

H₂O₂ Oxidation of Pre-Coagulated Semi Aerobic Leachate

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ABSTRACT: Heavily polluted wastewater from sanitary landfill presents the leachate characteristics that need special treatment and disposal. Concentration of chemical oxygen demand (COD), ammonia nitrogen (NH₃-N), heavy metal and other pollutant content are often larger than standard requirement after applying biological/physico-chemical treatment. Thus, the combination of coagulation-flocculation and chemical oxidation treatment has been investigated. Using the jar-test procedure and stirrer, the physico-chemical conditions were optimized. It concerns the most effective coagulant between ferric chloride (FeCl₃) and poly-aluminum chloride (PACl), the optimal pH and the H₂O₂ as the most effective chemical oxidant. The optimum pH and dosage of PACl and FeCl₃ were obtained as 7 and 2.0 g/L, 5 and 1.0 g/L respectively. Iron salts were proved to be more efficient than aluminum ones, resulting in COD reduction (up to 59%) whereas the corresponding values using alum was lower (50%). The optimum pH and dosage of PACl and ferric chloride for optimum oxidation process was; 300 mg/L at pH7 and 300 mg/L at pH 6 respectively. Oxidation process gave significant effect to the removal of suspended solids and turbidity (up to 94%) using supernatant contain with ion Fe³⁺ at pH 7.

Key words: Coagulation and flocculation, Alum, Ferric chloride, Oxidation, Hydrogen peroxide

INTRODUCTION

Sanitary landfill is commonly can be defined as an engineered method of disposing of solid waste on in a approach to protects the environment by spreading the waste in thin layers compacting it to the smallest volume, and covering it with soil by the end of each day or at more frequent as maybe necessary (O'Leary *et al.*, 1986). It is considered the simplest, and in many areas, the cheapest of the disposal methods (Tchobanoglous *et al.*, 1993). However, odor and leachate are the main problem associated with this method. Leachate contains with high organic matter, nitrogen (ammonia), suspended solids, salts and coloring matter (Agamuthu, 2001). Under normal conditions, leachate is found in the bottom of landfills. Without proper treatment, untreated leachate can flow into the nearest water bodies through percolation process. Various studies have been carried out to remove as much as undesirable constituents from landfill leachates. Variations in the composition of

deposited solid wastes, moisture routing through the landfill, specific climate conditions, the quality of refuse and mainly the aged of landfill influences the composition and concentration of contaminants in leachate (Chu *et al.*, 1994; Alkalay *et al.*, 1998). The presence of humic substances attributes the initial dark brown color of the leachate (Ntampou *et al.*, 2005). Several processes which were adapted from wastewater and drinking water have been applied for the treatment of landfill leachates such as anaerobic and/or aerobic biological degradation, chemical oxidation coagulation-flocculation, activated carbon adsorption, photo-oxidation, activated carbon adsorption and membrane process (Trebouet *et al.*, 2001). In general, the appropriate treatment methods are mainly based on specific characteristics of leachates (Lema *et al.*, 1988). A report adapted by O'Leary *et al.*, (1986) concluded that the composition of leachate changes over the life of the site and therefore

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treatment methods that are appropriate initially may not be satisfactory later. In general, leachate from newly deposited waste is more suitable to biological treatment than leachate from established fill areas. Coagulation has been an important component of high-rate filtration plants in the United States since the 1880s (Letterman *et al.*, 1999). The coagulation – precipitation process has been mainly examined by using stabilized or biologically pretreated landfill leachates for example, as a final polishing treatment leachate (Tatsi *et al.*, 2003). This process are used to remove such very small suspended particles from water and wastewater where these particles are induced to come together to form larger particles, which will settle rapidly enough to be removed by sedimentation process (Barnes *et al.*, 1981). By adding the coagulant in the coagulation process, colloidal particles were destabilized. This technique facilitates the removal of suspended solids and colloid particles from a solution. Normally, the approach for this technique includes pH adjustment and addition of coagulant, i.e. ferric/alum salts to overcome the repulsive forces between the particles (Ayoub *et al.*, 2001). Davis and Cornwell (1998) claimed that, the use of coagulation is to alter the colloids so that they can adhere to each other. Positive ion is added into the water during coagulation process in order to reduce the surface charge so that the colloids are not repelled from each other. Aluminum sulphate (alum), ferrous sulphate, ferric chloride and ferric chlorosulphate are commonly used as coagulants (Amokrane *et al.*, 1997; Barnes *et al.*, 1981; Davis and Cornwell, 1998). Aluminum and iron salts have long been used to remove color caused by natural organic material (NOM) and have been employed as coagulant chemicals since the beginning, with alum having the most widespread use (Letterman *et al.*, 1999). Nevertheless, FeCl_3 is more effective than alum as a coagulant (Amokrane *et al.*, 1997; Letterman *et al.*, 1999). On average, the percentage removal of COD and TOC archived by coagulation-flocculation is higher (56-65%) when it is applied to leachates of low BOD_5/COD ratio (stabilized leachates) while only 10-25% of COD and TOC removal with young leachates Amokrane *et al.*, (1997). Chemical oxidation effects are mainly to eliminate odor and sulphide (Amokrane *et al.*, 1997). Chlorine, ozone,

