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Performance Study of COD Removal of Landfill Leachate Using Granular Activated Carbon: A Review

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Abstract: The present study is conducted on the existing landfill site of Daddu Majra in Chandigarh. The landfill is not provided with the collection system of leachate and its treatment as this landfill site is not designed as an engineered system of Municipal Solid Waste disposal. The study was conducted to analyse the characteristics of the leachate produced by the landfill and one particular treatment method using granular activated carbon (GAC), GAC treated with sodium hydroxide (NaOH) and advanced oxidation process (AOP) using hydrogen peroxide (H₂O₂). The leachate was initially analysed for pH, colour, electrical conductivity (EC), chlorides, total hardness, total solids (TS), suspended solids, dissolved solids, alkalinity, chemical oxygen demand (COD) and biochemical oxygen demand (BOD).The leachate had a very low biodegradability ratio (BOD₃/COD) of 0.095, which suggested that direct biological treatment processes could not be applied to treat the leachate because it would be very toxic for the micro-organisms to work upon it. The GAC used was surface modified using NaOH to introduce additional basic oxygen-containing surface functional groups, responsible for its catalytic properties towards target compounds. The COD removal by the combined H_2O_2 and surface modified GAC treatment was evaluated, optimized and compared to that by H_2O_2 treatment alone and GAC treatment alone with respect to dose, contact time, pH, and biodegradability ratio(BOD₃/COD) in batch mode. The results showed that at an initial COD concentration of 12000 mg/L and BOD₃ of 1150 mg/L, the combined treatment has substantially achieved a higher removal (COD removal-85%) than the H_2O_2 oxidation alone (COD removal-38%), surface modified GAC adsorption alone (COD removal-60%) and as received GAC adsorption alone (COD removal-42%). Finally the optimized experimental conditions for the combined treatment obtained were 25 g/l of surface modified GAC dosage, 5 g/l of H₂O₂dosage, 60 minutes of contact time at 200 rpm of agitation speed and initial pH of the sample as 8.0. Although the combined H₂O₂ oxidation and surface modified GAC adsorption could treat leachate of varying strengths, treated effluents were unable to meet the local COD limit of less than 250 mg/l. However, the treatment significantly improved the biodegradability ratio of the treated leachate by 321% from 0.095 to 0.40, enabling the application of subsequent biological treatments such as Sequential Batch Reactor, UASB reactor etc. to further stabilize the target compounds in the leachate prior to their discharge as per the existing effluent discharge standards.

Keywords: Leachate, Granular Activated Carbon, Landfill, COD, BOD, Hydrogen Peroxide, NaOH.

I. INTRODUCTION

Pollution is the release of a waste matter and energy into the environment making it impossible to sustain life on earth. Pollution harms the earth's environment and its people in many ways. Land pollution is pollution of the earth's natural land surface by industrial, commercial, domestic and agricultural activities. Some of the main contributions to land pollution are deforestation, construction debris, industrial factories etc. Air pollution is the accumulation of harmful substances into the atmosphere that danger human life and other living matter on the earth. The number one way to prevent air pollution is to walk or bike more and drive less. This will prevent fossil fuels from further polluting the air. Water pollution is the introduction of chemical, biological and physical matter into large bodies of water that corrupt the quality of life that lives in it and consumes it. Oil spills, household chemicals, pesticides and fertilizers are the major sources of water pollution. The best way to prevent water pollution is to not throw trash and other harmful chemicals into our water supplies because it causes harm to the rivers and lakes.

With pollution in life, Earth's life supporting system is getting disturbed. Nevertheless, pollution is simultaneously endangering life on Earth. Pollution is becoming closer to put life on the threshold of death. These harmful actions have changed Earth, and they continue to do so today. Technology, each day has been evolving to make this world a better place. Nowadays, technology is being cleaner to preserve Earth. Also, it has been cleaning Earth through water treatment plants, air purifiers, etc. Technology will progress over the years to make Earth a healthier living experience. As a nation we have to learn to respect and salute the environment. We as individuals live in this environment and it is our sole responsibility to take care of it.



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Ground water is an important source of drinking water for more than half of the nation's population and nearly all its rural population. Ground water acts as a reservoir by virtue of large pore space in earth materials, as a conduit which can transport water over long distances and as a mechanical filter which improves water quality by removing suspended solids and bacterial contamination. In recent years, widespread reports of bacteria, nitrate, synthetic organic chemicals and other pollutants have increased public concern about the quality of ground water.

