Safe Disposal and Effective Utilization of Solid Wastes from Leather Industry

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Abstract: ***The leather industries produce large amount of solid organic wastes from raw hides and skins, semi-processed leather, as well as sludge as a result of wastewater treatment. If these solid wastes are not properly treated and disposed of, they can cause environmental damage to soil and groundwater as well as emissions of odour and poisonous greenhouse gases into the atmosphere. The chromium plays a vital role in the ground water contamination which is due to the solid waste expelled out from the leather industry. This project is about how to convert those harmful materials into Eco-Friendly materials. Chrome present in the solid waste has toxic nature when it is in the oxidation state of Cr^{6+}. So the project deals how to avoid the formation of Cr^{6+} in order to destroy the hazardous nature of the product formed from the solid waste by a method called pyrolysis. The observations on generation of no toxic compounds upon pyrolysis, suggests the suitability of this process towards achieving safe disposal of hazardous leather solid waste and to recover useful products. An attempt to use the generated residual ash as the replacement of cement and sand has been made and tested.***

Keywords: Chromium, Pyrolysis, Residual Ash, Blocks

1. Introduction

Leather industry, one of the polluting industries because of generation of huge amount of liquid and solid wastes, emits obnoxious smell because of degradation of proteinous material of skin and generation of gases such as NH_3, H_2S and CO_2.Treatment of solid wastes also is not cost effective, posing economic burden to the tanners.

Leather industry in the developing countries is facing lot of solid wastes problem and many tanneries closed for not meeting bio-chemical oxygen demand (BOD) and total dissolved solids (TDS) norms.

Leather industry has been characterized as one of the highly polluting industries and there are concerns that leather-making activity can have adverse impact on the environment. If the proteins and the other chemicals present in the solid wastes are not properly used then it will pose hazardous pollution problem to the environment.

Raw materials, Chemicals Used and Emission Factors in leather Industry

Raw material for leather industry is raw hide or skin. The salt used for preserving the skin/hide discharges huge amount of pollution load in terms of total dissolved solids (TDS) and chlorides. Other major polluting chemicals used in tanning industry are lime, sodium sulphide, ammonium salts, sulphuric acid, chromium salts and vegetable tanning materials.

Currently, about 6.5 million tons of wet salted hides and skins are processed worldwide annually. About 3.5 million tons of various chemicals are used for leather processing. A considerable part of this amount is discharged into the effluent. At an average consumption of 45-50 m^3 of the waste liquor 800kg of solid wastes per ton of raw hide are discharged by the leather industry.

Types of pollution in Leather Industry

Soil Pollution

Untreated wastewaters from tanneries have been applied on land merely to contain them at one place. The soils holding it directly and irrigated with contaminated groundwater lose productivity.

Atmospheric Pollution

Tanneries are proverbially known for generating malodor. The salted hides and skins emit odor of volatile fatty and amino acids evolved in the course of biological decomposition in the presence of water.

In addition, toxicity of hydrogen sulphide along with acids and etc., are predominant within tanneries. The venting out of malodorous substances to ambient air and subsequent transports to further distance are responsible for atmospheric pollution.

A. Methods of Solid waste disposal at present in the Leather Industry

1. Landfill Disposal

Disposal of land for waste disposal would be physically impossible since areas with the largest concentration of solid waste would also be the areas with serious scarcity of vacant land. The implications, therefore, is that if the current methods of solid waste disposal persist, the waste would have to be carried over long-distance, which would require the creation of a great deal of transport facilities and Infrastructure.

This would involve enormous additional finances. Land filling scenario faces the highest cost, which is explained by the combination of the overall high pollution emissions and low energy recovery. And also the available landfill sites rapidly reach their total capacity and the authorization for new site becomes difficult Indiscriminate land filling leads to deterioration of water quality in neighbourhood areas of land fill sites due to contamination by leachates from the landfill sites.

Landfill gas, which is 50-60%methane, contributes significantly to global warming. Hence, land fill disposal method has been discouraged by environmental experts and technological interventions were made.

2. Anaerobic Digestion of Animal Fleshing

Anaerobic digestion consists of break-down of biodegradable material by microorganisms in the absence of oxygen. This method has been applied for the treatment of solid waste (animal fleshing) and co-digested with secondary biological sludge.

