Original Article

Sludge Characterization of a Petrochemical Wastewater Treatment Plant, Iran

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Abstract

Background and purpose: Disposal of sludge from industrial wastewater treatment plants (IWWTPs) is a serious issue because it can affect human and animals' health, and also environmental quality. In this study, sludge from a petrochemical wastewater treatment plant was analyzed regarding its physicochemical characteristics and disposal options.

Materials and Methods: Grab sampling was used to collect 12 sludge samples biweekly (May-October 2012). One sample T-test was applied to analyze the obtained data. Canadian Soil Quality Guidelines (CSQG) and New Jersey Department of Environmental Protection Soil Cleanup Criteria (NJDEPSCC) were used to discuss the disposal fate of the generated sludge.

Results: The results showed that the order of the studied metals in the sludge was as: Fe>Al>Zn>Cr>Pb>Ni>Cd>Co>Cu>Mn>As>Hg. It was found that generated sludge compared with CSQG is not suitable for residential/parkland, agricultural, commercial and industrial applications. But compared with NJDEPSCC, studied sludge was suitable for residential and non-residential applications.

Conclusion: According to NJDEPSCC the studied sludge has potential to be used for residential and non-residential purposes. [Ahmadi M. Bayati N. Babaei A. *Teymouri P. **Sludge characterization of a petrochemical wastewater treatment plant, Iran.** IJHS 2013; 1(2):10- 18] http://jhs.mazums.ac.ir

Key words: Petrochemical wastewater treatment plant sludge, sludge characterization, sludge disposal, sludge reuse

1. *Introduction*

Industrial activities lead to the generation of large amounts of sludge the disposal of which is a serious environmental issue because it contains harmful level of pollutants including heavy metals(1). Heavy metals disposal is a big concern due to their being non-biodegradable and their tendency to bioaccumulation. Therefore, they can affect human and animals' health, and also environmental quality(2). Interest in such issues is constantly increasing because they have gradually been broadened with concepts such as sustainable development which implies ecological, economic and social responsibilities. Therefore ,handling sludge is one of the most important challenges in wastewater management (3). There are several methods to handle sludge, each with advantages and limitations such as land use (4,5), manufacturing construction materials (6,7) wastewater treatment reagents (8) sludge dewatering (9) and landfills. To select the most suitable method, it is important to know sludge properties. This study aims to determine some physicochemical characteristics of sludge from a petrochemical wastewater treatment plant (IWWTP) in southwestern Iran. A comparison of the heavy metal concentrations with Canadian Soil Quality Guidelines (CSQG) for the protection of environmental and human health (10) and New Jersey Department of Environmental Protection Soil Cleanup Criteria (NJDEPSCC) (11) was conducted. Finally, some sludge disposal methods have been discussed.

2. *Materials and Methods*

2.1. Study site

The studied Petrochemical Company located in Khuzestan, Iran. Toluene di-isocyanate and methylene diphenyl di-isocyanate are the main products, and HCl and sodium hypochlorite are the byproduct of this company. Petrochemical wastewater from the studied site has been collected and after pretreatment (Fig. 1), has been sent to the final treatment, along with the effluents of the other industrial companies in the area. The sludge from sedimentation tank has been collected and dumped somewhere outside the site.

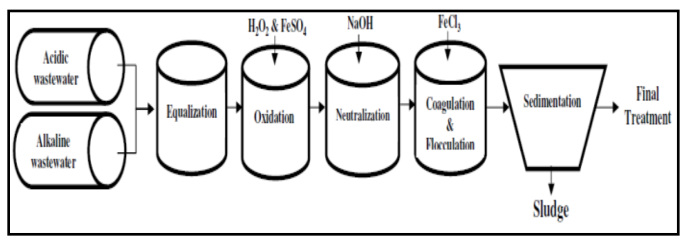

Fig.1. The studied site pretreatment process of petrochemical wastewater

1.1. Sampling

Grab sampling was used to collect 12 sludge samples biweekly (May-October 2012) from sedimentation tank of the pretreatment process. Samples transportation and storage were done according to Standard Methods for the Examination of Water and Wastewater (12).