Today urbanization has become a synonym of development and provides tremendous opportunities for growth, but simultaneously poses great challenges relating to delivery of adequate and efficient basic services in sustainable manner to a rapidly increasing population [30]. In the race of development and modernization, the man has in fact jumped headlong towards environment pollution impending towards crisis.

From the days of primitive society human have used the resources of the earth to support life and dispose off waste. In early times, the disposal of human and other waste did not pose a significant problem, because the population was very small and the amount of land available for the disposal of waste was large. But the ever increasing population has now lead to an increase in urbanization and industrialization consuming more and more natural resources, which results in the generation of large quantities of waste. These wastes can be classified as solid waste, liquid wastes and atmospheric emissions. Atmospheric emissions and liquid waste owing to their destructive nature have got focus. However, solid wastes as presently understood, methods of its safe management with environment friendly techniques are being worked out and as get in developmental stage.

Solid waste is generally categorized as domestic, industrial, agricultural, constructional, biomedical and commercial waste. The generation of solid waste has become an increasingly important global issue over the last decade due to the escalating growth in world population and large increase in waste production. This increase in solid waste generation poses numerous questions concerning the adequacy of conventional waste management systems and their environmental effects. Landfill disposal is the most commonly waste management method worldwide, and new methods are required to reduce green house gases emissions from landfills. Landfills have served as ultimate waste receptors for municipal refuse, industrial residues, recycled discards and waste water sludge.

II. IMPACTS FROM LANDFILLS

Landfills represent a significant threat to ground water resources as well the surrounding environment due to their nature of operation. Landfills and other disposal sites can threaten fresh ground water formations through the production of low quality leachate. Leachate is generated by precipitation percolating through a landfill and removing soluble components of disposed waste. The chemical composition of landfill leachate will depend on the following factors:

- Nature of the waste
- Leachate generation rate
- Age of the landfill

To curb pollution created by leachate, three preliminary measures are practiced today:

• **Prevention of leachate production**; leachate production can be minimized by installing a low permeability cover on the fill and by proper selection of the landfill site. These methods have met with limited success.

• **Recirculation of leachate back onto the sanitary landfill**; this method facilitates increasing moisture content of the solid waste and should aid in anaerobic biological stabilization of landfill contents.

• **Collection and treatment of leachate**; this is the most recent approach; leachate is collected and treated externally by biological or physical/chemical means [45].

• The need is to set up a secured landfill which is having proper liner systems, leachate collection and treatment facility so that the havoc which is being created due to the disposing of waste on the open dump is controlled. The secured or the engineered landfills are the sites which allows final disposal of waste in a secure manner by minimizing the impacts on the environment. The waste is spread out in a thin layer in the waterproof cells where they are leveled, compacted and covered periodically with soil or another inert material. Ditches all around the site deviate the surface water before it comes in contact with the waste. As for rainwater that infiltrates itself into the waste, it gets mixed with contaminants and increases leachate, which is collected at the bottom of the cells and is sent to the lagoons for treatment. After a few years, the degradation of the biodegradable part in waste produces landfill gas. This gas is captured by a network of wells installed all over the site and is burned or converted into energy.

III. OBJECTIVES AND STUDY AREA

The major thrust of this study was the characterization and treatment of the existing landfill leachate of the Daddu Majra landfill site as shown in Fig. 1. In the present study, a combination of Advanced Oxidation Process (AOP) using H_2O_2 and adsorption using surface modified Granular Activated Carbon (GAC), surface modification done using

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sodium hydroxide (NaOH), to remove the COD of the landfill leachate which proved to be a promising treatment method as shown by the results of the study. The adopted methodology improved the biodegradability ratio i.e. BOD/COD ratio of the leachate and hence can be employed as a preliminary step for further treatment methods which can employ the microbial treatments also, once a certain level of the BOD/COD ratio is achieved.



Fig. 1 Daddu Majra landfill site

IV. METHODOLOGY

The methodology adopted for the study includes:

1) Leachate Characteristics: This part is which includes the recent research being carried out throughout world with main focus on leachate characteristics and different treatment technologies used to treat leachate.

2) Field Investigation: This includes the sampling of leachate from the site and then testing all the parameters in the lab.

3) Proposed Treatment Method For Leachate.