hydrogen peroxide, potassium permanganate and calcium hypochlorite are normally used as oxidants. H_2O_2 is one of the most powerful oxidizers known; stronger than chlorine, chlorine dioxide, and potassium permanganate. Through catalysis, H_2O_2 can be converted into hydroxyl radicals (OH^{\bullet}). It is also has been applied in the treatment of various inorganic and organic pollutant (Venkatadri and Peters, 1993). This study focuses on the leachate generated from Pulau Burung Landfill Site (PBLs). Pulau Burung Sanitary Landfill (PBLs) was semi aerobic landfill. Leachates that produce at PBLs were treated using coagulation-flocculation process, adsorption by activated carbon and limestone and leachate recirculation. Although the leachate was treated, but the effluent characteristics still did not comply with Standard B for wastewater. Thus, this study was conducted to find the alternative of leachate treatment by means of coagulation-flocculation followed by oxidation process. More specifically, the aim was the determination of most appropriate condition for combined action, coagulation-flocculation; dosage, pH, speed and contact time rapid and slow mix using FeCl_3 and PACl as coagulant followed by chemical oxidation; dosage, pH and contact time.

MATERIALS & METHODS

Leachate was obtained directly from leachate collection pond 1 at PBLs. Leachate samples were collected in plastic container. It was transported to the laboratory and stored at 4°C in cool room for preservation. Temperature and pH of the leachate was taken on site. Raw leachate samples were analyzed for pH, color, turbidity, suspended solids (SS), chemical oxygen demand (COD) and ammonia nitrogen ($\text{NH}_3\text{-N}$). These characteristics were analyzed using HACH spectrophotometer and the experimental standard according to HACH standard which was adapted from the Standard Method of Water and Wastewater (APHA, 2005).

Coagulation-flocculation experiments were performed with Scientifica jar-test apparatus equipped with six paddles (2.5cmx7.5cm) for 1 liter high shape beakers. According to jar-test procedure, PACl (50 g/L) or FeCl_3 (50 g/L) was added into 500mL raw leachate sample. The coagulation process consisted of three subsequent

stages; the initial rapid mixing stage took place for 5 min at 200 rpm, followed slow mixing for 30 min at 60 rpm and the final settling step lasted for another 30 min to 60 min. The pH values of the samples were adjusted to the desired levels by adding appropriate amounts of NaOH or H₂SO₄. After the settling period, the supernatant was withdrawn from the beaker using pipette from a point located about 2 cm below the top liquid for analysis the supernatant. This experiment was proceeding with oxidation process after the optimum condition for coagulation-flocculation was obtained. Leachate sample was coagulated in optimum condition (optimum dosage, pH, rapid and slow speed also contact time) before continue to oxidation process. 100mL supernatant was collected and transferred into volumetric flask. H₂O₂ (5 mg/L) was added into the sample and stirred using hot plate magnetic stirrer at 350 rpm for 30 minutes. The sample was let to settle for about 30 min before the supernatant could be analyzed as leachate characterization.

RESULTS & DISCUSSION

The leachate treated in this study originated from Pulau Burung Sanitary Landfill. Table 1 lists the average analysis results performed on samples.