1.1. Analytical Methods & Instruments

Total suspended solids (TSS), total dissolved solids (TDS) (dried at 103–105 °C), pH (781 pH meter, Metrohm, Switzerland), electrical conductivity (712 Conductometer, Metrohm, Switzerland), turbidity (Nephelometric method, Turb 355IR, WTW, USA) total hardness (TH) (EDTA titration) were determined. COD was also measured using a thermo reactor and a spectrophotometer (DRB200, Hach, USA) and Metal content including Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn (ICP-OES OPTIMA 4000 Series, Perkin Elmer, USA), As (4100ZL Graphite AAS, Perkin Elmer, USA), and Hg (Flow Injection Mercury System (FIMS) 400, PERKIN ELMER, USA) were also determined in the sludge samples. Metals content except for As and Hg were determined using ASTM (D5198-92) and EPA (3050B and 6010 C) standards (13), and the other parameters were measured according to the Standard Methods for the Examination of Water and Wastewater (12). All chemicals used in this study were of analytical grade and were purchased from Merck Chemical Company (Germany) except for HgSO4, which was of ACROS Company production (USA).

1.2. Sample Preparation & Digestion for Heavy Metal Analysis

1 liter of each sample was filtered. 2.5 g of sludge (on the filter) was incinerated in a furnace at 500˚C. Then, the resulted ash was digested with a mixture of concentrated HCl and concentrated HNO_3 on a hot plate. The suspension was cooled and filtered through an ash free filter paper. The filtrate was diluted to a volume of 100 ml with deionized water.

1.3. Statistical Analysis

In order to analyze data, at first Explorer command, stem and leaf graph were used to exclude outlier data. Then Kolmogorov-Smirnov Z analysis was performed to assess the normality of the data. One sample t-test was applied to compare metals concentration with the standard values. Since there are no standards, regulations, or legal restrictions available for soil clean-up levels in Iran, CSQG and NJDEPSCC were used for this purpose.

3. Results

3.1. Sludge characteristics

Table1 shows the result of physicochemical characteristics of the studied sludge. As this table shows, the number of samples for Co and Cr is 11, which is due to omitting the outlier data (Table 1). Metals behavior in soil and their uptake by organisms can be strongly affected by pH (14). The pH of the studied sludge was slightly alkaline. Considering using NaOH for neutralizing the oxidation chamber effluent to pH 7.5-8.5, the slightly alkaline nature of sludge is justifiable. The EC amount for the studied sludge was higher than some other sludge samples reported by different researchers (4, 15, 16). But, Bahremand et al. (2003) obtained approximately similar EC for their studied sludge (17). Higher EC means higher salinity, which makes the studied sludge unsuitable for land application. Table 1 also shows a high concentration of COD, TSS and TDS in studied sludge.

Table 1. Physicochemical characteristics of the slurry sludge

Parameter	Unit	Samples no.	Mean±SD
pH	-	12	8.25±0.36
EC	ms/cm	12	13.4±6.78
Turbidity	NTU	12	6610±1846.69
T.H.	mg/l	12	1142.58±190.76
COD	mg/l	12	17950.50±3853.17
TDS	mg/l	12	8047.50±4046.97
TSS	mg/l	12	13915.83±4189.35
Al	mg/kg dry solid	12	533.83±144.08
As	mg/kg dry solid	12	0.548±0.234
Cd	mg/kg dry solid	12	18.33±9.04
Co	mg/kg dry solid	11	10.74±3.08
Cr	mg/kg dry solid	11	115.09±24.57
Cu	mg/kg dry solid	12	3.53±1.18
Fe	mg/kg dry solid	12	14391.58±5490.04
Hg	mg/kg dry solid	12	0.405±0.246
Mn	mg/kg dry solid	12	2.24±0.75
Ni	mg/kg dry solid	12	30.65±9.11
Pb	mg/kg dry solid	12	56.20±21.44
Zn	mg/kg dry solid	12	497.36±159.57

