

REDUCTION OF CHEMICAL OXYGEN DEMAND AND POTENTIALLY TOXIC METALS IN LEACHATES GENERATED FROM ISOLO DUMPSITE USING DIFFERENT COAGULANTS

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ABSTRACT

Leachate samples were collected from Isolo dumpsite within a seven month period, at eight different times after rainfall. The characterization of the leachate shows that they were sourced from an old landfill. The highest concentration of chemical oxygen demand (COD), biological oxygen demand (BOD) and total organic carbon (TOC) in the most polluted leachate samples were 392 mg/L, 203 mg/L and 5090 mg/L respectively. The levels of Fe, Pb, Cu and Zn were 19.7 mg/L, 2.06 mg/L, 2.18 mg/L and 3.50 mg/L respectively. Three different coagulants: ferric chloride, ferrous sulphate and aluminium sulphate were used to treat the most polluted leachate sample. Different pH and concentrations were investigated to obtain the optimal dosage for the most effective coagulant. The experimental results showed that at a neutral pH, 96% COD, 66.2% Fe, 94.3% Zn reductions were achieved at the lowest concentration of 1000 mg/L of $Al_2SO_4.14H_2O$ while $FeCl_3$ and $FeSO_4$ gave <96% reduction at a high concentration of 25,000 mg/L. The pH of 3, 5, 9 and 11 at optimal dosage of $Al_2SO_4.14H_2O$ gave 14%, 78%, 82%, 88% reduction of COD respectively. The result therefore indicates that $Al_2SO_4.14H_2O$ is the most effective of the three coagulants with optimal pH and dosage of 7 and 1000 mg/L respectively.

Keyword: Coagulant, COD, Leachate, Potentially Toxic Metals

INTRODUCTION

One of the simplest and cheapest methods of disposing waste is the landfill which is adopted by most low-to medium- income developing nations. The management of landfill has become one of the main focus of waste management because decomposing organic wastes in the landfills generate greenhouse gases (methane and carbon dioxide) with attendant impact on climate and potential health hazard (Aljaradin and Persson, 2012). In addition to air pollution, solid waste disposed in landfills is usually subjected to series of complex biochemical and physical processes which lead to the production of leachates (Olsson et al, 2009). Leachates are generated by direct or indirect mixing of rainwater, snowmelt and groundwater together with liquids produced from the waste itself through hydrolysis and solubilisation, brought about by a series of complex biochemical reactions during decomposition of organic wastes. Leachate refers to any liquid percolated through deposited waste and seeped from or contained within a landfill consisting of many different organic and inorganic compounds that may either be dissolved or suspended. The landfill leachate is a secondary contamination related to landfills. Leachate spends many years infiltrating through the landfill and during this time, it will make contact with various substances such as paints, plastic, oil among others within the landfill. The resulting liquid leaches and dissolves various constituents until it contains a load of heavy metals, chlorinated organic compounds and other substances. The leachate water quality reduces after rainwater washes the landfill (Abbas *et al.*, 2009, Kangsepp and Mathiasson, 2009).

When leachate becomes highly concentrated, the wastewater that results is a potential threat to the quality of groundwater as it could migrate or seep from the landfill either through direct infiltration on site or by infiltration of leachate-laden runoff offsite. The extent of the risk posed to groundwater-fed drinking water sources is usually considered in terms of waste composition, quality of leachate produced and leachate migration - attenuation and dilution. This implies that water bodies around the landfill site are likely to be polluted with various constituents of the leachate. The presence of the non- biodegradable compounds in leachate after biological treatment, calls for an alternative treatment method that reduces both biodegradable and non-biodegradable constituents. The treatment of such leachates by physical or chemical methods achieves this. This treatment method is sometimes, applied after biological treatment method to improve leachate treatment efficiency (Aziz *et al.*, 2007).