Table1. PBLs raw leachate characteristics

Parameters	Concentration	*Average
pH	8.42 – 8.74	8.58
NH ₃ -N(mg/L)	1470 - 2060	1765
COD(mg/L)	1700 – 2565	2133
SS (mg/L)	180 - 208	194
Turbidity	200 – 238	219
Colour	3660 -4390	4025
Iron (mg/L Fe)	4.0 -4.8	4.4
Aluminium (mg/L Al ³⁺)	0.1 – 0.2	0.15

* Average of samples taken between 5/1/06 – 15/12/07

Quality of leachate is difficult to predict because there are many influence factors as stated by Chu et al. (1994) and Alkalay et al. (1998). Tchobanoglous et al. (1993) said that, the characteristics of collected leachate can vary so widely. Thus, a number of options have been used for the treatment of leachate. Pulau Burung Sanitary Landfill was developed based on semi aerobic system and leachate recirculation has been applied to this site. These conditions give reasons to the changes of leachate characteristics.

Although it just short period time sampling, the leachate characteristics showed the different concentration of COD, NH₃N, turbidity, color and suspended solids. Leachate taken from PBLs considered partially stabilized as the COD/BOD ratio within 0.15 (Aziz et al., 2004).

Several coagulant dosages were test on sample at pH7 and 4 using PACl and FeCl₃ as coagulant. The results are shown in Fig.1 (a), (b), (c) and (d). According to Shahin (2004) and Aziz et al., (2007) finding, pH 7.5 and 4 were the optimum pH for PACl and FeCl₃ respectively. Barnes et al., (1981) claimed that optimum pH for aluminum salt with moderate alkali is likely to be 6.0 to 7.0 while for iron salt generally 4.5. Poor coagulation using alum occurs in the range 7 to 8.5. According to Fig.1 (a), the optimum dosage was 1.0 g/L with about 49% COD removal, 18% NH₃-N removal, 70% suspended solids removal, 71% turbidity removal and 85% color removal. It also shown that, after the optimum dosage, the reduction for all the considered parameter became lesser. However, at pH 7, removal of the constituents become higher with the increasing of coagulant dosage as showed in Fig.1 (b). Corresponding to COD removal at pH 7, up to 57% COD could be removed could be using FeCl₃, with higher dosage; 6.0 g/L. This may be result to the large supernatant iron content. Fig.1(c) showed that, using PACl as coagulant give better result at pH 7 but not at pH 4 (Fig.1 (d)). The addition of Al³⁺ ions leachate samples with pH control at 7 resulted in COD reduction (Tatsi et al., 2003), when PACl were in the range higher dosage (3.5-7.0 g/L), further COD reduction was not observed. Based on result presented in Fig.1(c), the COD reduction at 2.0 g/L and 2.5 g/L did not give significant different with 52% and 53% COD reduction respectively. Therefore, the optimum PACl dosage was 2.0 g/L. The sludge produced during the physical-chemical treatment of wastewaters, is proposed by the amount of originally suspended organic matter and solids, as well as by the compounds formed due to the possible of chemical reagents. The amounts and the characteristics of the sludge produced during the coagulation-flocculation process are highly depending on the coagulant used and the operating procedure (Tatsi et al., 2003).