Table 1 also represents that the order of the studied metals in the sludge was as follows:

Fe>Al>Zn>Cr>Pb>Ni>Cd>Co>Cu>Mn>As>Hg

Fe had the highest concentration amongst the studied metals, which is due to using $FeSO_4$ and $FeCl_3$ as the co-oxidator and coagulant in the present treatment plant, respectively. Among the heavy metals, Zn and then Cr were the ones with the highest concentrations. Comparing our results with those of Wang et al. (2005)(18) revealed that Cd, Cr and Pb in our studied sludge were higher, and Ni, Zn and Cu were lower than these heavy metals in their studied sludge samples. Differences in the nature of sludge samples can be the reason for such dissimilarity in the results.

3.1. IWWTP Sludge Disposal

Sludge quality requirements depend on the sludge management methods ,that is, the disposal and reuse practices (19). In our study, a comparison of the studied heavy metals with the standards determined by CSQG and NJDEPSCC showed that according to CSQG, Cr concentration in the studied sludge was significantly beyond the acceptable values for residential/ parkland, agricultural, commercial and industrial applications (see Table 2). Table 2 also shows that Zn concentration in the studied petrochemical sludge is significantly higher than CSQG standards for residential/ parkland and agricultural applications which restricts its use for such applications.

Table 2. Statistical results of comparing the studied heavy metals with the standards determined by CSQG and NJDEPSCC

Heavy metal	CSQG								NJDEPSCC			
									soil direct exposure			
	Residential/ parkland		Agricultural		Commercial		Industrial		Residential		Non Residential	
	Standard (mg kg^{-1})	PV*	Standard (mg kg^{-1})	PV*	Standard (mg kg^{-1})	PV*	Standard (mg kg^{-1})	PV*	Standard (mg kg^{-1})	PV*	Standard (mg kg^{-1})	PV*
As	12	<0.0001↓	12	<0.0001↓	12	<0.0001↓	12	<0.0001↓	20	<0.0001↓	20	<0.0001↓
Cd	10	0.009↓	1.4	<0.0001↓	22	0.188↓	22	0.188↓	39	<0.0001↓	39	<0.0001↓
Cr	64	<0.0001↑	64	<0.0001↑	87	0.004↑	87	0.004↑	-	-	-	-
Cu	63	<0.0001↓	63	<0.0001↓	91	<0.0001↓	91	<0.0001↓	600	<0.0001↓	600	<0.0001↓
Hg	6.6	<0.0001↓	6.6	<0.0001↓	24	<0.0001↓	50	<0.0001↓	14	<0.0001↓	270	<0.0001↓
Ni	50	<0.0001↓	50	<0.0001↓	50	<0.0001↓	50	<0.0001↓	250	<0.0001↓	2400	<0.0001↓
Pb	140	<0.0001↓	70	0.05↓	260	<0.0001↓	600	<0.0001↓	400	<0.0001↓	600	<0.0001↓
Zn	200	<0.0001↑	200	<0.0001↑	360	0.017↓	360	0.017↓	500	0.896↓	1500	<0.0001↓

***P-value<0.05 is considered as significant.**
↑ And ↓ indicate that the measured amounts are higher and lower than the standards, respectively.

3.2.1. Land Use

Land use is defined as the use of the upper soil zone to manage waste. Wastes for land disposal need to have organic and easily biodegradable material. Wastes with hazardous or toxic nature are not advisable to apply this method. To prevent accumulation of pollutants in the soil, it is necessary to consider the concentrations of pollutants in the sludge and the loading rate of a pollutant applying to the land. Only sludge within the recommended concentrations should be applied to land. Land use is a relatively simple and cost effective method that uses natural processes to recycle waste and can potentially improve soil structure (20). Yadav and Grac studied the feasibility of food industry sludge for vermin-composting. According to their results, good quality manure could be derived from this sludge by vermin-composting if mixed up to 30% with cow dung. They found that Fe concentration in final vermin-compost was significantly higher than that of the initial feed mixtures. Cu, Zn and Mn concentration did not follow such pattern(21). Shumar et al., in their study revealed that 35 sewer and industrial sludge samples from Gaza strip were clean of heavy metals, except for Zn that in 85% of samples exceeded the standards for land application (5). In the preset study, as mentioned before, compared with CSQG standard for park land and agricultural use, Cr and Zn concentrations in the studied sludge was higher which make it unsuitable for agricultural application.

