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ENLISTING EFFLUENT SLUDGES FROM PHARMACEUTICAL INDUSTRIES AND WASTE VALORIZATION AT HAZARDOUS WASTE MANAGEMENT FACILITY

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Abstract
Pharmaceutical formulation and its content are basically mass-produced in several batch processes resulting in the presence of different products in the effluents which are resultant of various operations. These ample quantities of water are used for process like washing of solid cake, extraction, washing of kit etc. Recovery, reuse and recycling of sludge from pharma industrial effluent treatment plant (ETP) sludge, are commonly practiced in India and other industrialized countries largely by virtue of low-cap investment. Characterization of the sludge generated from effluent treatment plants of the different industries reuse / recovery is important in deviating the path of ETP sludge depends on either reuse / recovery. Interests are raised to get the best possible way in discarding of these wastes to make sure ecological contemplations. Attention should be given on utilizing sludge as a resource that can be recycled or reuse, which ultimately serves purpose of waste valorisation. In this study the effluent sludge from various industrial sources are broadly categorized and quantified based on its source and physico-chemical characteristics and finger print analysis etc. which will ultimately plan to reuse or dispose in hazardous waste management facility.

Keywords:Pharma industries, Hazardous wastes, Inventory, ETP sludges

Introduction
India is one of the major countries producing pharmaceutical products which hold fifth place in global pharmaceutical markets. In terms of volume the Indian Pharma industry stands 3rd in position and 14th in rapports of value. It is projected that the industry is worth about 4.5 Billion USD and escalating at an annual rate of 8 to 9 % [1-3]. The pharmaceutical development in the country is accompanied by various operations. It includes pharmaceutical drugs manufacturing, production of excipients, production and evaluation of raw materials and finished dosage forms [4]. These operations produce various pharmaceutical effluents which generates sludge. Managing these pharmaceutical wastes generated all over country becomes a major challenge for Indian pharmaceutical industry. The Bulk drug manufacturing sector has experienced the escalating consumption and drug's impervious nature evident of their presence in Pharmacy, clinics, hospitals and in municipal waste water and surface water streams. Moreover, the recalcitrant chemicals of such drugs escape from the water treatment plants and enter the environment through effluent or in the form of Sludge [5,6].
Sludge is generated from the treatment of wastewater in on-site (e.g. septic tank) and off-site (e.g. activated sludge) systems. The solids from wastewater treatment may contain concentrated grades of contaminants that were initially contained in the wastewater. The sludge that comes out of waste water treatment plant has water content between 97 % and 99.5 %. Here, we have broadly categorized the sludge based on their source as Primary sludge, Secondary sludge, Biological sludge, mixed organics sludge and ETP sludge.
Primary sludge consists of suspended solids and organics acquired from the primary treatment process through gravitational sedimentation, normally by a primary clarifier and is delivered through the mechanical wastewater treatment process. It happens after the screen and the grit chamber collect complex wastewater contaminants. The secondary sludge is generated as by-product of the biological treatment [7] and consists predominantly of excess biomass produced during the biological process

[8]. Biological sludge has several fractions of water with sludge solids, which are mostly related to microorganisms [9]. In general, the ETP sludge comes out from industrial effluent treatment plant in the form of semisolid or solid form [10]. Mixed organic and putrescible sludge contains multiple industrial effluent wastes[11].