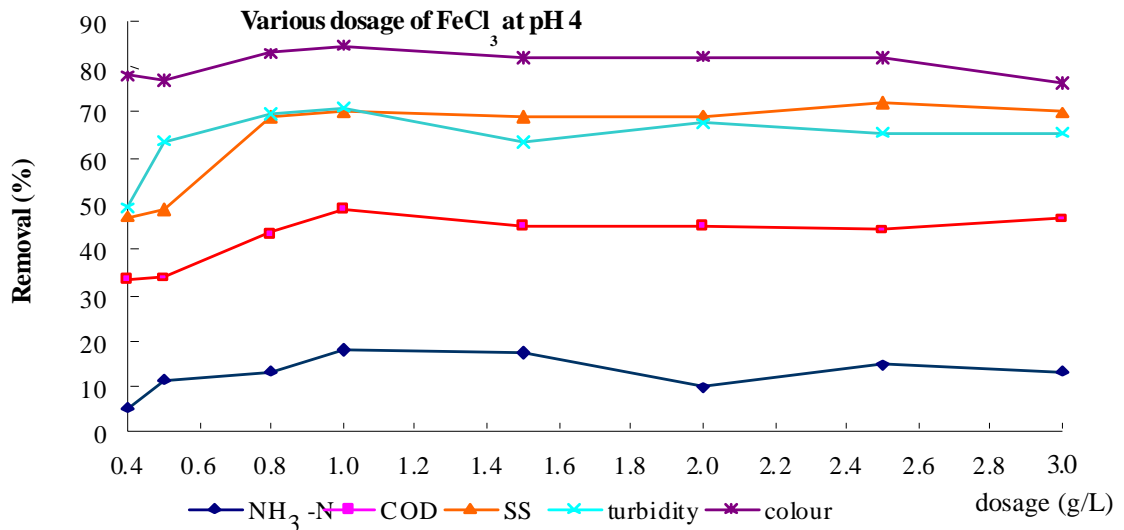


Fig. 1. (a) Percentage removal of COD, NH₃N, SS, turbidity and color at different dosage using FeCl₃ and PACl as coagulant at pH 4 and pH 7 respectively

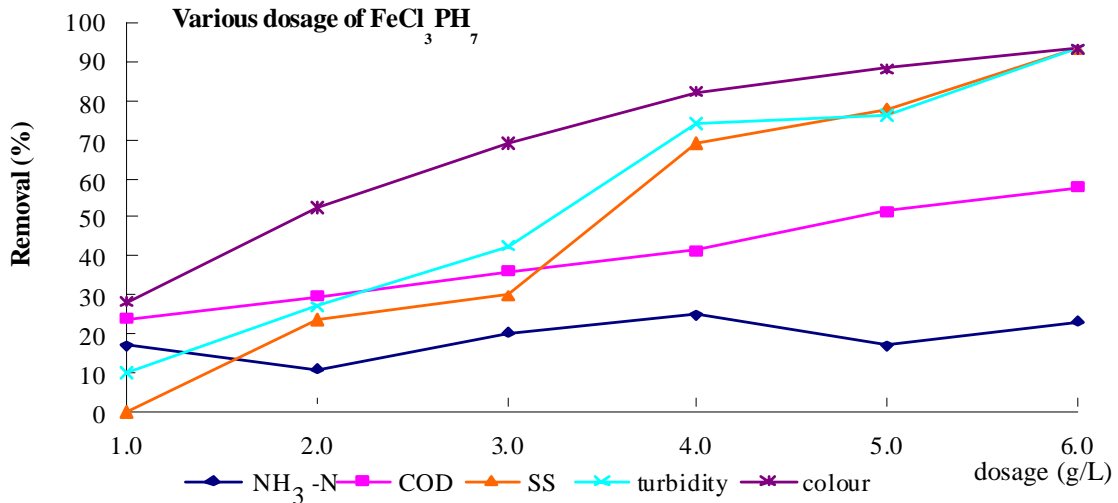


Fig. 1.(b) Percentage removal of COD, NH₃N, SS, turbidity and color at different dosage using FeCl₃ and PACl as coagulant at pH 4 and pH 7 respectively