Coagulation and flocculation treatment process is a widely used technique effective in removing high concentration of organic pollutants, heavy metal and anions (Wang *et al.*, 2002). The process involves destabilization and aggregation of colloidal dispersion to permit particle removal by sedimentation and filtration (Dewall and Chain, 2006). The chemistry of coagulation reaction may be considered in two stages:

dissociation of the coagulant into positively charged ions which combine with the negatively charged colloids, neutralizing their charge thereby permitting agglomeration and formation of insoluble complexes (floc) by the reaction of the metal ions with the hydroxide ions (and other available ions such as phosphates, sulphates and chlorides). The most widely used coagulants for wastewater treatment are the salts of iron and aluminum (both supply cations and have positive Zeta potential (Amokrane *et al.*, 1997). The objectives of this research are to examine the efficiency of coagulation-flocculation processes for the removal and/or reduction of metals and COD in the landfill leachate and to study the optimal conditions for the removal using three coagulants.

MATERIAL AND METHODS

Study Site

Isolo dumpsite is an inactive landfill situated close to the General Hospital, Isolo, Lagos with GPS coordinates of 6° 31' 52' N and 3° 19' 4' E. The total area of the dumpsite is about 0.3 km². The dumpsite shares boundary with an abattoir, a mechanic workshop and food stuff shops. Solid and liquid wastes from the dumpsite and other areas connected to it, find their ways into the Oke-Afa canal which is a few meters away from the dumpsite. This dumpsite is not well-designed and has no leachate collection point.

Sampling

Eight leachate samples were collected at the sampling site between September 2013 and March 2014. The leachate samples were collected from two point sources connecting drainage point to the Oke-Afa canal. The leachate samples were collected in clean dry plastic containers and stored in the refrigerator (< 4 °C) prior to analysis to keep the microbial load constant. Physicochemical analysis was carried out on all the leachate samples according to standard methods (Ademoroti, 1996). Before the analysis, the leachate samples were removed from the refrigerator and conditioned for about three hours under ambient temperature. All chemical reagents used for analysis were of analytical grade. The coagulants used were FeCl₃.6H₂O, FeSO₄ and Al₂(SO₄)₃.14H₂O. After the physico-chemical analysis, the leachate samples were treated with the different three coagulants.

Physicochemical analyses

The methodology for the determination of the physico-chemical parameters such as, pH, total hardness, total dissolved solids, chlorides, chemical oxygen demand, conductivity, alkalinity, sulphates, phosphates, nitrates. such as copper, Iron, zinc, copper, nickel and lead were determined using standard methods (Oluseyi *et al.*, 2011) as shown in Table 1.

Table 1. Analytical methods applied for the determination of physico-chemical parameters

Parameter	Unit of measurement	Analytical method
pH	-	Potentiometry
Conductivity	µs/cm	Conductimetry
Total hardness	mg/L	Titrimetry
Chemical oxygen demand (COD)	mg/L	Titrimetry
Total dissolved solids (TDS) And Total Solids (TS)	mg/L	Gravimetry
Alkalinity	mg/L	Titrimetry
Chlorides	mg/L	Titrimetry
Sulphates	mg/L	UV Spectrophotometry
Phosphates	mg/L	UV Spectrophotometry
Nitrates	mg/L	UV Spectrophotometry
Potentially toxic metals (Fe, Pb, Cu, Zn and Ni)	mg/L	Atomic absorption spectrometry

Determination of Chemical oxygen demand

50.0 mL of leachate sample was placed in a reflux flask containing antibumping granules. 5.0 mL of conc. H₂SO₄ and powdered HgSO₄ was added and swirled until the mercuric sulphate has dissolved. The reflux flask

was placed in an ice bath and 25.0 mL of 0.025 N $K_2Cr_2O_7$ was slowly added with swirling. This was later followed by addition of 70 mL of sulphuric acid-silver sulphate solution to the cooled reflux flask, using slow addition with swirling motion. Heat was applied to the flask and refluxed for 2 hours. The flask was allowed to cool and the content was transferred to a 500 mL Erlenmeyer flask, washing out the reflux flask 3 times with distilled water. The acid solution diluted to about 300 mL with distilled water and the solution allowed to cool to room temperature. 8 to 10 drops of ferroin indicator was added to the solution and titrated with 0.25 N ferrous ammonium sulphate solution to the end point with a colour change from a blue-green to a reddish hue.