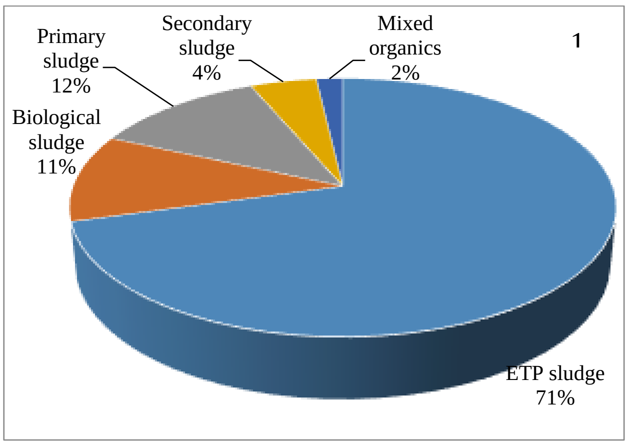
Many research groups and their scientific works were focused on applying sludge from different industrial sources as an amendment with vermin composting, agriculture residues, cattle dung and saw dusts [12-14].Suthar, [15]suggested that if the industrial sludge can be mixed with a bulky material in a suitable ratio and may result in a potential vermi-compost. Using suitable composting technology, the sludge can be treated properly by removing putrescible substances and other toxic compounds. Other experiments are carried out to involve waste products with conceivable practical applications, where in rubber formulations with marble sludge are used as filler that can supplant calcium carbonate as a tyre compound making it a value added product [16]. This paper focuses on the receiving quantity of industrial sludge in a waste management facility, disposal criteria and its suitability to be used as an alternative fuel.

Methodology

The present study investigates the inventory of the hazardous wastes received at the waste management facility from different industries within the range of 5 to 250km [17]. The inventory data displayed the quality received, available treatment process for each hazardous waste and its further disposal. Inventory analysis was done based on the type of waste received, nature, quantity (MT) and source of waste generation. As and when the waste was received at the facility in loaded trucks, a representative sample was collected by using coning and quartering method for reducing sample size, was homogenized and sent for finger print analysis [18]. The finger print analysis included parameters with their methods namely pH(SW-846-9045C), bulk density (ASTM-D5057-90), Loss of ignition (LOI)(APHA 2540 E), Loss of drying (LOD)(APHA 2540 B), Calorific value (CV)(IS 1350:1970), Sulphur (%) (SW-846) and Chloride (%)(SW-846) and finally compared with CPCB acceptance co-processing criteria to reuse in cement kilns.

Result and Discussion

As explained through figure 1(a), it was observed that the higher frequency of wastes that comes to the facility are from different pharmaceutical industries in the region, constitutes 71% of ETP sludge. The frequency of other wastes received at the facility are in descending manner as per inventory percentage including primary sludge(12%), biological sludge(11%), secondary sludge(4%), and mixed organics(2%). However, the quantity (MT) of waste received at the facility in the form of sludge from different industries is presented in figure 1(b). Such types of sludge are highly toxic and hazardous in nature. The quantity of sludge coming to the facility are



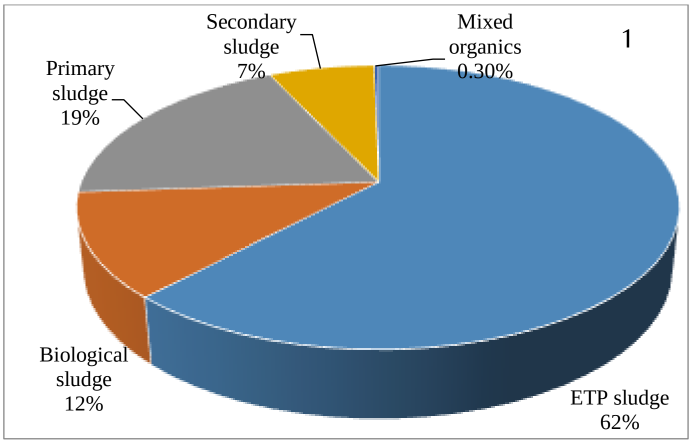


Figure 1: (a) Frequency of waste received (inventory) in the facility and (b) Quantity HW received to the facility

as follows ETP sludge529,752 MT (62%) of total HW received at facility, primary sludge 163640MT (19%), biological sludge 101355 MT (12%), secondary sludge 57160MT (7%)and Mixed organics 2545MT(0.30%).As witnessed, the quantity of ETP sludge waste is on higher percentage. This may be due to presence of more number of pharma and other industries operating there captive effluent treatment plant in the surrounding area of the waste management facility.

