

Treatment of landfill leachate by electrochemical oxidation for removal of color and chemical oxygen demand (COD)

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Abstract - Electrochemical technologies, which use electrons to remove contaminants through redox reactions, can provide an elegant contribution to environmental control. The primary goal of electrochemical oxidation has been to produce carbon dioxide from oxidizable molecules. Leachate is a complicated effluent that comes from landfills and has the potential to have a significant influence on the environment. In order to comply with inland disposal regulations, this study attempts to treat the landfill leachate. In an electrochemical method, the removal of contaminants was investigated using various anode materials. In a batch electrolytic parallel plate reactor, leachate from two different packages were treated by electrochemical oxidation. The electrochemical process was carried out individually, using graphite as cathode and anode electrodes. The effects of the operating factors such as current density, Dilution factor, reaction time, chloride ion concentration that influence the removal of pollutant from Leachate electrochemically were studied.

Key Words: contaminants; electrochemical oxidation; electrodes; Landfill leachate; redox

1. INTRODUCTION

Ai wabel et al., (2011) said that the Landfill leachate is an important pollution source originated in municipal landfill sites. Landfill leachate is defined as those aqueous streams generated as a consequence of rainwater percolation through wastes, biochemical processes in the waste's cells and the inherent water content of the wastes themselves. Leachates may contain large amounts of organic matter, of which humic type constituents are an important group, as well as ammonia- nitrogen, heavy metals and chlorinated organic and inorganic salts. Rajan Gandhimathi et al., (2013) discussed that the discharge of landfill leachate can lead to serious environmental problems as they may percolate through soils and sub soils, causing extensive pollution of ground and surface waters if they are not properly treated and safely disposed. Leachate becomes ahead of wastewaters as being the most difficult to treat as it is a wastewater with a complex and widely variable content generated within a landfill. Therefore, many pre-treatment and combined treatment methods have been proven to treat leachate. Yun nen chen et al., (2012) discussed that the type of leachate depends on factors such as age and type of landfill, pH, and BOD5/COD ratio.

2. ELECTROCHEMICAL OXIDATION

Huankai li et al., (2023) investigated that due to its effectiveness and ease in operation, electrochemical oxidation process has recently received significant attention for wastewater treatment. The process has shown its efficacy for the destruction of refractory pollutants such as cyanide and EDTA, and also for colour removal. In general, pollutants can be destroyed electrochemically by direct anodic oxidation or by indirect oxidation. Many researchers have investigated the electrochemical oxidation of different wastewaters with various types of compounds. These include textile wastewater, p-chlorophenol and p nitrophenol phenolic wastewater and Tanyolac, olive oil wastewater tannery wastewater et al., and paint wastewater.

Xianni song et al.,(2023) discussed that the treatment of CLBE by EO with Ti/RuO₂-IrO₂ as the anode can achieve concomitantly organic carbon removal (COD) and nitrogen removal (NH₃-N). The statistical analysis revealed that current density, A/V, and Cl-concentration were significantly and positively correlated with the removal of COD, NH₃-N and TN, while d showed a nonmonotonic effect on them. The initial pH showed a non-monotonic effect on the removal of COD that was first weakened and then promoted, and was significantly and positively correlated with the removal of NH₃- N and TN. 17 Panizza et al., (2023) discussed that in all anodes except graphite, ammonium removal dominated over organic oxidation. A Ti/PbO₂ anode is found as a better anode than Ti/Ru-SnO₂ though BDD showed best performance among the three anodes for both COD and ammonium removal as well as in terms of current efficiency and operating cost.