Leachate treatment

The initial pH of the sample was 6.63 and later adjusted to pH 7 by adding an appropriate amount of NaOH solution. At constant pH, four different concentrations of each coagulant were added to the 100 mL of leachate sample, shaken vigorously, centrifuged at 100 rpm for five minutes and then filtered. The required filtrate volume was withdrawn with the aid of a pipette. This solution was characterized and the reduction levels of the pollution parameters were compared with the raw leachate sample. Each of the three coagulants was used to treat the leachate firstly at constant pH of 7 and varying concentration of 1000, 5000, 10000 and 25,000 mg/L respectively. The coagulant with a high COD removal was selected and the pH was varied at 3, 5, 9, and 11 to obtain the optimal pH while maintaining a constant concentration of the coagulant. The sample with the highest COD removal employing the optimal pH and concentration was digested with aqua regia and analysed to ascertain the reduction level for the metals.

RESULTS AND DISCUSSION

The characterizations of the raw leachate samples are shown in Table 1. It was observed that these leachate samples had pH which ranged from 6.6 – 7.1, indicating a weakly acidic to a slightly alkaline leachate sample. This is due to the fact that leachate generally tends towards alkaline as the age of the landfill increases. The concentration of pollution parameters, chemical oxygen demand (COD) and potentially toxic metals (PTMs) in the leachates were also found to be high and above permissible limits when compared to the LASEPA discharge standard.

Table 2: Physicochemical parameters of untreated leachate samples

Physicochemical Parameters	A1	A2	A3	A4	B1	B2	B3	B4
pH	7.1	7.0	6.6	6.9	7.1	6.9	6.9	6.6
Temperature (°C)	26.9	27.3	27.3	27.0	27.3	27.1	27.6	26.5
Conductivity (μ s/cm)	1190	1330	1580	1610	1340	2160	1700	1100
TDS (mg/L)	600	650	790	380	670	1100	840	500
TS (mg/L)	1560	1790	2300	5950	1060	1980	1340	1370
Chloride (mg/L)	234.0	230.0	298.0	284.0	268.0	504.0	376.0	255.0
Total hardness (mg/L)	12.0	16.0	14.80	56.0	12.40	38.0	33.20	40.0
Sulphate (mg/L)	79.0	49.6	35.8	28.3	104.0	158.0	101.0	56.4
Phosphate (mg/L)	2090	3090	2360	1980	5450	1140	1350	1570
Nitrate (mg/L)	41.4	53.4	21.0	13.8	64.2	28.5	44.4	ND
COD (mg/L)	220.0	152.0	392.0	104.0	44.0	36.0	52.0	160.0
Alkalinity (mg/L)	7.44	8.80	10.10	4.81	7.61	8.01	6.64	5.61
Iron (mg/L)	16.60	10.60	19.70	9.40	3.74	3.22	3.52	ND
Lead (mg/L)	1.40	1.50	2.06	ND	0.18	ND	0.48	1.70
Copper (mg/L)	1.94	1.92	2.18	2.44	0.54	1.22	2.72	1.62
Zinc (mg/L)	3.24	2.98	3.50	3.00	0.92	1.58	2.22	2.77
Nickel (mg/L)	ND	ND	ND	ND	ND	ND	ND	ND

Note: ND = not detected.

A1, A4, A3 and A2 represent leachate samples collected at the same point source on 13th September 2013, 20th November 2013, 17th February 2014 and 12th March 2014 respectively.

B1, B4, B3 and B2 are for the other point source on the same date as for sample A.

From the results shown in Table 2, Sample A3 which had the highest concentration of COD of 392.0 mg/L and the PTMs, so it was chosen for further treatment with the three coagulants with the pH maintained at 7. The percentage reduction of COD using the three coagulants are shown in Table 3.

Table 3: COD values of sample A3 at constant pH 7 after treatment with the coagulants

Coagulant concentration	Treatment with $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$	Treatment with FeCl_3 (mg/l)	Treatment with FeSO_4 (mg/l)
1000 mg/L	16.0	352.0	816.0
5000 mg/L	32.0	336.0	384.0
10,000 mg/L	64.0	272.0	192.0
25,000 mg/L	384.0	96.0	64.0

Note: Initial COD value before treatment was 392 mg/L

COD reduction was 96% and 2% using 1,000 mg/L and 25,000 mg/L $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ respectively, FeCl_3 achieved 10% and 76% reduction respectively. Also 84% reduction was achieved at high concentration of 25,000 mg/L for FeSO_4 , while at low concentration of 1,000 mg/L an approximately three (3) times fold increase of initial COD was observed (to 816 mg/L) because at low concentration of FeSO_4 its floc is not yet formed and the solubility of ferric hydroxide is not exceeded and therefore no reduction of COD at low concentration. This implies that for FeSO_4 treatment, an increase in concentration (that is more quantity of FeSO_4), will achieve 84% COD reduction. The disadvantage of this is that more dosage will increase the chemical residue of the solution, thereby interfering with coagulation process during filtration and as such it will not be economical.