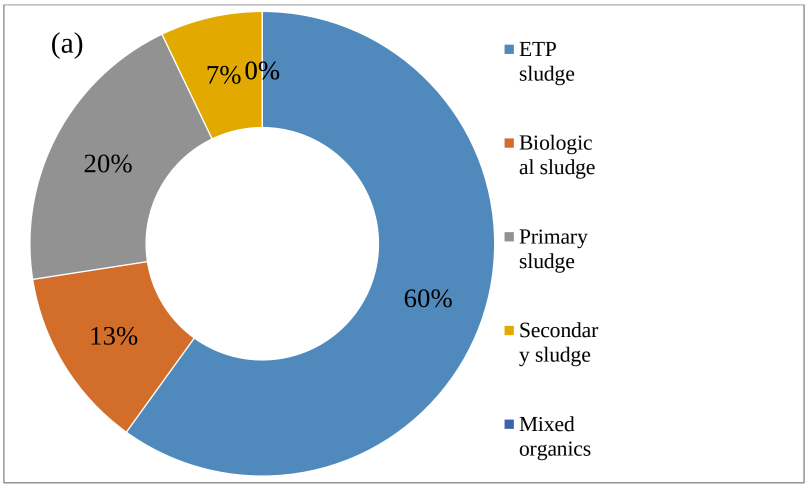
The Figure 2 indicates percentage of HW sent to each type of treatment facility like landfill after treatment (LAT), direct landfill (DL), incineration (Inc) and alternate fuel (AF). In Figure 2 (a) shows the percentage of hazardous waste disposed at landfill after treatment which encompasses ETP sludge (60%), primary sludge (20%), biological sludge (13%), secondary sludge (7%) and mixed organic sludge (0%).The figure 2 (b) indicates that the ETP sludge having a quantity of 10886 MT hazardous waste going into the direct landfill. The quantity of around 36690 (MT) ETP sludge is utilizing in AFR as shown in figure 2 (c) and only mixed organics with a value of 2545MT waste is sent to incineration as given in figure 2 (d).

In the study the considered amount of total waste coming to the facility is 854452 (MT), out of which the maximum share holds by ETP sludge with a worth of around 529752 (MT) (62%). Now this ETP sludge is further segregated to be sent to various treatment processes based on its initial characterization. As per the study around 91 % of ETP sludge is disposed to landfill after treatment, while 6.9% of the ETP sludge is disposed to AFR and only 2.1 % of the ETP sludge is going direct landfill.

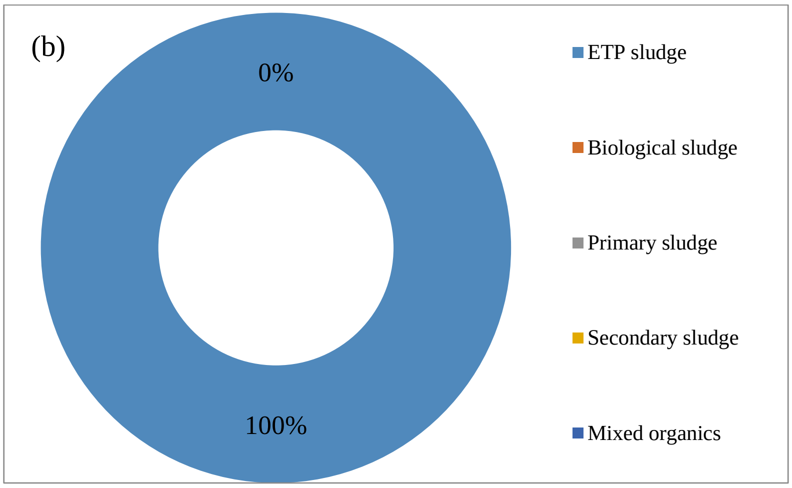
Table 1: Standards for pharma effluents and acceptance criteria for Industrial wastes

S.No	Industry	Parameter	Standard
		Effluent standards	Limiting concentration in mg/l, except for pH
1	Pharmaceuticals (Manufacturing and Formulation Industry)	Compulsory Parameters	
		pH	6.0-8.5
		Oil & grease	10
		BOD (3 days 27 °C)	100
		Total suspended solids	100
2	Specification of HW for use of energy recovery (Guidelines on Co-processing in Cement/Power/Steel Industry, CPCB (2010)	Calorific Value As received basis	2,500kCal/kg
		pH	4-12
		Chloride	< 1.5 %
		Sulphur	< 1.5 %