Nidhesh et al., (2023) said that Leachate treatment using electrochemically activated persulfate by externally added ferrous ions into the leachate system have been carried out effectively. The treatment processes include anodic oxidation of Pt/ Ti, sulphate

radical generated from the cathodic reduction of persulfate and its activation via externally added Fe^{2+} ions in water medium. Hydroxyl radicals and active chlorine stimulated in the system due to anodic oxidation and indirect electro-chemical oxidation processes accordingly enhance COD reduction in leachate. %ICE relies on persulfate concentration and escalates with augmentation of COD removal rate. Huian su et al.,(2023) said that the pollutants such as COD, $NH_4^+ - N$, S^{2-} , turbidity, and heavy metals could be significantly removed by the electrical flocculation and electrochemical oxidation in the BEF-O system. Additionally, EBR was used to deeply treat BEF-O system effluent and achieved a satisfactory treatment effect on the mature landfill leachate. Shen et al., (2006); Irdemez et al., (2006); Li et al., (1995) Isa et al.,(2008) investigated that the Electrochemical degradation of stabilized landfill leachate was investigated by employing a flow electrochemical reactor and using TiO_2 anode and Ti cathode.

Many types of electrodes have been investigated for electrochemical treatment such as TiO_2 , Ti, Fe, PbO_2/Ti , SnO_2/Ti , graphite and aluminium. Abdulhussian A abbas et al.,(2016) said that the electro degradation was an alternative means to breakdown recalcitrant organic compounds in landfill leachate. Due to high energy consumption, however, this technology is more 18 expensive than other treatment methods. As a result, this treatment technique has been investigated less extensively for the treatment of stabilized leachate.

Chiang et al. (1995) investigated that compared the efficacy of four anode materials in terms of COD and ammonium nitrogen removal of a low BOD/COD ratio (0.2) landfill leachate and the efficacy order has been obtained as Sn-Pd-Ru oxide-coated titanium (SPR) > Ru-Ti oxide-coated titanium (DSA) > Ti/PbO_2 > graphite due to high electrocatalytic activity of SPR anode. They have confirmed the production of chlorine/hypochlorite as main responsible species for organic oxidation and ammonium nitrogen removal using all the anodes by conducting experiments using saline water. Fernandes et al. (2016) investigated that during the initial period of electrolysis, organic oxidation reaction dominated over ammonium removal but later, after 50% COD removal, ammonium removal rate get accelerated through hypochlorite (ClO) formation. Fernandes et al. (2016) also compared the performances of $Ti/Pt/PbO_2$, $Ti/Pt/SnO_2-Sb_2O_4$ and BDD anodes where $Ti/Pt/PbO_2$ anode was found as most suitable anode material yielding lower energy consumption, higher nitrogen removal, and lower nitrate formation than BDD anode. The indirect oxidation through chlorine/hypochlorite was the dominant mechanism.

There are three main directions in the development of electrochemical treatment process applied to wastewaters containing various impurities. They are as follows:

- 1) Removal of dissolved impurities (mostly organic matter) from waste effluent in the form of non-toxic (or less toxic) and in some cases, water insoluble products as a result of anodic oxidation and cathodic reduction.
- 2) Removal of dissolved impurities (mainly inorganic matter) from wastewaters by electro dialysis, simultaneously utilizing recovered products.
- 3) Removal of dissolved and finely divided in dispersed state (including emulsified) insoluble impurities (both organic and inorganic) by electro coagulation methods and electro flocculation process (Deng and Englehardt, 2006).

2.1 ADVANTAGES OF ELECTROCHEMICAL PROCESS

The advantages of electrochemical oxidation are:

- A. Less land area required and pollution free.
- B. Does not leave any residue and no additional reagents are required.
- C. Continuous process with relatively high flow rates can be designed.
- D. No phase changes are required and high current efficiencies can be attained.

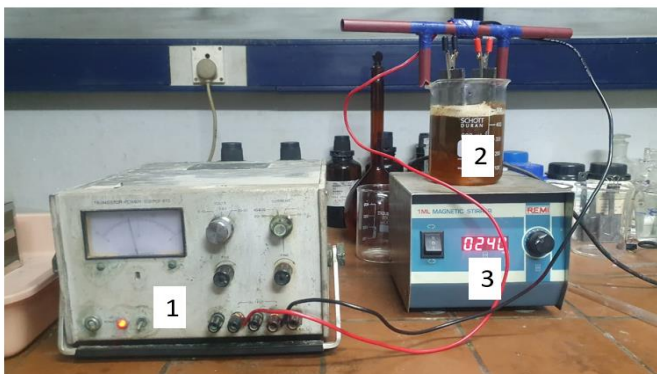
2.2 LIMITATIONS OF ELECTROCHEMICAL PROCESS

- a) Electricity requirement and high pH may affect the electrodes.
- b) It is usually necessary to do a multiple pass of the electrolyte to achieve a high removal of its ionic contents. A single pass usually removes less than 50% (Bhaskar Raju et al., 2009).

