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Physicochemical characterization of CETP sludge

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In this current study, tannery waste have been characterized and chemically analysed for several applications. The present study might propose the usage of tannery waste in polymerization and immobilizing the chromium present in the sludge. The characterization studies of CETP sludge reveals the composition of heavy metal, sulphate, chlorides, pH of the sludge, total chromium present in the sludge, leachability to hexavalent chromium, physical properties etc. Instrumental method of analysis like FTIR, XRD, XRF, AAS, UV-spectrophotometer analysis have been carried out to analyse the characteristic properties of the sludge. FTIR anlaysis peaks confirms the presence of calcium in the form of sulphate and carbonate. SEM-EDX analysis were carried out to study the morphology and structural composition of the sludge. The results of the study revealed that the concentrations of metal ions in the sludge were low, but the concentrations of chloride and sulphate ions were found to be high. The concentration of the chromium in the sludge is found to be high than the admissible limit with no further oxidation to hexavelent chromium. The amount of calcium content in the CETP sludge is found to be high and it can add a major advantage in easy binding of CETP sludge with inorganic polymers.

Keywords: CETP sludge, XRF, AAS, UV-spectrophotometer, FTIR, XRD, SEM-EDX, leachability test.

Introduction

With the increasing urbanization the quantity of waste sludge has been increasing day by day and due to the lack of landfill sites, the disposal and reuse the sludge is becoming an important and immediate concern. The annual sludge production in India is increasing day by day due to increasing economic growth.

Tanning process consists of the transformation of animal skin into leather. The skin of the animals is subjected to different processes to eliminate meat, fat and hair. Different chemicals like sodium hydroxide, sodium hypochlorite, lime, chlorides, sulphuric acid, formic acid, ammonium salts, enzymes, and other compounds were added during the processing of the hides. The hides thus obtained after the treatment were further treated with chromium sulphate, mineral salts and colors to obtain well finished leather. Only about 20% of the chemicals used in the tanning process is absorbed or utilized during the leather processing and the rest is released as wastes[1–3]. Tanning industries generates a large quantities of solid wastes like raw skin trimmings, hair fleshing, splitting waste, pickle trimmings, chrome shavings, crust trimmings, finished leather trimmings and sludge during the leather manufacturing process. The chrome salts, dyestuff residues, fat liquoring agents, syntans and other organic matter are also considered to be the major pollutants of post tanning process (UNEP 1991). Sludges from leather processing contains inorganic matter and organic residues. Direct usage of tannery sludge has limited its application in agricultural field[4], considering the organic and inorganic pollutant mainly of chromium present in it. Tannery sludges are generally disposed off by land filling, ocean dumping and incineration or solidification[5,6], considering the environmental impacts and economic costs[7]. However, this method might not be the suitable method considering the problems associated with land applications of sludge due to the odors and potential pathogens in sludge. The major reason includes the non availability of suitable site and also on the quality of both soil and sludge with respect to toxic organic chemicals, salts and heavy metals[6,8]. The another important problem that must be taken for consideration is the high concentrations of heavy metals in sludge. As the heavy metals are adsorbed by soil they get accumulated in soil causing the major pollutant of soil[9,10]. This may create an adverse effect including metal toxicity to plant, microbial population of soil and eutrophication. Therefore, minimizing the amount of tannery waste or by recycling into useful products has become a major concern.

The priority for waste sludge management and treatment studies have been carried out investigating the direct usage of sludge both in construction, agriculture and ceramic industry. It has been reported, that tannery sludge mixed with clay is used in the production of bricks, tannery sludge is used for construction purpose as the partial replacement of cement in concrete, recovery of Cr_2O_3 from sludge, recovery of chromium[11,12] extracted chromium III from tannery sludge by mineral acids, using detoxified sludge on agricultural lands by recycling plant nutrients and organic matter of soil for crop production[13]. Therefore, from the view point of solid waste management practice, the chemical composition and characterization studies of the solid wastes generated from tanneries can still propose an appropriate tannery waste sludge management options.

Materials and methods:

For safe disposal of the tannery sludge without affecting the natural environment attempts are being made to utilize the sludge rather than dumping it to somewhere else. The tannery sludge is utilized in geotechnical applications such as partial substitution in concrete, as a sub-base material in ceramic industry, etc. in bulk only. For this, an in-depth study of the physical and chemical properties and leaching behavior are required to get the thorough knowledge of the sludge.

Chemicals: Analytical grade reagents are used for this analysis of the CEPT tannery sludge studies.

Collection of tannery sludge sample: The tannery sludge waste for this analysis was collected from tannery effluent treatment plant, Ranipet, India. The samples were air dried in an oven at 100°C for nearly 2 h to remove the moisture. The dried samples were finely powered and they are sieved using 150 μm sieve size. The sieved samples were stored in air tight bags and further used for the characterization studies of the sample.