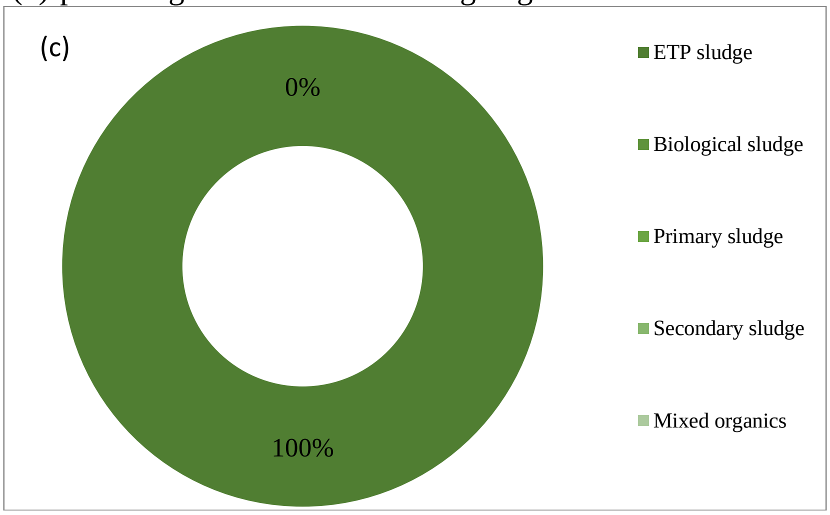
Source:[19,20]



(a) percentage of hazardous waste disposing at landfill after treatment



(b) percentage of hazardous waste going into direct landfill



(c) percentage of hazardous waste accepted for AFR

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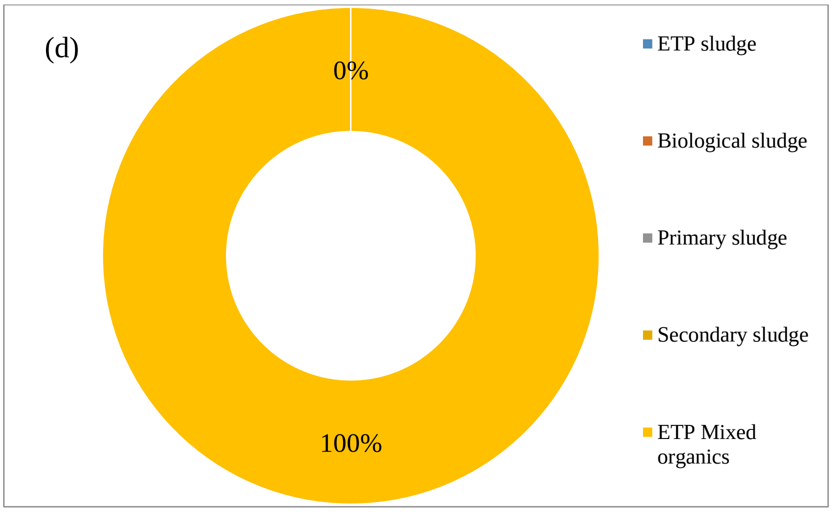

(d) percentage of hazardous waste under incineration

Figure 2: Percentage of HW with reference to each type of treatment methods

Disposing of waste through AFR is a preferred & superior alternative as it is an eco- friendly way of waste disposal when compared to others like incineration & / or landfill. This method maybe the response for disposing the waste and also help in reducing the burden over landfills. It also profits in using energy and material value of wastes in turn complete consumption of wastes. This results in cost-effective and also eco-friendly solution to HW disposal which finally leads to sustainable management.

[21] Studied the utilization of sewage sludge as a secondary fuel (pet coke) for the cement kiln. Several research groups studied energy efficiency of different types of wastes that can be utilized as alternative fuels in cement industries by replacing traditional fuels. Vidya, [22] characterized the electroplating sludge generated from automotive industry and reported its pH as 9.6, LOI-3.8% and Organic content-6.7%. Shiva Prasad, [23] worked on Solar Evaporation Pond (SEP) sludge, which comes under schedule-III (Part B) that generated from agro based industry, which mainly contains distillation bottom residues. It was characterized to have a CV-7238 cal/g and sulphur-0.8 %.