3. ELECTROCHEMICAL REACTOR ASSEMBLY

The experiment was conducted by batch process. An undivided cell of 500ml capacity (Glass Beaker) were used throughout the study. The experimental apparatus was constructed. The anode and cathode were positioned vertically and parallel to each other with an inner electrode gap of 2 cm. These electrodes were dipped in the electrolyte solution in submergence of 7 cm. Wires were used for making connections between the electrodes and DC power system. The positive terminal is connected to the anode and negative terminal to the cathode. The reactor was kept in a glass bowl containing water to maintain constant temperature of the electrolyte cell. The solution was kept constantly stirred with a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution as shown in Figure 1

Figure 1: Electrochemical Reactor assembly



- 1 – Transistor DC power supply (Max 30V;2A)
- 2 – Leachate sample in 600ml Borosilicate glass beaker [Reactor]
- 3 – Magnetic stirrer

Table -1: Characteristics of leachate

S.NO	PARAMETER	SAMPLE 1	SAMPLE 2	METHOD/EQUIPMENT
1	pH	7.8	7.93	Electrometric method
2	EC (μ S/cm)	5710	12810	Microprocessor
3	TDS (mg/L)	2850	6150	Gravimetric method IS 3025-part 15
4	TSS (mg/L)	2150	4812	Gravimetric method
5	BOD	450	1563	Winkler's method IS 3025-part 44
6	COD (mg/L)	1211.8	4218.8	Open Reflux method
7	Total Hardness as CaCO ₃ (mg/L)	1531.8	1700	APHA, 1992, 3500
8	Calcium hardness(mg/L)	466.2	1200	EDTA Titration
9	Colour	0.680	0.690	Spectrophotometric method
	436nm	0.267	0.289	
	526nm	0.122	0.146	
	620nm			
10	Magnesium Hardness(mg/L)	1065.6	500	EDTA Titration

11	Calcium	186.48	480	APHA, 1992, 3500-Ca
12	Magnesium	258.94	121.5	APHA, 1992, 3500-Mg
13	Sulphate	345.78	586.7	Colorimetric method APHA, 1992, 4500-SO ₄
14	silica	552	1245	Colorimetric method
15	chlorides	1149.65	7867.7	Argentometric method

Note: Sample 1 is the leachate sample collected from Package 1 from Perungudi dumpsite.

Sample 2 is the leachate sample collected from Package 3 from Perungudi dumpsite.

Source: APHA (2005) and APHA-AWWA-WPCF (1998)

The results show that the values are obtained by characterisation of sample. The sample was collected from perungudi dumpsite package 3. The sample was found to be slightly alkaline in nature at pH of 7.8. The sample was found to have higher COD and chlorides of 1228.8 mg/L and 1149.65 mg/L due to presence of inorganic pollutants and other persistent organic pollutants. The sample has shown higher conductivity of 5710 μ S due to presence of chlorides. The samples will be treated with electrochemical oxidation and compared with the standards of leachate as per municipal solid waste management rules 2016.

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3.1. ELECTRODES

Graphite is an electric conductor, consequently, useful in such applications as arc lamp electrodes. Commonly used inert electrodes: graphite (carbon). It can conduct electricity due to the vast electron delocalization within the carbon layers (a phenomenon called aromaticity). These valence electrons are free to move, so are able to conduct electricity. The electrode material that will be employed in the present study will be graphite with the dimension of 10 X 5 cm. The effective area of the cathode will be 50.0 cm².

3.2. POWER SUPPLY

A stabilized DC power supply (0-50V) is preferred as the source of electric current for the experiment.