3.2.2. Residential, Commercial & Industrial Uses

Table 2 shows that Cr in the studied sludge was significantly higher than CSQG standard for residential, commercial and industrial uses. On the other hand, according to NJDEPSCC, the studied sludge can be used for residential and non-residential purposes. Some residential and non-residential applications of sludge have been discussed below:

3.2.2.1. Being Used As Building & Construction Materials

Incinerated sludge ash contains predominant amount of Si, Al, Ca, and Fe. Thus, it can be used as raw material for manufacturing construction materials such as bricks, tiles and blocks (22). Vieira et al.,(2006) studied the composition of a fine steel sludge from an integrated steel making plant into real ceramics. They found that the incorporation of 5 w.t% of waste is beneficial to ceramic. But, they did not consider the heavy metal contents of the sludge (6). Silva et al., in their study used stabilized/ solidification technology to treat sludge from an electroplating industry and the resultant was used as raw material to build concrete block. They revealed that the block constituents have very low metal leach ability and solubility indicating a low environmental impact (7).To reduce the potential health threats from exposure to sludge, FDEP guidance allows sludge blending with uncontaminated soils provided that the resulting mixture is still appropriate for beneficial use.

FDEP recommends Eq.1 to determine the appropriate blend ratio (ratio of blend material to sludge) for lowering the concentrations of a contaminant in the sludge (23):

$$(1) \quad Blend\ Ratio = \frac{(A-B)}{(B-C)}$$

Where, A stands for contaminant concentration in the sludge, mg/kg, B is the blended material target concentration, mg/kg, C is contaminant concentration in the material used for blending, mg/kg.

3.2.2.2. Being Used in Wastewater Treatment

Sludge has some other applications, too. For example, Huang et al., used sulfuric acid to optimize aluminum leaching condition from a textile sludge incineration residue. The leaching solution was investigated for its coagulant effect on textile wastewater treatment. Their results showed that it can be used as a textile wastewater treatment agent(8). Ning et al., used tannery sludge incineration slag (TSIS) as a skeleton builder in combination with cationic polyacrylamide (CPAM) to condition tannery sludge. Their results indicated that pre-treating the sludge with a combination of TSIS and CPAM improved sludge dewaterability over CPAM conditioning alone (9).

3.2.2. Other Sludge Uses

As another reuse practice, sludge with high concentration of heavy metal or toxic chemical can be technically converted into oil by a pyrolysis process. But capital and running cost of such process is high (24).

3.3. Land filling

For that sludge which cannot be reused landfilling is the ultimate disposal method. Such sludge's usually contain heavy metals or toxic chemicals. Therefore, lining of the landfill with suitable lining materials such as clay or plastic liner may be needed to prevent groundwater contamination(24). Current management of sludge from the studied IWWTP is discharging in an unlined dumping site. Such wastes can contribute to landfill leachate, pollute groundwater, enter the food chain and cause health problem. Yagout suggested lined evaporation ponds as an economical and safe method for industrial liquid and sludge disposal in arid climates (25).

4. Discussion

In this study, some physicochemical characteristics of a petrochemical wastewater sludge was studied and the results showed that Fe had the highest concentration amongst the studied metals and amongst the heavy metals, Zn was the one with the highest concentrations. The measured parameters were compared with international standards and the results were reported. Compared with CSQG, the investigated sludge was polluted for residential/parkland, agricultural, commercial and industrial use because of its high Cr concentration. According to NJDEPSCC, the studied sludge was suitable for residential and non-residential applications. It should be noted that there are other parameters in CSQG and NJDEPSCC than those studied in this study including different organic and inorganic compounds, and it would be better for these parameters to be considered in future studies.

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