance of PACl as coagulants was tested using samples from two different sites. The results show that, pH optimum for KLS was obtained at pH 7 while KSLs at pH 6. In this study, optimum dosage of PACl for KLS and KSLs leachates was concluded at 500 mg/L and 1000 mg/L respectively. At optimum dosage, PACl successfully removed 98% SS, 92% turbidity, and 70% COD, with a complete removal of colour, in KLS leachates while percentage removal of SS, turbidity, colour

and COD in KSLs leachate were 94%, 96%, 95%, and 70% respectively. Better performance was exhibited by PACI in removing SS and colour from KLS leachates compared to KSLs leachates. However, the results only show a slight difference from each other. This small difference may be due to the similar range of landfill age. PACI application as coagulant has shown a good removal efficiency for SS, turbidity, colour and COD. However, PACI performance in removing NH₃-N is lower

compared to these parameters. NH₃-N in KSLs leachate has a removal efficiency of 60% while KLS removal efficiency was 43%. This may be related to the cationic nature of NH₃-N and PACI which prevent PACI from neutralized positive charges surrounding NH₃-N particles. Thus, addition of coagulant aids to enhance coagulation-flocculation process and increase the removal percentage of NH₃-N in landfill leachates is recommended.

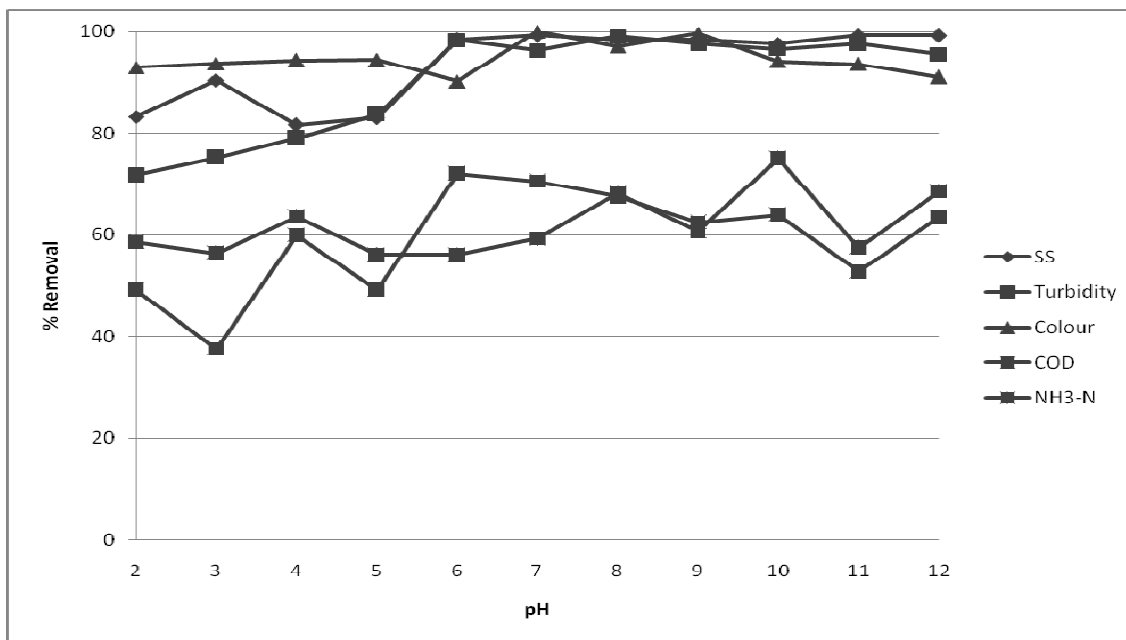


Figure-3
 Percentage removals of SS, Turbidity, Colour, COD and NH₃-N vs pH for KLS leachates

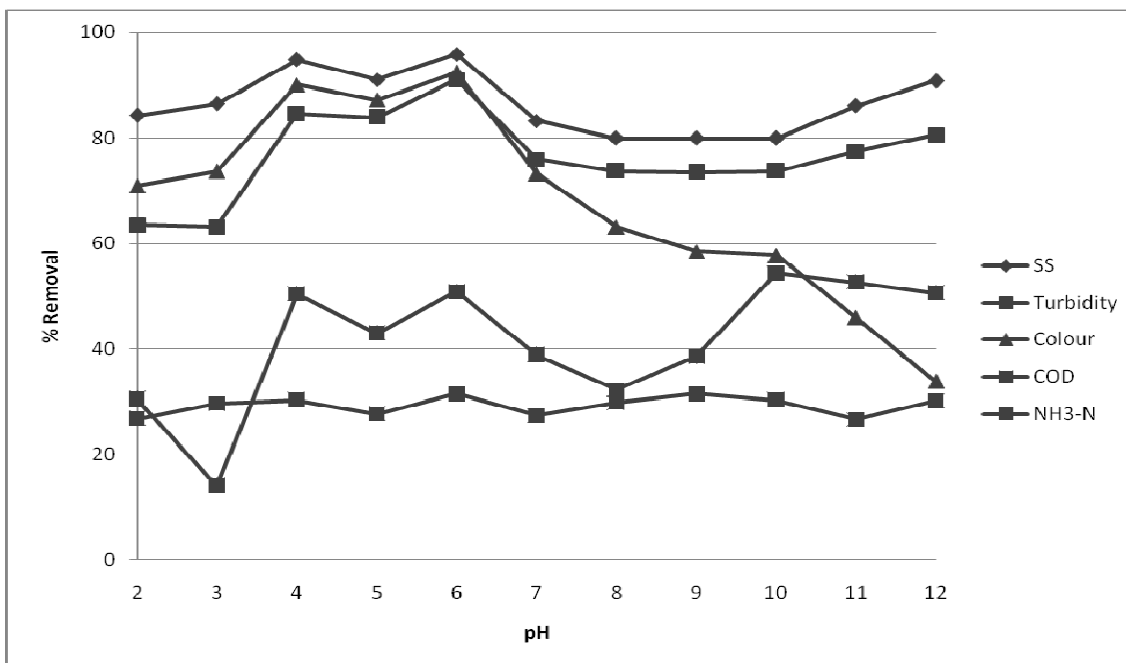


Figure-4
 Percentage removals of SS, Turbidity, Colour, COD and NH₃-N vs pH for KSLs leachates

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