V. RESULTS AND DISCUSSIONS

A. Leachate Characterization

Leachate from the landfill was tested to study the various characteristics of the leachate. The results are shown in the Table I below:

S.No.	Parameters	Units	Results
1	pН	-	8.0
2	Colour	-	Black brown
3	EC	µmho/cm	12550
4	Chlorides	mg/l	7482
5	Total hardness	mg/l	8000
6	TS	mg/l	9200
7	Suspended Solids	mg/l	2760
8	Dissolved Solids	mg/l	6440
9	Alkalinity	mg/l	9000
9	COD	mg/l	12000
10	BOD ₃	mg/l	1150
11	BOD/COD ratio	-	0.095

11 BOD/COD Tatio

B. Treatment of leachate using $\rm H_2O_2$ and GAC

1) Effects of reaction time on COD removal

To find the optimum time for maximum removal of COD, initially a GAC dosage of 15 g/l was applied and the %COD removal was calculated while varying the contact time from 10 minutes to 60 minutes. An initial pH of 8.0 was maintained during this experiment and an agitation speed of 150 rpm was maintained and initial COD being 12000 mg/l. It was observed that a 30% COD removal happened with this dosage as shown in the Fig. 2.

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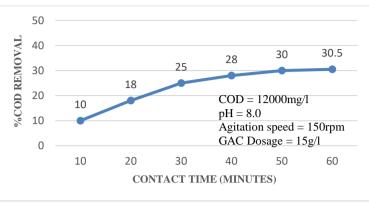


Fig. 2 Effects of reaction time on COD removal

2) Effects on COD removal w.r.t. agitation speed

After determining the optimum time of 60 minutes, to determine the optimum agitation speed at the same GAC dosage of 25 g/l and time of contact as 60 minutes, the agitation speed was varied from 50 rpm to 250 rpm maintaining the initial pH 8.0. It was observed that the %COD removal varied from 14% to 32% at the agitation speed of 50 rpm and 200 rpm respectively as shown in the Fig. 3. So for the maximum COD removal an agitation speed of 200 rpm was adopted.

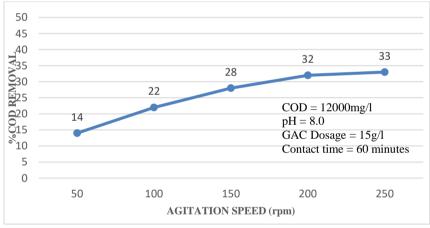


Fig. 3 Effects on COD removal w.r.t. agitation speed

3) Effects on COD removal w.r.t. GAC dosage at optimised conditions

To determine the optimum dosage of GAC, at a contact time of 60 minutes, initial pH of 8.0 and agitation speed of 200 rpm, the GAC dosage was varied from 10 g/l to 30 g/l. The %COD removal varied from 24% to 60% at GAC dosage of 10 g/l to 25 g/l respectively. So the maximum COD removal was observed at GAC dosage of 25 g/l as shown in Fig. 4.

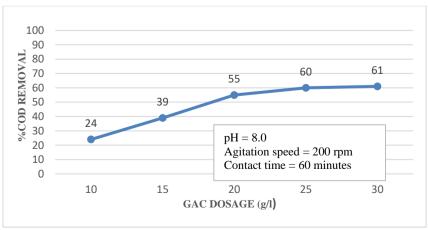


Fig. 4 Effects of GAC dosage on COD removal

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4) Effects of COD removal w.r.t. H₂O₂ dosage alone at optimized conditions

A complete removal of target compounds requires an optimum dose of H_2O_2 for the oxidation process. Therefore, it is necessary to determine its optimum dose to maximize catalytic oxidation. In this study, the dose of H_2O_2 was varied from 1 to 6.0 g/l, while the dose of GAC was kept unchanged at 25 g/l and the initial pH at 8.0. The effects of the H_2O_2 doses on COD removal are shown Fig. 5 below. It was observed that the %COD removal varied from 8% to 38% at the H_2O_2 dosage of 1 g/l and 5 g/l respectively. So the maximum COD removal was observed at 5 g/l.

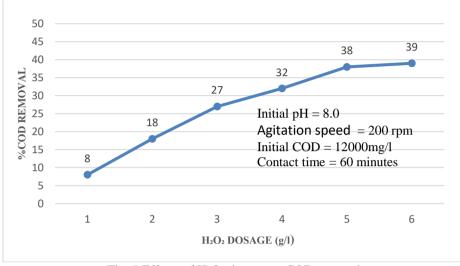


Fig. 5 Effects of H₂O₂ dosage on COD removal

5) Combined effect of GAC and H₂O₂ on COD removal

At the optimised conditions of 60 minutes of contact time and 200 rpm of agitation speed, initial pH was maintained at 8.0 and the combined effect of GAC and H_2O_2 was observed on the COD removal. It was observed that at the GAC dosage of 25 g/l, when the H_2O_2 dosage was varied from 1 g/l to 6 g/l to study the combined effect, the %COD removal varied from 35% to 85% at the H_2O_2 dosage of 1 g/l and 5 g/l respectively as shown in Fig. 6. The agitation speed was maintained at 200 rpm and the pH was 8.0 and the initial COD being 12000 mg/l.