The result for FeSO_4 and FeCl_3 at pH 7 indicates that a high reduction of COD can only be achieved at a high concentration (25,000 mg/L). Even at this, the percentage COD reduction is less compared to that obtained at low concentration using $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$. The reason $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ usage gave a better reduction at least concentration investigated (1000 mg/L) and pH 7 is that at this concentration, the solubility limit of aluminium hydroxide has been exceeded favouring the formation of floc. It is this floc that adsorbs particles in the wastewater. This condition therefore enables the activity of aluminium floc and hence the consequent reduction of COD value to 96%. At a higher concentration the activity of aluminium floc begins to reduce thereby resulting to a lower COD reduction value as observed in 5000, 10,000 and 25,000 mg/L, which gave 92%, 84% and 2% COD reduction respectively. As shown in Figure 1 the highest COD reduction was achieved at pH 7 and 1000 mg/L of $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$.

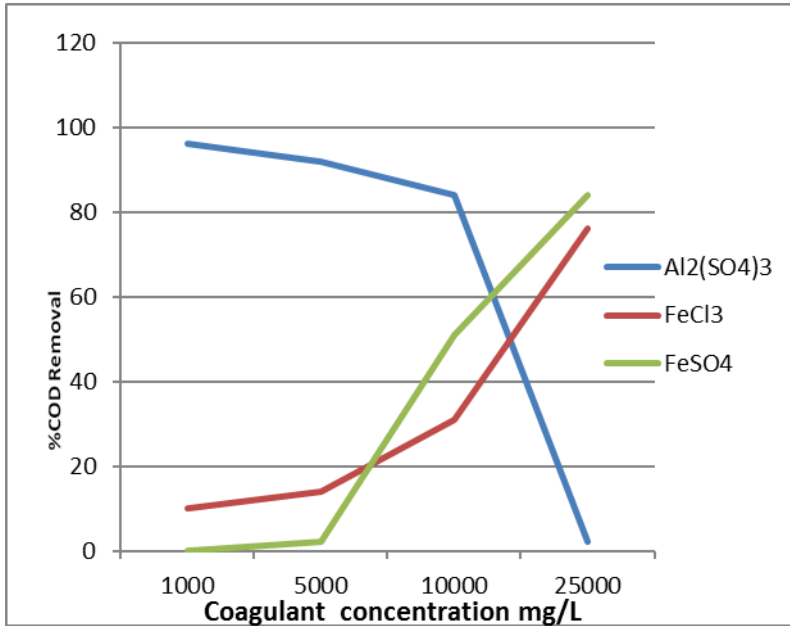


Figure1: Percentage COD Reduction at different coagulant concentrations

When the concentration of the coagulant was kept constant at 1000 mg/L and the pH was varied between 3 and 11, COD reduction of 14%, 78%, 88% and 82% were observed. At pH values of 3 and 5, COD reduction increased, while a decrease was observed in pH 7 and 9. It also further confirmed that at low pH, COD reduction is minimal, and at a higher pH beyond 7, it starts decreasing steadily. The COD removal efficiency thus increases with increasing pH up to the pH of 7 beyond which the removal efficiency starts decreasing gradually as shown in Figure 2. This confirms that coagulation treatment process is pH dependent as observed by Trebouet *et al.*, (2001) and Silva *et al.*, (2004).