This process has advantage that it reduces the emission of greenhouse into the atmosphere. Anaerobic digestion can be regarded as a non-conventional energy source because the process produces methane and carbon-di-oxide rich biogas suitable for energy production helping to replace fossil fuels.

The methane can be burnt to produce both heat and electricity, usually with a reciprocating engine or micro turbine. The residuals left after anaerobic digestion is nutrient-rich and can be used as organic manure.

The negative aspects of anaerobic digesters are the careful control of the temperature, pH and organic loading rate of the influent and technical expertise. The biogas contains hydrogen sulphide which causes dry corrosion in the burners and thus it is required to scrub the gas before considered as fuel gas, adding to the capital cost. High capital costs and lower process efficiencies have limited industrial level application of this process.

Anaerobic digesters fed with animal fleshing generated methane gas 46 L/kg and electrical power of 6 w/kg of animal fleshing.

3. Thermal Incineration

Capital investment of the thermal incineration process is only about 1/6th of the total cost for the land filling scenario. Therefore, tannery wastes like sludge, shavings and buffing dust can be thermally treated to reduce the volume to be disposed-off.

The thermal treatment of wastes involves incineration, gasification and Pyrolysis as a mean of disposal, while also recovering energy from waste. So the thermal incineration is considered as the cheapest alternative and attractive method for its simultaneous energy production and volume reduction of solid waste.

The thermal incineration of solid wastes from tanneries needs a special attention on the issues such as release of toxic chromium (VI), halogenated organic compounds, poly aromatic hydrocarbons etc. into the environment. The major species formed from Cr (III) during thermal incineration of solid waste are $Cr_2(SO_4)_{3(s)}$, $CrOCl_{2(g)}$ and $Cr_2O_{3(s)}$ which later accounts a path for the formation of Cr (VI).

The highly toxic properties of ash prohibit its direct land co-disposal. Therefore, an effective solidification and stabilization of bottom ash was resorted to change potentially hazardous solid wastes into less hazardous or non-hazardous solids before it is disposed-off as landfill.

Solidification is another process that has been considered as an alternative solution to the wastes containing heavy metals. In the present study the bottom ash was solidified and stabilized using Portland cement, fine aggregate, coarse aggregate and blue metal dust.

The focal theme of the present investigation was on

(i) To arrest oxidation of trivalent chromium to hexavalent chromium with simultaneous energy utilization from organic fractions in thermal incineration.
(ii) Solidification and stabilization (s/s) of bottom ash of calcined chrome shavings and its leachability studies.

Chromium in the solid waste

Basic chromium sulphate (BCS) is the most widely used tanning material for converting putrescible collagen fibres into non putrescible leather matrix. Only 60% of chromium salts applied for tanning process react with the raw materials and the rest of chromium salts disposed along with the waste material and also into the waste water.

Hazardous chromium

The energy content of tannery leather solid waste is more than 50% in comparison to hard coal, is normally 20 MJ/kg in dry basis. The chromium content in solid leather wastes (wet blue leather), is approximately 30gmkg^{-1} (w/w). Brazilian Environmental Council (CONAMA) classified chromium containing leather waste material as a category-one waste, one of the most dangerous and harmful wastes if discarded into the environment without any further treatment.

Causes and effects

Chrome containing leather waste is carcinogenic in nature and it causes clinical problems like

1. Respiratory tract ailments
2. Ulcers
3. Perforated nasal septum
4. Kidney malfunction
5. Lung cancer

Because of this, such a material needs a special disposal, which is very expensive. In the absence of any economically viable technology to dispose the solid leather waste, land co-disposal, thermal incineration and anaerobic digestion methods are currently being practiced.

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A double pyrolysis approach was used in this study to assess the mass of the residual carbonaceous material, gases and value added products.

The residual-ash generated from the pyrolysis method can be used in various forms. The Generated ash can be mixed with the sand and cement i.e., the ash is replaced by various percentages for both cement and sand.

Since there are some possibilities for the chromium to leach out, the residual ash is densified and standardized by mixing it with a Nanoparticle and the pH is brought to 6.8-7 which is a neutral value, such that there wouldn't be any possibility for the chromium to leach out.

Mortar mixes were casted and the compressive strength of the mortar was tested. Leachability test were also been carried out for the samples.

1:3 mix proportions is chosen for the mortar blocks.

Figure 1: Carbon mixed mortar cubes

Compressive strength of Mortar cubes:

Compressive strength of mortar cubes are tested by using the compressive strength testing machine (CTM) shown in figure 1.