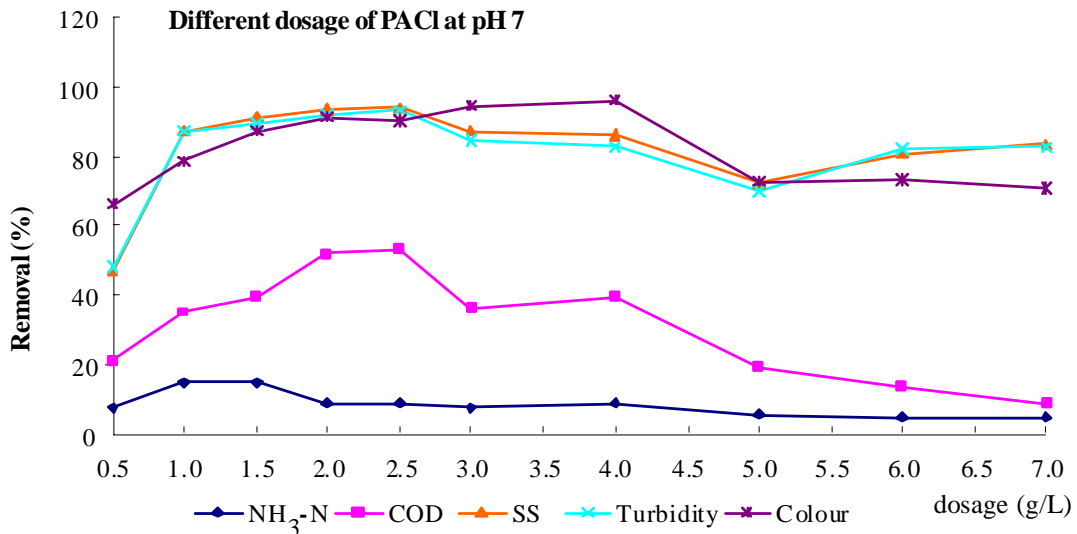


Fig. 1.(c) Percentage removal of COD, NH₃N, SS, turbidity and color at different dosage using FeCl₃ and PACl as coagulant at pH 4 and pH 7 respectively

Using OpCd, experiment results were shown in Fig. 2 (a) and (b) indicate that the optimum pH for FeCl₃ and PACl were 5 and 7 correspondingly. Turbidity and suspended solids reduction was less efficient in the alkaline region than that in the pH 5 for FeCl₃ but pH 7 for PACl. Supernatant pH samples were decreased when the coagulant

were added and gave a value 3.5 and 6.5 for FeCl₃ and PACl respectively. Acidic character of Al³⁺ and Fe³⁺ (acid of Lewis) can explain the decreasing of the pH. By reacting with OH⁻ ions of leachate, aluminum or iron precipitate in form of Fe(OH)₃ or Al(OH)₃ (Amokrane *et al.*, 1997; Tatsi *et al.*, 2003).