Other studies revealed the alternate fuel with a calorific value of more than 7100 kJ/kg which is generally used in 80% of cement industry furnaces [24]. Punmathari, [25] reported that, the sludge generated from an iron forging industry had a pH of 8.85, suggested that such sludge had a potential to be used as a raw material in cement industries. The bottom tank petroleum sludge contains sulphur (wt. %) ranges from 0.51 to 1.17.If the sulphur content is high in selected waste, it leads to blockage of cement kilns, unbalances the kiln/pre heater system and increases the probability of formation of kiln lumps and also affects the quality of cement.

Table 2: Fingerprint analysis of ETP Sludge in the hazardous waste management facility

Parameters	Methods	Results (ranges)
pH at 25.2 °C	SW-846-9045C	8.14-8.27
Calorific Value cal/gm	IS 1350:1970	2640-3050
Chlorides as Cl %-	SW-846	0.4-0.6
Total Sulphur as S %	SW-846	0.10-0.12
LOD % at 105 °C	APHA 2540 B	67.3-72.5
LOI % 550 °C	APHA 2540 E	62.8-76.5
Bulk density gm/cc	ASTM-D5057-90	1.1-1.3

Rahman, [26] cites an example of Lafarge Cement that has adopted to use hazardous waste as an alternate fuel, where they have set the parameters for CV value 14 MJ/kg, Chlorine <0.2% and Sulphur content is less than2.5% have been fixed. In case the chloride content is high in the selected waste,

there are chances of formation of sticky lumps in the pre heater, which leads to blockage in the system. Countries like Germany and Austria fixed the maximum value for chloride content as 1.5% in AFR[27,29].
In the present study, the samples that were examined for finger print analysis were differentiating physical and chemical analysis[28]. In physical analysis parameters such as CV, LOI, LOD and Bulk density were studied while in chemical analysis parameters such as pH, Sulphur and Chloride were considered. The findings acquired were summarized in Table 2 and also contrasted in conclusion with CPCB acceptance criteria. Industrial solid waste (ISW) contains huge amounts of sludge having combustible organics. The highest fraction of waste for energy recovery was found in organic sludge from wastewater treatment plant as well as in polymeric waste. The advantage of combination of organic sludge and saw dust to increase CV value for use as alternative fuel is a cost-effective method and has environmental benefits. The application of these industrial wastes in co-processing may reduce the burden on landfill and make value addition as alternative fuel for the cement industry. It can be concluded that, the ETP sludge received at the facility fits into the CPCB criteria as an alternative fuel with suitable blending components which further can be co processed in cement industry or any other heat intensive industries.

Conclusion
As per CPCB acceptance criteria and standards for pharma effluents as mentioned in Table 1, the pH of hazardous waste sample ranges between 4-12, whereas in the present study it ranges from 8.14 to 8.27, the calorific value mentioned by CPCB should be >2500 kcal/kg, while in our study it ranges between 2640 to 3050kCal/kg. Similarly, in case of both sulphur and chloride percentage, the CPCB suggests value < 1.5% and in the present study it is ranging between 0.4 to 0.6 % for chloride and 0.10 to 0.12 % for sulphur respectively. These obtained values were also compared with other published research literatures. All these analysed values indicate the possibility in use of these pharma effluents for energy recovery through AFR. Advantage can be taken to reuse these wastes in various alternatives methods especially in cement kilns.

The above study also suggests promoting the utilisation of wastes to convert the ETP sludge going for landfill after treatment to reuse the waste through AFR with suitable binding material to increase the CV and also to make the homogenized composite sample to fit the acceptance criteria of CPCB, 2010. Heat intensive industries particularly cement industries are playing a vital role in the utilization of HWs for energy requirements, thus reducing the load on both the fuel due to waste utilization, which would otherwise end up in landfills.

Conflict of interest
The authors state no conflict of interest for this work.

Declaration
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