4. ELECTROCHEMICAL OXIDATION PROCESS

Leachate sample of 500 ml each was taken for batch analysis from the perungudi dumpsite. The samples were transported to the laboratory and stored in a refrigerator at 4oC prior to use in the experiments. The electrodes were placed vertically and parallel to each other in the electrolytic reactor containing 450 mL of leachate sample. The distance between the cathode and anode was 2cm. Electrolyte, sodium sulphate NaCl was added at a concentration of (0.05mM to 0.2mM) to the samples before each experiment. DC power supply at current density of 20 mA/cm² was applied initially to the reactor. At different time intervals the sample was collected and stored in air tight container for further analysis in the laboratory. The sample collected was analysed for COD and colour. By varying the voltage to the reactor, the maximum removal efficiency was obtained.

5. OPERATIONAL PARAMETERS

5.1 REACTION TIME

The study was carried out till the optimal level of leachate attained. With varying time interval. The range of reaction time was [0- 240] mins.

5.2 CURRENT DENSITY

The effect of current density was varied from [20 - 80] mA/cm²

5.3 DOSE

The effect of addition of electrolyte NaCl was added to enhance removal of pollutant from landfill leachate. The dosage was [0,500,1000 mg/L].

5.4 DILUTION

The effect of dilution was carried out at various ratios raw leachate with no dilution [No addition of distilled water], 1:1[250ml leachate sample + 250ml distilled water] dilution, 2.3:1[350ml Distilled water + 150ml leachate sample] dilution.

6. RESULTS AND DISCUSSIONS

6.1. Cod Reduction from Leachate by Batch Electrochemical Oxidation Process

The batch EO process was conducted to check the removal of COD from the leachate [Package 3 and package 5]. The chemical oxidation demand of the effluent sample is determined by open reflux method, using COD digestion apparatus. The absorption of the sample is recorded to measure color on Spectrophotometer, recording the spectra over 190nm to 1000nm range.

6.2. Final Optimization for Package 3 (Sample 2):

The optimized condition for reaction time 2 hours has removed 75.4% of COD. but the COD value does not meet the standards of leachate mentioned as per municipal solid waste management rules 2016. The final value of COD is 561.72 mg/l, whereas minimum COD value to be maintained as per Municipal solid waste management rules 2016 is 250 mg/l.

By increasing the reaction from 2 hours to 4 hours, The COD removal increased drastically from 75.4% to 95%, the value is 120.2 mg/l, which is favorable to meet the minimum COD value as per MSW rules 2016.

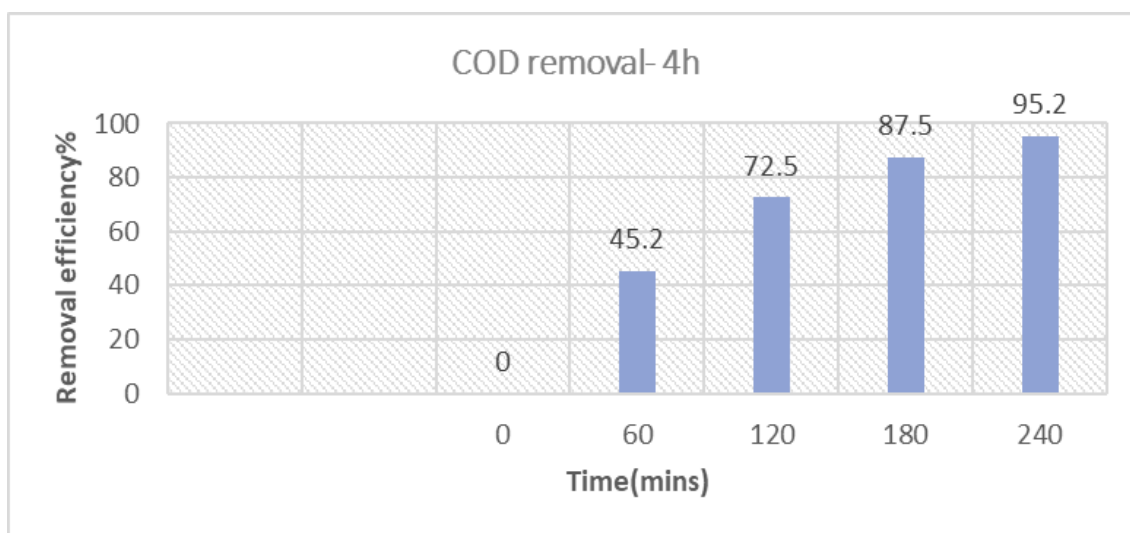


Figure 2: Maximum reduction of COD

Color removal has slightly increased when compared to 2 hours of reaction time. In 2 hours of reaction time, the absorbance values were calculated. Only 19.2% of color at 526nm, 7.1% of color at 436nm, 5.8% of color removal at 620nm has been removed which is not that much significant.