Characteristic properties of sludge: Characteristic features of the tannery sludge like moisture content, volatile matter, total dissolved solids, density, specific gravity, water absorption test etc. were found using standard procedure and the results are given in the Table I.

Instrumental analysis: The heavy metal composition in the tannery sludge was found, using XRF analysis. The surface morphology and chemical characterization of tannery sludge were studied using SEM-EDX with high resolution. The amount of chloride and sulphate present in the sample was analyzed using international standard method APHA 4500 IS 3025 part 32 using Argentometric method and IS 3025 part 24 turbidity method using a spectrophotometer at 420 nm. Leachability test was conducted to find the hexavalent chromium present in the sludge by spectrophotometry method using the sludge sample to react with diphenyl semicarbazide in acidic medium. The red-violet colour exhibits the presence of hexavalent chromium. The total chromium present in the sludge was analysed using AAS by acid digestion method.

Total chromium present in the sample mg Cr/l =

$$\frac{\mu\text{g of Cr (in 100 ml of the final solution)}}{V}$$

where V = volume in ml, of the sample used.

FTIR spectra is used in the study of absorption features, which can be related qualitatively of the given sludge. Absorption features result in the detection of vibrational modes, i.e. lattice vibrations and or molecular group vibrational modes. The FTIR were recorded from pellets of sludge containing 2 mg of the freeze-dried humic acids with 250 mg of dry KBr using Perkin-Elmer FTIR spectrophotometer covering a wavenumber range of 400–4000 cm^{-1}. There are several methods which may be used to determine the phase and phase composition of the sludge. X-Ray powder diffraction method is highly suitable for both qualitative and quantitative phase analyses of sludge.

Results and discussion

Characteristic features: Physical properties help in classifying the sludge for engineering properties. The chemical properties of the sludge mainly influence the environmental impacts that may arise out of their usage and disposal nature of the sludge. The adverse impacts include contamination of surface and subsurface water with toxic heavy metals present in the sludge, loss of soil fertility etc. Some of the properties discussed below.

Density: The density of the sludge is an important parameter as it controls the strength, compressibility and permeability. Density of the sludge seems to be 240.9 kg/m^3 and it improves the engineering properties.

Table I. Characterization of the CETP tannery sludge

Parameter	Values
Color	Brownish
Moisture (%)	8.8
Total solids (%)	91.2
Volatile solids (%)	28.62
Water absorption	0.15–0.20
pH	Above 7

Specific gravity: The specific gravity of tannery sludge is around 2.56. Because of the low value specific gravity of tannery sludge compared to soils, it tend to result in low dry densities. The reduction in unit weight is advantage so that it can be used as a backfill material.

Particle size: Tannery sludges are predominantly fine sized with coarse particles. Finely grind sludge particles passed through the 150 μm sieve size.

pH: The sludge having higher calcium content and alkaline oxides shows higher pH values. The sludge is mostly alkaline, so it can be used in reinforced cement concrete which will be corrosion resistant.

FT-IR analysis:

FT-IR spectrum is able to predict the main chemical constituents in the tannery sludge. The FT-IR spectrum of tannery sludge at 3747 cm^{-1}, is related to O-H group stretching vibration. Absorption band at 3630 cm^{-1} may be assigned to calcium hydroxide group. A broad peak with less intensity at 3296 cm^{-1} may be assigned to chromate group. A very weak absorption band near 2360 m^{-1} is related to C=O stretching band. The peak at 1676 cm^{-1} may be correlated to Si-O-H bending mode of vibration. Absorption band at 3630 cm^{-1} may be assigned to calcium hydroxide group. A broad peak with less intensity at 3296 cm^{-1} may be assigned to chromate group. A very weak absorption band near 2360 m^{-1} is related to C=O stretching band. The peak at 1676 cm^{-1} may be correlated to Si-O-H bending mode of vibration. The intense band at 1458 cm^{-1} is the characteristic peak of calcium (ν_3) vibrational mode. The very weak and broad at 1107 cm^{-1} and 1077 cm^{-1} may be assigned to sulphates and chromium sulphates. The very sharp peak at 873 cm^{-1} is assigned to Al-O stretching vibration. A weak and less intense absorption band is found at 606 m^{-1} may be assigned to C=S stretching vibration of sulphides and (ν_4) vibrational mode of sulphates. The band centered around 750 cm^{-1} shows the alkaline (Na, K) nature in sample. A less intense peak around 550 cm^{-1} and 720 cm^{-1} is assigned to the Cr^{3+} present in the tannery sludge. As the Cr^{3+} content in the sludge is very less, the peak intensity is found to be very less.