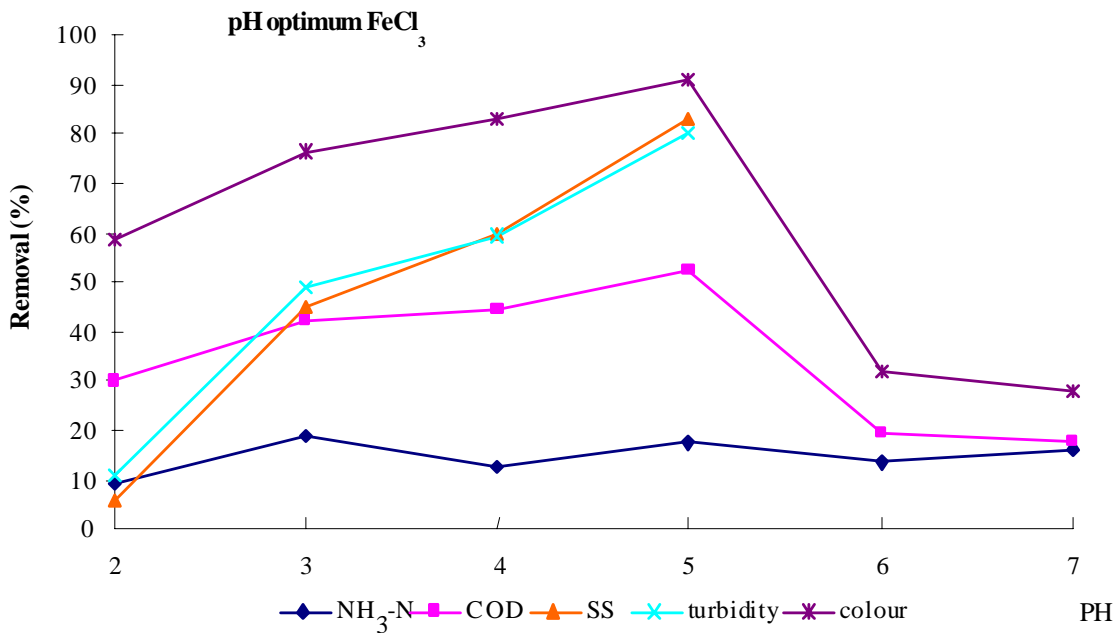


Fig. 2. (a) Optimum pH for FeCl₃

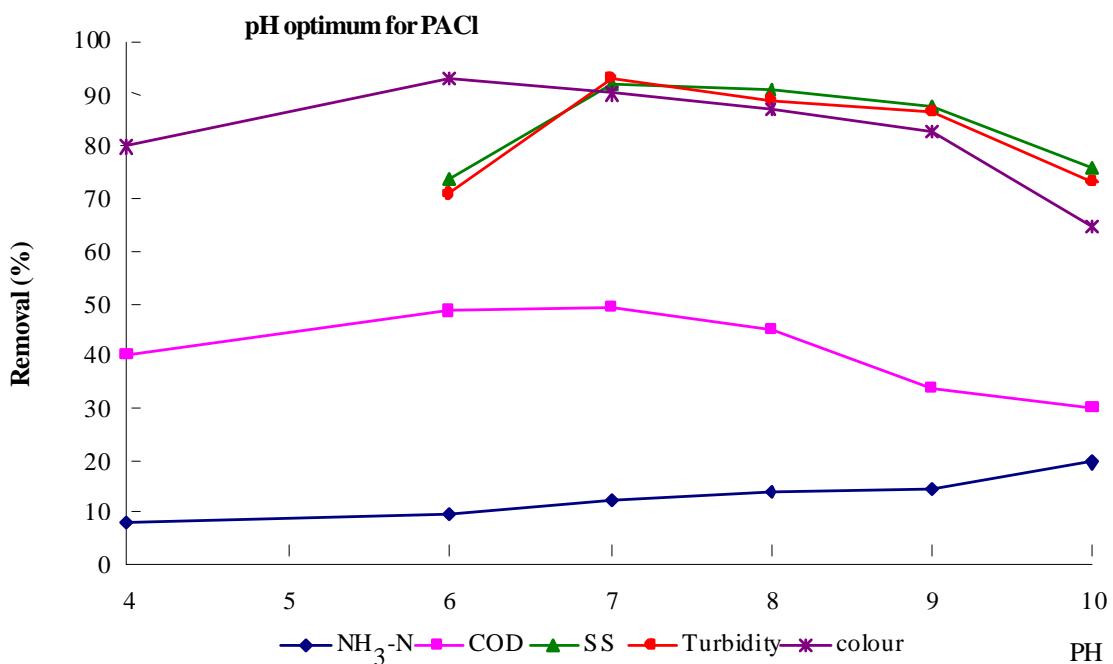


Fig. 2. (b) Optimum pH for PACl

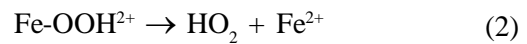
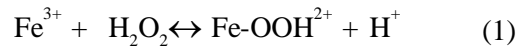
Coagulation was carried out to determine optimum pH at optimum dosage; 1.0g/L for FeCl₃, 2.0g/L for PACl. Speed and contact time rapid and slow mix was done at optimum dosage and optimum pH. Optimum coagulation condition was summarized in Table 2 below.

Table 2. Optimum coagulation condition

Coagulant	FeCl ₃	PACl
Optimum dose	1.0 g/L	2.0 g/L
Optimum pH	200 rpm	7
Optimum rapid mix (speed)	2 min	200 rpm
Optimum contact time (rapid)	20 rpm	3 min
Optimum rapid mix (speed)	20 min	30 rpm
Optimum contact time (slow)	20 min	30 min
Optimum settling time	20 min	30 min

After the samples was coagulated through coagulation process, and remain about 60 minutes for settling, the supernatant was sampled to proceed for the second process. In this second process, H₂O₂ (supplied by Merck) as oxidant was added to let the oxidation process occurred. The pH sample was controlled at pH 7 to determine the optimum concentration of H₂O₂ Fig. 3 (a) and (b) showed that the optimum concentration of H₂O₂ was 300 mg/L for both (supernatant contain iron or alum). It also showed that turbidity and

suspended solids gave significant removal when H₂O₂ applied to the sample contain iron. Neyens and Baeyens (2003) said that the reaction of hydrogen peroxide with ferric ions is referred as Fenton-like reaction (reaction 1 and 2):



Further oxidation happened as H₂O₂ can react with OH₂. The ferrous ions generated react with hydroxide ions to form ferric hydro complexes. Within pH 3 and 7, dissolved suspended solids are captured and precipitated. Large amounts of small flocs are observed. This study agreed with this statement. This was because when the pH samples were varied to pH 3 until 7, to determine optimum pH, large small flocs can be seen after stirring. The flocs took time to settle about 45 minutes to 60 minutes. After the settling time, clear supernatant was obtained. According to Table 3. iron content in supernatant after coagulation using FeCl₃ was high. However, after adding with H₂O₂, there was reduction in iron content in the supernatant. This finding is agreement with Amokrane *et al.*, (1997). H₂O₂ dose was optimized to remove maximum residual iron. Conversely happened to supernatant contain with alum. This was because, no significant removal archived after adding with H₂O₂.