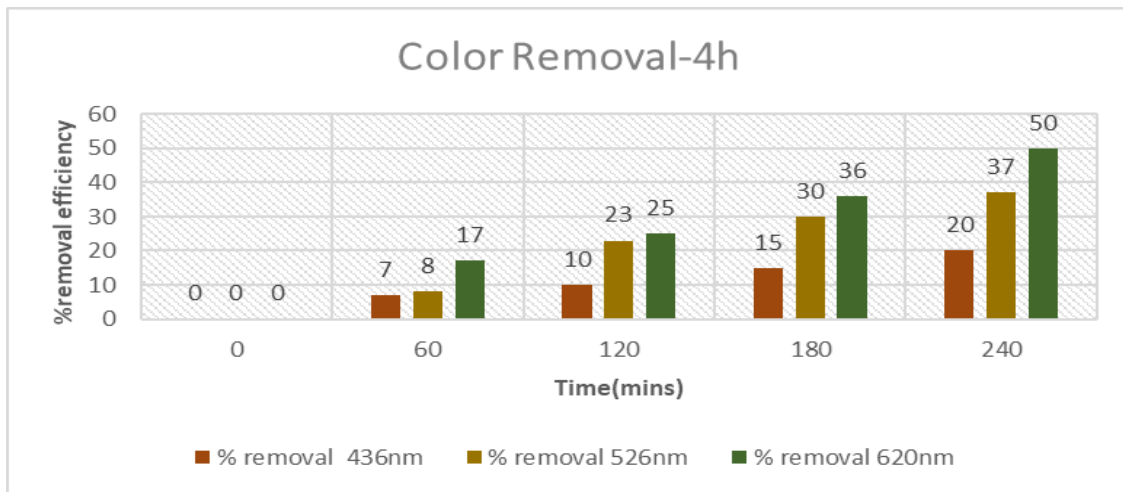


Figure 3 : Maximum reduction of Color

In order to increase the color removal, Reaction time has been increased from 2 hours to 4 hours in optimized condition. From the reaction of 4 hours, Colour removal has been absorbed in different absorbance values which are 20% colour removal at 436nm, 37% colour removal at 526nm and 50% colour removal in 620nm. which is significant. If the reaction time further increased the colour removal also increases.

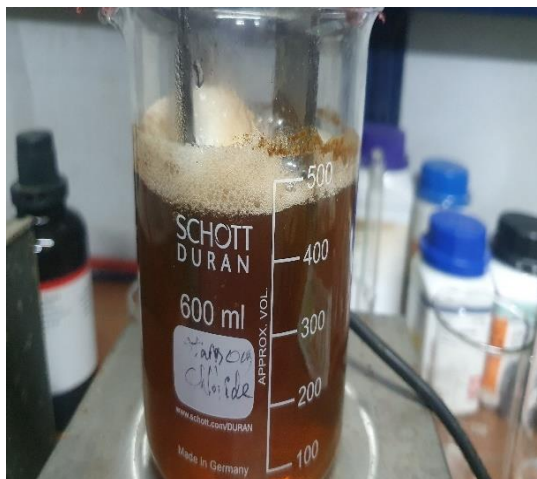


Figure 4: Before treatment of leachate [Package3]