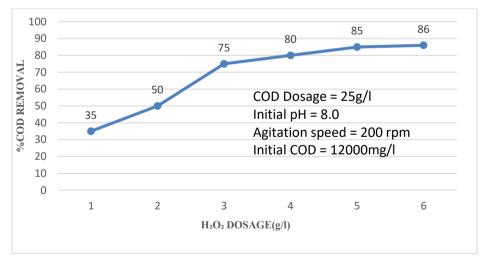


Fig. 6 Effects of combined treatment using GAC and H₂O₂ on COD removal

6) Effect of initial pH of sample on COD removal using $\mathrm{H_2O_2}$ alone

To study the effect of initial pH of the sample on the COD removal, the pH was varied from 2.0 to 9.0 to find the optimum pH for maximum COD removal. The agitation speed of 200 rpm was maintained at contact time of 60 minutes, initial COD was 12000 mg/l, and the H_2O_2 dosage was 5 g/l. It was observed that the %COD removal varied from 5% to 38-39% when the pH was raised from 2 to 8-9 respectively. So the maximum COD removal was observed at the pH of 8.0 as shown in the Fig. 7.

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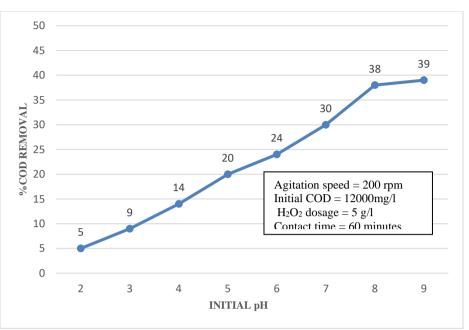


Fig. 7 Effects of initial pH on COD removal using H₂O₂ alone

7) Effect of initial pH of sample on COD removal using combined treatment of GAC and H₂O₂

To study the effect of initial pH of the sample on the COD removal, the pH was varied from 2.0 to 9.0 to find the optimum pH for maximum COD removal. The agitation speed of 200 rpm was maintained at contact time of 60 minutes, initial COD was 12000 mg/l, and GAC dosage was 25 g/l, the H_2O_2 dosage was 5 g/l. It was observed that the %COD removal varied from 7% to 85% when the pH was raised from 2 to 8-9 respectively. So the maximum COD removal was observed at the pH of 8.0 as shown in the Fig. 8 below using the combined treatment of GAC and H_2O_2 .

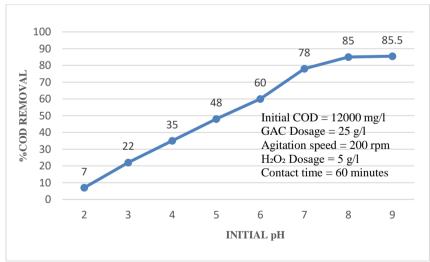


Fig. 8 Effects of initial pH on COD removal using combined treatment of GAC and H₂O₂

8)Variation of biodegradability ratio(BOD₃/COD) of leachate w.r.t. time of contact with treatment of H₂O₂ alone To study the effect of H₂O₂treatment on the biodegradability ratio of the leachate, the time of contact was varied from 10 minutes to 60 minutes, the H₂O₂ dosage was 5 g/l, pH 8.0, initial BOD₃ as 1150 mg/l, initial COD as 12000 mg/l, hence BOD₃/COD = 0.095, agitation speed of 200 rpm. In the study it was observed that when the time of contact was varied from 10 minutes too 60 minutes, the BOD₃/COD ratio varied from 0.095 to 0.15, which showed that not a very significant change was observed, being a change of only 57%. However, the combined treatment of GAC and H₂O₂ would be a very significant change. The variation is shown in the Fig. 9.