Figure 2: Testing of cubes in CTM

Carbon replaced for Cement:

Table 1: Load and Stress calculations for different % of Carbon Replaced for Cement

%of C	%of Sand	%of Cement	Load(kN)-7days	Stress (MPa)-7days	Load(kN)-28 days	Stress (MPa)-28 days	Wt. of blocks (gm)
5	75	20	41.10	8.24	73.86	14.80	733
6.25	75	18.75	17.70	3.54	39.06	7.82	717
7.5	75	17.5	19.96	4.00	44.76	8.98	725
8.75	75	16.25	12.40	2.48	40.46	8.10	703
10	75	15	25.30	5.00	50.14	10.06	701
11.25	75	13.75	06.38	1.29	16.64	3.32	693
12.5	75	12.5	07.10	1.42	18.88	3.70	692

Carbon replaced for Sand:

Table 2: Load and Stress calculations for different % of Carbon Replaced for Sand

%of C	%of Sand	%of Cement	Load(kN)-7days	Stress (MPa)-7days	Load(kN)-28 days	Stress (MPa)-28 days	Wt. of blocks (gm)
15	60	25	16.30	3.26	53.62	10.74	684
18.7	56.2	25	32.10	6.00	70.04	14.04	663
22.5	52.5	25	45.58	9.14	77.86	15.62	644
26.2	48.7	25	54.12	10.84	80.22	16.08	642
30	45	25	57.96	11.62	99.18	19.88	640

Leachability Test

Leachability test for the mortar cube samples were carried out. The broken pieces of samples were collected in a cover for 10 grams and tested for leachability and it was observed that the chromium doesn't leach out and not detected.

Figure 3: Samples for Leachability

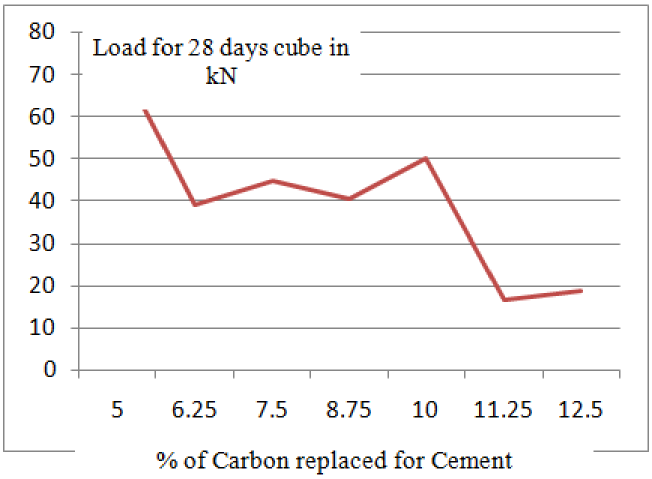

Figure 4: Graph depicting about the strength of 28 Cubes (Cement partially replaced by Carbon ash)

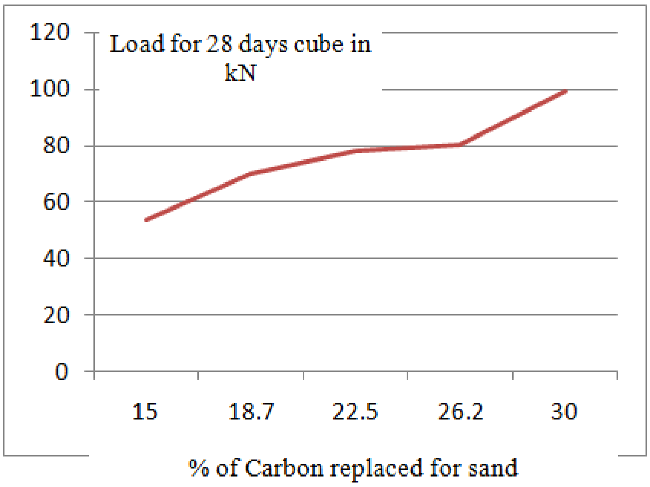

Figure 5: Graph depicting about the strength of 28 Cubes (Sand partially replaced by Carbon ash)

2. Conclusion

Based on the strength of the mortar cubes and the leachability results it can be concluded that the solid waste can be successfully disposed of and the useful products can also be derived from the solid waste before disposing.

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