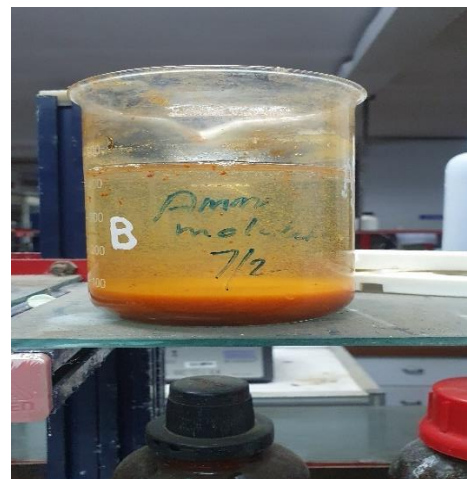


Figure 5: After treatment of leachate [Package3]

6.3. Final Optimization for Package 1 (Sample 1):

The optimized condition for the reaction time 2 hours has removed 87% of COD where the value of COD is 162.7 mg/l which is met the standards of municipal solid waste management rules 2016. Whereas the colour removal is not much efficient when compared to COD. To enhance the colour removal the reaction time has increased from 2 hours to 4 hours. The final COD value is 90.4 mg/l.

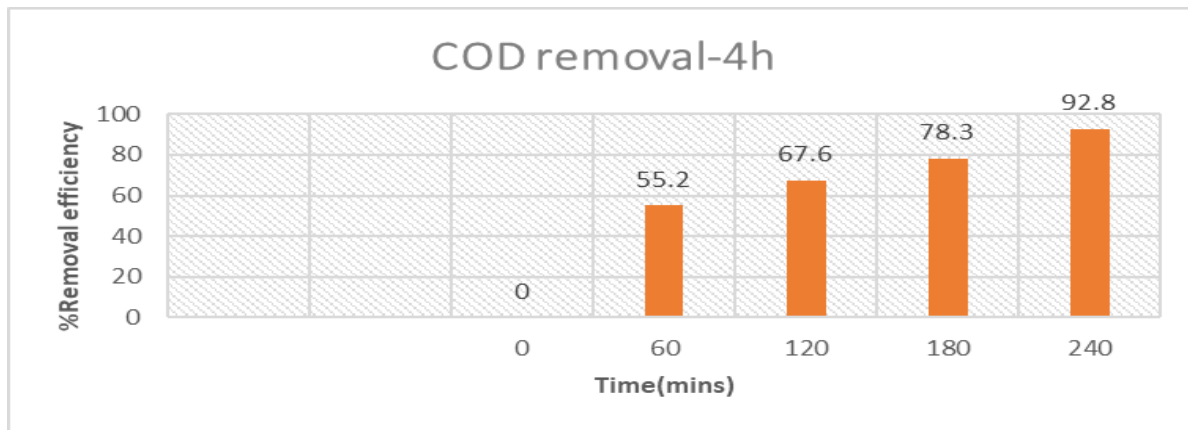


Figure 6 : maximum COD reduction

Colour removal has slightly increased when compared to 2 hours of reaction time. In 2 hours of reaction time, the absorbance values were calculated. Only 23.3% of colour at 526nm, 17% of colour at 436nm, 50.3% of colour removal at 620nm has been removed which is not that much significant. In order to increase the colour removal, Reaction time has been increased from 2 hours to 4 hours in optimized condition.

From the reaction of 4 hours, Colour removal has been absorbed in different absorbance values which are 43.5% colour removal at 436nm, 62% colour removal at 526nm and 63% colour removal in 620nm. which is significant. If the reaction time is further increased, the colour removal also increased.