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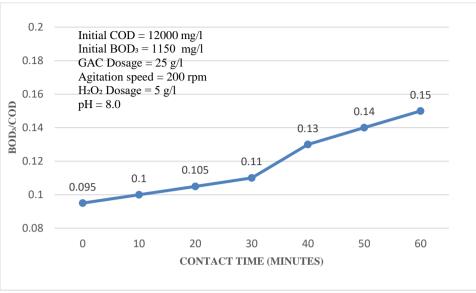


Fig. 9 Variation of biodegradability ratio w.r.t. time with treatment of H₂O₂ alone

9) Variation of biodegradability ratio(BOD₃/COD) of leachate w.r.t. to time of contact with combined treatment of GAC and H₂O₂

To study the combined effect of GAC and H_2O_2 treatment on the biodegradability ratio of the leachate, the time of contact was varied from 10 minutes to 60 minutes, the H_2O_2 dosage was 5 g/l, COD dosage was 25 g/l, pH 8.0, initial BOD₃ as 1150 mg/l, initial COD as 12000 mg/l, hence BOD₃/COD = 0.095, agitation speed of 200 rpm. In this study, it was observed that when the time of contact was varied from 10 minutes too 60 minutes, the BOD₃/COD ratio varied from 0.095 to 0.40, which showed a change of 321% which is a very significant change for further treatment of the leachate. The variation is shown in the Fig. 10.

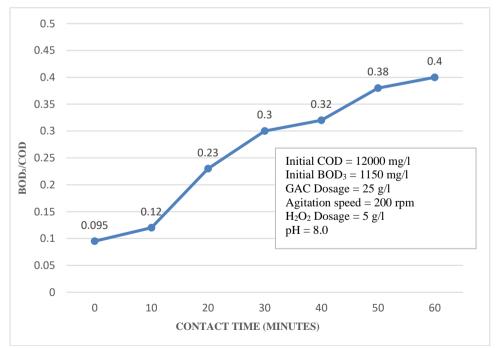


Fig. 10 Variation of biodegradability ratio w.r.t. time with combined treatment of GAC and H_2O_2

10) Effect of contact time on COD removal using H₂O₂ alone

To study the effect of H_2O_2 treatment on COD removal of the leachate, the time of contact was varied from 10 minutes to 60 minutes, the H_2O_2 dosage was 5 g/l, pH 8.0, initial BOD₃ as 1150 mg/l, initial COD as 12000 mg/l, agitation speed of 200 rpm. In the study, it was observed that when the time of contact was varied from 10 minutes to 60 minutes, the

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%COD removal varied from 10% to 38% respectively. After 60 minutes, no significant variation was observed. The variation is shown in the Fig. 11.

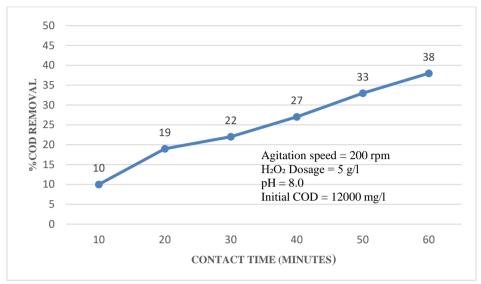


Fig. 11 Effects of contact time on COD removal using H₂O₂ alone

11) Effect of contact time on COD removal using GAC alone:

To study the effect of GAC treatment on COD removal of the leachate, the time of contact was varied from 10 minutes to 60 minutes, the GAC dosage was 25 g/l, pH 8.0, initial BOD₃ as 1150 mg/l, initial COD as 12000 mg/l, agitation speed of 200 rpm. In the study, it was observed that when the time of contact was varied from 10 minutes to 60 minutes, the %COD removal varied from 20% to 60% respectively. After 60 minutes, no significant variation was observed. The variation is shown in Fig. 12.

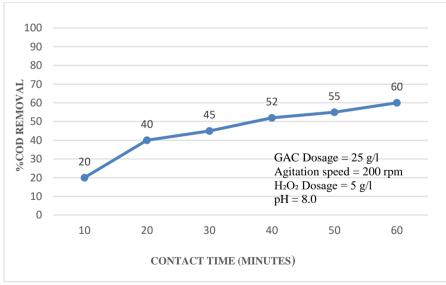


Fig. 12 Effects of contact time on COD removal using GAC alone

12) Effect of contact time on COD removal using combined treatment of GAC and H₂O₂

To study the effect of combined GAC treatment of GAC and H_2O_2 on COD removal of the leachate, the time of contact was varied from 10 minutes to 60 minutes, the GAC dosage was 25 g/l, H_2O_2 dosage was 5 g/l, pH 8.0, initial BOD₃ as 1150 mg/l, initial COD as 12000 mg/l, agitation speed of 200 rpm. In the study, it was observed that when the time of contact was varied from 10 minutes to 60 minutes, the %COD removal varied from 22% to 85% respectively. After 60 minutes, no significant variation was observed. The variation is shown in Fig. 13.