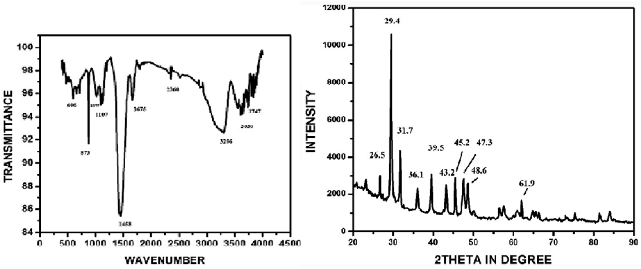

Fig. 1. FTIR and XRD analysis of the tannery waste.

XRD analysis:

From the FTIR analysis calcium is found to be high composition with respect to other elements present. As the sludge samples contains calcium in sulphate form calcium sulphate can have more than one crystal phases. The high intense peak with 2θ = 29.4 value predicts the monoclinic phase of calcium sulphate hemihydrate. Sharp peaks denotes the crystalline nature of the sludge sample.

XRF analysis: The average concentration of metal ions, in the sludge is confirmed by the XRF analysis (Table 2).

Table 2

Heavy metal	Mo	Nb	Zr	Fe	Cr	Ti
% Comp	0.063	0.063	0.22	0.544	3.772	0.20

Sulphate and chloride:

The high concentration of sulphate and chloride concentrations in the sludge reveal that due to the use of significant amount of sodium sulphide salts during the liming and unhairing stages of leather processing. The high concentrations of sulphate in the tannery sludge may also result from many auxiliary chemicals used. During soaking, pickling and chrome tanning elevated level of chlorides are used. The chloride values of the sludge were found to be higher than the ISW-BDS-ECR (1997) standard (600 mg/L). The high values of chloride in the sludge might be due to the chloride salts used in hide and skin preservation, and also in the pickling process. The present study indicates that the amount of sulphate is found to be 17500 ppm and chlorides is 38174 ppm respectively. Both the values are very high compared to the standard limits EN 12457-2, indicating chloride pollution.

Leahability test: The leachability in solution of the sludge was analysed for hexavalent chromium. The observed values were found to be below the detection limit as per the comparision with the standard values.

Atomic absorption spectroscopy: The total Cr present in the sludge is determined by AAS. The sludge is digested using nitric acid and the sample is directly aspirated to the atomizer with air acetylene flame using hollow-cathode lamp at wavelength 357.9 nm. From the aspirated sample solution the absorbance is measured which gives the total Cr present in the sample. The total Cr content in the sludge was calculated to be 5787 ppm.

SEM-EDX analysis:

The compositions of the sludge at the mesoscopic scale were attained using SEM-EDX. The surface texture appeared to be smooth, granular, dense to highly porous morphology is seen and the surfaces had sometimes coating of chromium. This analysis of the sludge indicates the presence of total chromium. EDX analysis shows the presence of trivalent chromium (Cr^{3+}) with corresponding peak at 5.5 keV. There was no peak for hexavalent chromium at 5.9 keV confirming that (Cr^{3+}) is not further oxidized to (Cr^{6+}). The amount of calcium is found to be high compared to any other metal ion which gives an intense peak in the EDX spectrum.

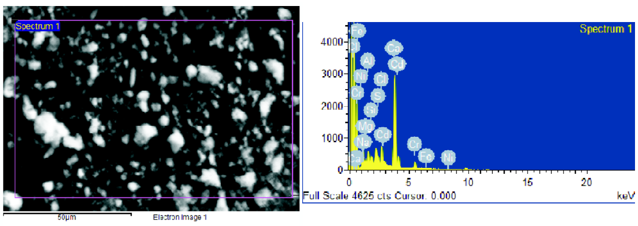

Fig. 2

Conclusion

Based upon data recorded, it can be concluded that the combined physical and chemical properties of the CETP tannery sludge was found to be optimum with less content of heavy metals. The pH of the sludge seems to be higher and found to posses more alkaline oxide which favors the reinforcement with the cementitious material. FTIR analysis of the sludge predicts the high content of calcium in the form of sulphates and carbonates. A very less intense peak was observed for the Si=O bond. Likewise in the XRD analysis the 2θ values shows a very high intense peak for calcium sulphate hemi hydrate and the sharp band are observed and the sludge is found to be crystalline phase. The amount of chloride and sulphate content in the sludge is detected to be in higher level than the toxic limit, which might cause chloride pollution. The SEM images of the tannery sludge depicted the granular, smooth and chromium mixed structure. The EDX results shows the high amount of calcium content in the sludge along with chromium. The Cr^{6+} in the sludge is found to be below the detection limit and proves that there is no further oxidation occurred to Cr^{3+}. This CETP sludge with appropriate proportion of elemental composition and physical nature can be proportioned with cementitious material. The chemical, physical and mineralogical properties of CETP tannery sludge may have appreciable effects on performance of the sludge in polymerization.

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