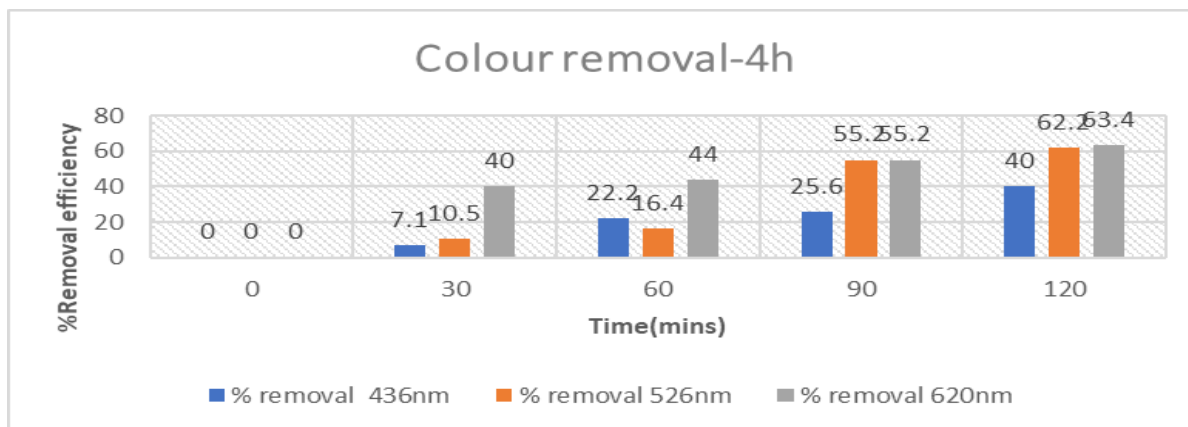


Figure 7 : Maximum Color reduction

Increase in reaction time, the chloride concentration in leachate gets converted to hypochlorite/chlorite after prolonged period of time, this hypochlorite/chlorite ion is converted to hypo chlorate/chlorate precipitate which agglomerates with dissolved and suspended solids in the solution, thereby colour removal occurs.

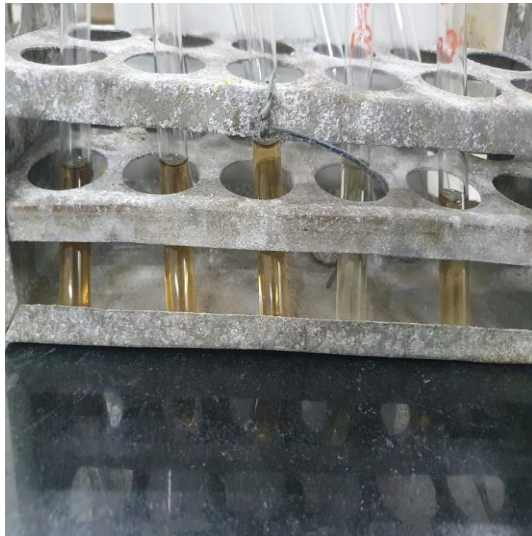


Figure 8: Before treatment of leachate package 1

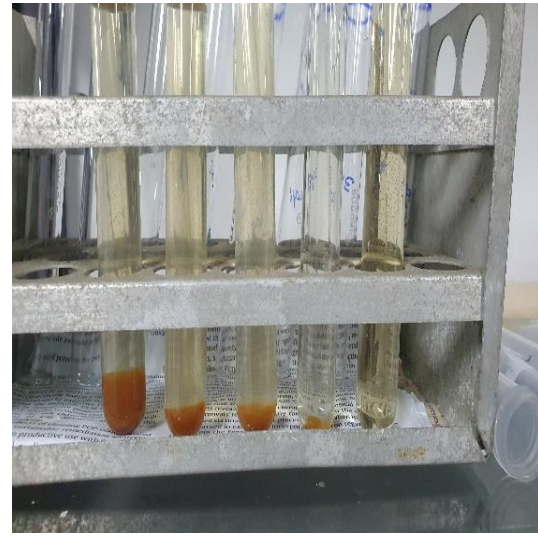


Figure 9: After treatment of leachate package 1

7. CONCLUSIONS

The highest removal efficiency of colour 63.4% at 620nm, 62.2% at 526nm and 40% at 436nm for optimum conditions of variables viz, pH = 3.4 and contact time at 240mins at 60mA/cm² have been recorded for leachate sample from package 1. The highest removal efficiency of colour 20% at 436nm, 37% at 526nm and 50% at 620nm for optimum conditions of variables viz, pH = 3.4 and contact time at 240mins at 60mA/cm² have been recorded for leachate sample from package 3.

The effective percentage removal of COD was 75.4% for reaction time of 2 hours and 95.2% for reaction time of 4 hours for leachate sample Package 3. The effective percentage removal of COD was 87.2% for reaction time of 2 hours and 92.5% for reaction time of 4 hours for leachate sample Package 1.