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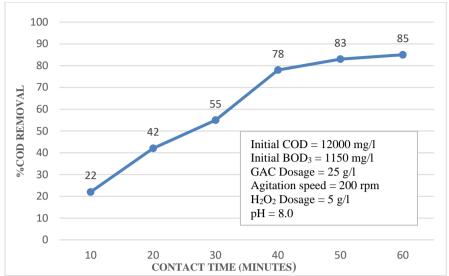


Fig. 13 Effects of contact time on COD removal using combined treatment of GAC and H₂O₂

13) Effect of contact time on COD removal:

The combined effect of contact time on COD removal are shown in Fig. 14, which gives a clear indication of the importance of the combined treatment of H_2O_2 and GAC to remove a significant amount of COD from the stabilised landfill leachate, so that it can be further treated.

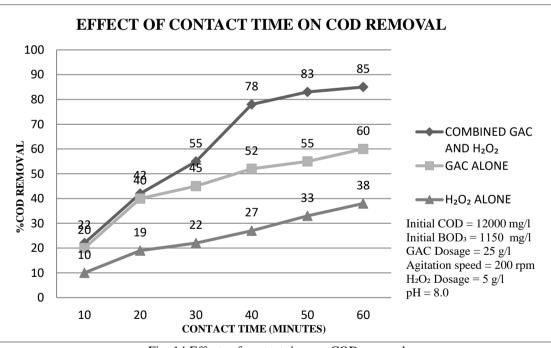


Fig. 14 Effects of contact time on COD removal

VI. CONCLUSIONS

Based on the experimental work conducted in this study the following conclusions can be drawn:

1) The leachate of the landfill when analysed for the pollutional parameters showed a pH of 8.0, black brown colour, EC of 12550µmho/cm, chlorides value 7482 mg/l, total hardness as 8000 mg/l, total solids as 9200 mg/l, suspended solids ranging to 2760 mg/l, very high amount of dissolved solids i.e. 6440 mg/l. Alkalinity was found to be 9000 mg/l and a very high COD value of 12000 mg/l was observed along with 1150 mg/l of BOD₃ value.

2) The biodegradability ratio i.e. BOD/COD value was found to be 0.095 before the treatment and so the leachate is highly toxic for the micro-organisms.

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3) The high COD value which is an indicator of the refractory compounds in the leachate makes the treatment process of leachate very expensive as lot of resources are needed to be employed to treat it up to a desired extent.

4) A pH value of 8.0 i.e. slightly alkaline, suggests that the landfill has entered into methanogenic phase.

5) The application of the integrated H_2O_2 oxidation and GAC adsorption treatment is technically applicable and economically attractive for the removal of refractory compounds from landfill leachate.

6) GAC in this study was coconut shell based which is otherwise a waste material. So it is economically more advantageous to use such a material for the treatment of leachate.

7) Surface modification using NaOH proved very significant because as received GAC alone could only reduce COD by 42%, whereas after the surface modification using NaOH, as observed in the present study, the %COD removal was 60% which is an increment of 17% clearly. So, it can be concluded that the surface modification of GAC using NaOH proved to be a very significant process for the removal of the recalcitrant compounds from the landfill leachate.

8) The leachate had very low biodegradability ratio i.e. 0.095, which is very toxic for the microorganisms. This ratio is so low that that a biological process alone is not effective enough to remove the bulk of refractory pollutants. For this reason, an integrated leachate treatment with other technologies such as advanced oxidation process (AOP) or physico-chemical treatments like adsorption was adopted which converted recalcitrant materials to relatively more biodegradable and improved its treatability. After the treatment the biodegradability ratio raised to 0.40 i.e. an increase of 321% enabling the use of subsequent biological treatments such as SBR, UASBR etc.

9) Combinations of the two treatments have been proved to be more efficient and effective than individual treatment in improving the effluent quality. This could be due to the fact that a two or more-step treatment has the ability to synergize the advantages of individual treatments, while overcoming their respective limitations. It has been proved in this study.

10) Recalcitrant organics which contained in mature landfill leachates, are not amenable to conventional biological processes and the high ammonia content might also be inhibitory to microorganisms. As to encounter these problems, advanced oxidation processes (AOPs) have been used as effective alternative treatment for mineralization of recalcitrant wastewater organics and biodegradability improvement. Biological processes are effective for removal of biodegradable organics and nitrogenous matter from wastewater.

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