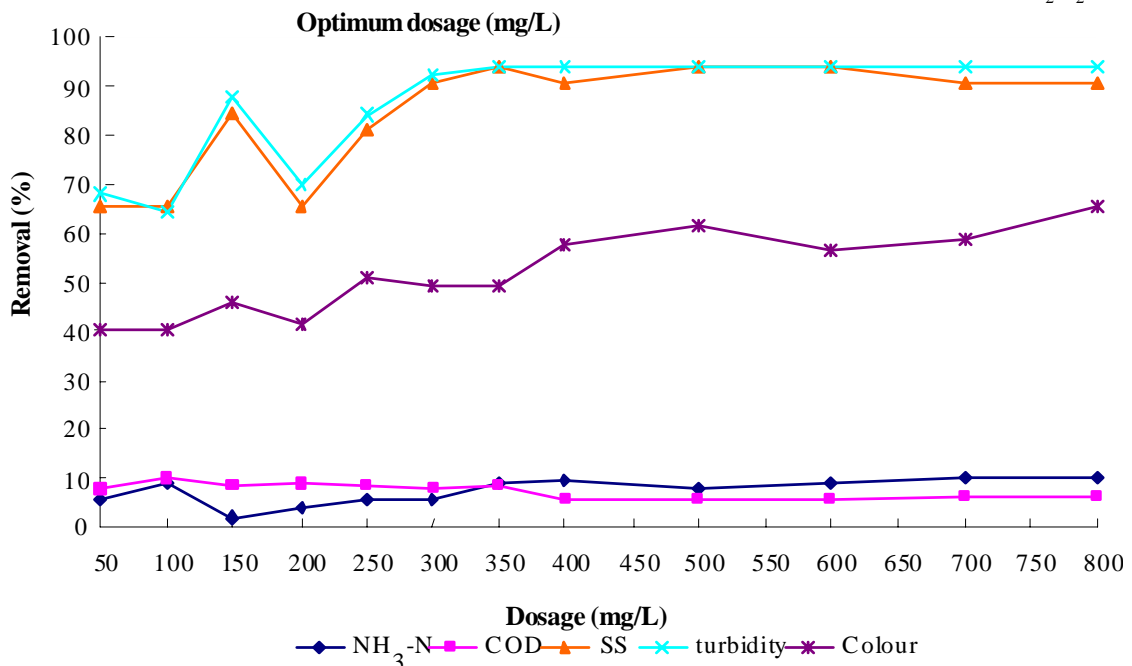


Fig. 3. (a) Different concentration of H₂O₂ applied on supernatant contain iron

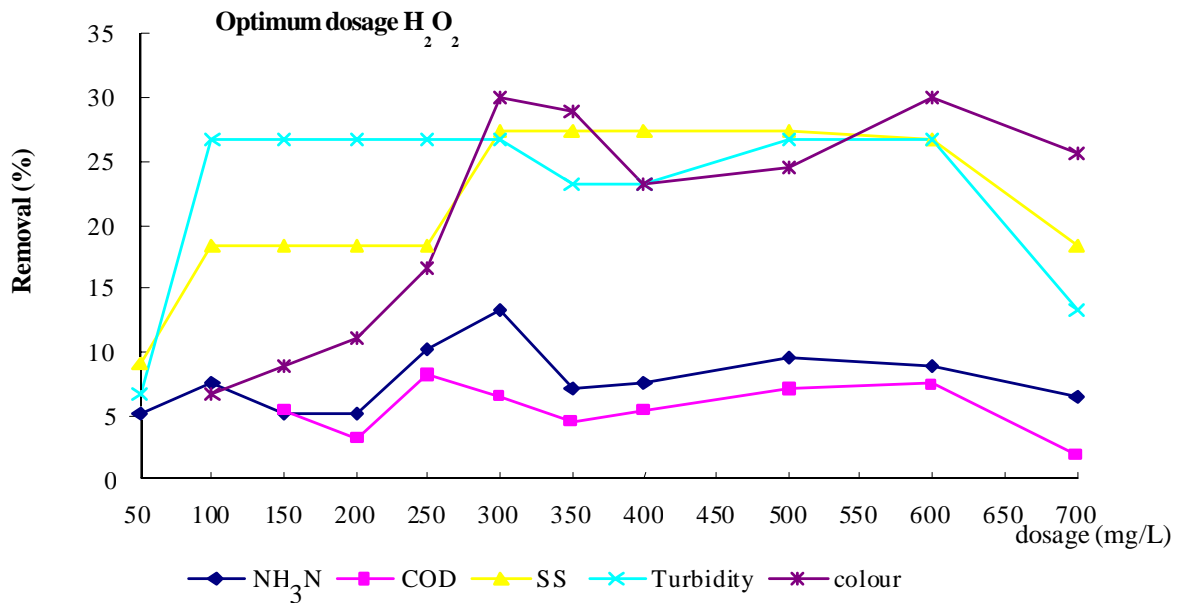


Fig. 3. (b) Different concentration of H₂O₂ applied on supernatant contain alum

Table 3. Percentage removal of COD, NH₃-N, SS, turbidity and color, concentration of Fe³⁺ and Al³⁺ after coagulation, oxidation and after both treatment using PACl

Parameter	% removal					
	After coagulation		After oxidation from coagulation		After coagulation and oxidation	
	% removal	Conc	% removal	Conc	% removal	Conc
NH ₃ -N	7.1	1580	16.5	1320	22.4	1320
COD	52.5	1040	9.1	945	56.8	945
SS	94.4	10	80	2	98.9	2
Turbidity	94.8	12	66.7	4	98.3	4
Colour	90	425	22.4	330	92.2	330
Fe ³⁺ (conc)	0.2		0.4		0.4	
Al ³⁺ (conc)	0.1		0.1		0.1	

Table 4. Concentration of NH₃-N, COD, SS, turbidity and color after coagulation process followed by chemical oxidation

Parameters	Coagulant		Standard B
	FeCl ₃	PACl	
NH ₃ -N (NH ₃ -N Nessler)	1290	1320	0.9-2.7
COD (mg/L COD)	800	945	50-100
SS (mg/L)	2	2	150-300
Turbidity (FAU)	2	4	-
Colour (PtCo APHA)	270	330	-
Fe ³⁺	4.0	0.4	5
Al ³⁺	0.1	0.1	0.5

CONCLUSION

Table 4 concludes the result of all the parameters taken after applying both treatments compare to standard B, wastewater effluent. Coagulation-flocculation followed by chemical oxidation was

studied as partially stabilized leachate treatment at PBLs. It was found that, the optimum dosage for FeCl₃ and PACl were 1.0g/L and 2.0g/L respectively at pH 5 and 7 with FeCl₃ give higher COD removal than PACl about 59% and 50%.

Optimum rapid speed for FeCl₃ and PACl was 200 rpm with contact time 2 min and 3 min respectively. While the optimum slow speeds was 20 rpm for 20 min using FeCl₃ but 30 rpm for 30 min using PACl. Further treatment was preceding using H₂O₂ as chemical oxidation applied to the supernatant contain with ferum or alum. The optimum concentration for H₂O₂ was 300mg/L, pH 7 with contact time 45 min for FeCl₃ and 300 mg/L, pH 6 with contact time 45 min for PACl. According to Table 3. the effluent of this combination treatment still not fulfills the wastewater Standard B requirement. Further study has to be done to bring down the pollutant consists in leachate as maximum as it can.

Several recommendations have been presented here for further improvement and investigation. These recommendations were listed as below:

1. According to the result, FeCl₃ can be used as coagulant for further study for this combine treatment by using jar-test apparatus for both processes sequentially (coagulation and oxidation).
2. Used H₂O₂ from new and unopened bottles for the experiments. This is because H₂O₂ easily can be changed to the form of H₂O and O₂. Thus, it can give effect to the experimental result.
3. Applying ammonium stripping in order to remove NH₃-N after coagulation process because it was already proved that, NH₃-N could be removed trough coagulation-flocculation process.

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