Increase in reaction time increases the COD and colour removal efficiency and graphite electrodes helps in reducing the organic contaminants of leachate and also other pollutants. The electrode is cheap, economically available and easy to handle.

Graphite electrode is sensitive for chloride concentration and maximum operating hours of 7 hours. Electrochemical oxidation provides several advantages for the prevention and remedy of pollution problems. The inherent advantage is its environmental compatibility as it uses a clean reagent, the electron, and there is little or no need for addition of chemicals. Likewise electrochemical oxidation is generally characterized by simple equipment, easy operation and brief retention time.

REFERENCES

- [1] D. Kornack and P. Rakic, "Cell Proliferation without Neurogenesis in Adult Primate Neocortex," *Science*, vol. 294, Dec. 2001, pp. 2127-2130, doi:10.1126/science.1065467.
- [2] M. Young, *The Technical Writer's Handbook*. Mill Valley, CA: University Science, 1989.
- [3] R. Nicole, "Title of paper with only first word capitalized," *J. Name Stand. Abbrev.*, in press.
- [4] K. Elissa, "Title of paper if known," unpublished.
- [5] Amokrane, A., Comel, C. and Veron, J. (1997) 'Landfill leachate pre-treatment by coagulation flocculation', *Water Research*, Vol. 31, pp.2775-2782.
- [6] APHA (2005) *Standard Methods for the Examination of Water and Waste Water*, 21st ed., American Public Health Association, Washington DC.

- [7] APHA-AWWA-WPCF (1998) Standard Methods for the Examination of Water and Waste Water, 20th ed., American Public Health Association, Washington DC.
- [8] Aziz, H.A., Alias, S., Adlan, M.N., Asaari, F.A.H. and Zahari, M.S.M. (2007) 'Color removal from landfill leachate by coagulation and flocculation process', *Bioresource Technology*, Vol. 98, pp.218–220.
- [9] Bhaskar Raju, G., Thalamadai Karuppiah, M., Latha, S.S., Priya, D.L., Parvathy, S. and Prabhakar, S. (2009) 'Electrochemical pretreatment of textile effluents and effect of electrode materials on the removal of organics', *Science Direct, Desalination*, Vol. 249, pp.167–174.
- [10] Deng, Y. and Englehardt, J.D. (2006) *Electrochemical Oxidation for Landfill Leachate Treatment*, Department of Civil, Architectural and Environmental Engineering, McArthur Building, University of Miami, USA.
- [11] Enzminger, J.D., Robertson, D., Ahlert, R.C. and Kosson, D.S. (1987) 'Treatment of landfill leachate', *Journal of Hazardous Materials*, Vol. 14, pp.173–182.
- [12] Mishra, R., Gedam. N., Waghmare. S., Masid, S. and Neti, N.R. (2009) 'Landfill leachate treatment by the combination of physical-chemical and electrochemical methods', *Journal of Environ Science & Engine*, Vol. 51, No. 4, pp.315–320.
- [13] Nisha Priya, M., Esakku, S. and Palanivelu, K. (2005) 'Electrochemical treatment of landfill leachate', *Indian Chemical Engineer, Centre for Environmental Studies, Anna University*, pp.272–276.
- [14] Rajkumar, D., Palanivelu, K. and Balasubramanian, N. (2004) 'Combined electrochemical degradation and activated carbon adsorption treatments for wastewater containing mixed phenolic compounds', *Journal of Environ Eng Science*, Vol. 4, pp.1–9.
- [15] Tatsi, A.A., Zouboulis, A.I., Matis, K.A. and Samaras, P. (2003) 'Coagulation-flocculation pre treatment of sanitary landfill leachate', *Chemosphere*, Vol. 53, pp.737–744
- [16] Vadivu, R. (2007) *Management of Reverse Osmosis Reject from Textile Industry*, ME Thesis, Centre for Environmental Studies, Anna University, Chennai, India.
- [17] Vlyssides, A.G., Israilides, C.J., Loizidou, M., Karvouni, G. and Mourafeti V. (1998) 'Electrochemical oxidation of textile dye and finishing waste water using Pt/Ti electrode', *Journal of Environment Science and Health*, Vol. A33, No. 5, pp.847–862.