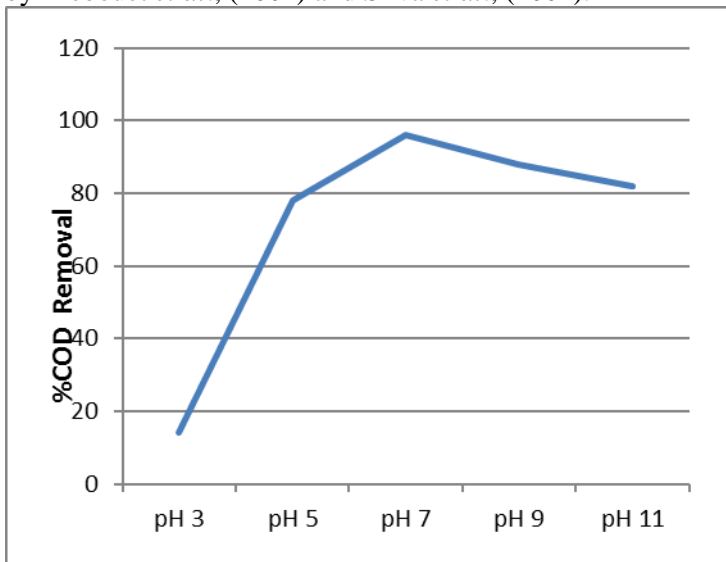


Figure 2: Percentage COD reduction at different pH values

The pH influence on the coagulation treatment process is evident by a competition between hydrogen ion, hydroxide ion and the metal species on the adsorption site of the metal. At low pH, H⁺ competes with the metal species generating substances that do not easily precipitate. The resultant effect is a poor removal. While at a neutral pH, there is equal balance between OH⁻ and H⁺, giving the coagulant active action on the water and also since the region of best coagulant activity for Al₂SO₄.14H₂O range from 6.5 to 7. At a higher pH, OH⁻

competes with the other compounds for metal adsorption site causing precipitation of metal hydroxide to occur by precipitation (Silva *et al.*, 2004).

Therefore, the optimal dosage and pH for achieving the highest COD reduction was 1000 mg/L and pH 7 using $\text{Al}_2\text{SO}_4 \cdot 14\text{H}_2\text{O}$ as coagulant. At this same coagulant condition, the concentration of TDS, TS, conductivity and metals (Zn, Pb, Ni, Cu and Fe) also reduced close to various discharge limits set by LASEPA as shown in Table 4. The results showed that 24%, 66% and 94% reductions were observed in the TS, Fe and Zn concentration respectively. The concentrations of Pb, Ni, and Cu were too low to be detected after the treatment. The reduction in TS was greater than LASEPA discharge limit, due to the fact that addition of coagulant must have increased the total solid content in the wastewater. Also the TDS content increased after treatment due to the fact that addition of coagulant also increased the dissolved salt content of the water (Adlan *et al.*, 2004).

Table 4: Results of leachate after treatment with 1000 mg/L $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$.

Physicochemical parameters	Leachate before treatment	A3 Leachate after treatment	LASEPA discharge Limit
pH	6.63	7.0	6.5-8.8
TDS (mg/L)	790	880	500
TS (mg/L)	2,300	1760	525
COD (mg/L)	392.0	16	30
Zn (mg/L)	3.50	0.02	2
Fe (mg/L)	19.70	0.60	10
Pb (mg/L)	1.06	ND	0.5
Ni (mg/L)	ND	ND	0.05
Cu (mg/L)	2.18	ND	0.5

ND = not detected.

CONCLUSION

From the results obtained in this experiment, the application of coagulation-flocculation treatment process for untreated leachate collected from Isolo dumpsite was effective. The treatment process performed at fixed centrifuging condition, constant pH, varying coagulant dosage and at varying pH showed that $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ as coagulant gave the best reductions when compared with other coagulants used. $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ when conditioned at an optimal pH of 7 and concentration of 1000mg/L gave a 96% COD reduction, 94% Zn reduction, 66% iron reduction, and subsequently a crystal clear solution (compared to the dark colour before treatment) was achieved. Pb, Ni, and Cu were not detected after treatment. This reduction level achieved is below LASEPA discharge standard. FeCl_3 and FeSO_4 coagulants on the other hand gave 76% and 84% COD reduction respectively at pH 7 and a high dosage of 25,000 mg/L. Their usage is not economical and will increase chemical sludge in solution whereas $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ gave a better reduction at low concentration of 1000 mg/L approved to be the more economical coagulant.

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