

Solidification and Stabilization of Petrochemical Flocculation Effluent (Sludge) after Treatment with Activated Carbon

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Abstract: Petrochemical flocculation effluent (sludge), pose serious environmental and health risks in its use, storage, transportation and disposal. A brief exposure to this effluent has been associated with adverse effects such as: birth defects, nervous disorders, cancer and even fatalities. The objective of this study is solidification and stabilization of Petrochemical flocculation effluent after treatment with activated carbon. Characterization of petrochemical flocculation effluent shows concentrations of toxic substances as follows: Arsenic (0.005 mg/l), Barium (7mg/l), Cadmium (0.023mg/l), Chromium (0.162 mg/l), Lead (0.18 mg/l) Mercury (0.98 mg/l), Selenium (0.12 mg/l), Silver (0.04 mg/l) and Zinc (2.9 mg/l). The sludge was mixed with activated carbon and allowed to stand for sixty minutes as a treatment procedure. Characterization of the treated sludge was carried out and the concentrations of the toxic substances were ascertained and then used as a baseline for further treatment. The treated sludge was solidified and stabilized by mixing with Portland cement in the ratio of 1:4 (that is 20 percent of cement to 80 percent of pre-treated sludge). Characterization was carried out on the samples after 7, 14 and 28 days curing time, respectively. pH as a characteristic feature of toxicity of a substance was also determined at the various intervals of characterization. The solidified and stabilized treated sludge showed concentrations of: Arsenic (0.03mg/l), Barium (4mg/l), Cadmium (0.017mg/l), Lead (0.06mg/l), Mercury (0.30 mg/l), Selenium (0.09mg/l), Silver (0.02 mg/l) and Zinc (1.5 mg/l). The reduction in the concentration of the toxic substances was determined as the ratio of the final concentration to the initial concentration presented in percentage values as follows: Arsenic (< 66.67%), Barium (45.25%), Cadmium (62.94%), Chromium (7.86%), Lead (96.67%), Mercury (30%), Selenium (88.89%), Silver (< 95%) and Zinc (76.67%). These met the permissible limits of the Department of Petroleum Resources standards 2002 [which is the regulatory standard for Petroleum or hydrocarbon related waste in Nigeria] and the International Statutory requirements for remediation of toxic substances with exception of mercury.

Keywords— Solidification; Stabilization; Petrochemical Flocculation Effluent; Activated Carbon

1. INTRODUCTION

Petrochemical flocculation effluent (sludge) is a complex emulsion of various petroleum hydrocarbons (P.H.C.s), water, heavy metals and solid particles resulting from petroleum related activities [1]. Petrochemical industries use relatively large volumes of water especially for cooling systems this gives rise to high volume of sludge. The refineries also generate polluted waste waters containing BOD₅ and COD levels of approximately 150 to 250 mg/l and 300 to 600 mg/l; oil levels of 5000mg/l in tank bottoms, benzene levels of 1 – 100mg/l, benzo(a)pyrene level of less than 1 – 100 mg/l and heavy metals (chrome and lead levels of 0.1 – 100mg/l and 0.2 – 10 mg/l respectively) and other pollutants. The waste and sludge generation are of range 3 – 5 kg/ton of petroleum processed and eighty percent of which may be considered toxic [2]. They are of great environmental concern and thus are referred to as toxic substance [3].

Solidification involves the addition of reagents (binders) to a toxic material to impart physical/dimensional stability to contain toxic substances in a solid product and reduce access by external agents (e.g. air, rainfall) [4]. Stabilization refers to a chemical process that involves the addition of reagents (binders) to a toxic material (e.g. soil or sludge) to bind the matrix of the toxic substances such that it is immobilized resulting in more physical and chemical stability [5]. The primary aim of a typical remediation process involving solidification and stabilization is to reduce (to minimum acceptable levels) the actual or potential impact of toxic substances on the environment

Solidification and stabilization has considerable technical merit. Selection of solidification and stabilization is also supported by recent developments in the environmental regulations such as the Resource Conservation and Recovery Act (RCRA), The Toxic Waste and Solid Waste Amendments (HSWA), The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA); and the Superfund Amendments as they pertain to the S/S of toxic waste, [5];[6].

Solidification and Stabilization (S/S) is an established remediation technology for contaminated soils and treatment technology for toxic wastes in the United States of America and some European Union member States.

2. MATERIALS AND METHODS

2.1 Materials

The materials required for this study are outlined below:

- Petrochemical flocculation effluent (sludge) was collected from a Petro – Chemical Company in Eleme, Rivers State, Nigeria.
- Powdered activated carbon was obtained from wood charcoal.
- The binder used in the study was Ordinary Portland Cement (OPC – grade 42.5). It conformed to BS EN 196-6[7].

2.2 Methods

Characterization was carried out on a 5g sample size of petrochemical flocculation effluent (sludge) using the Atomic Absorption Spectrophotometer (AAS). This test gave the concentration of toxic substances in the sludge. The pH of the sludge was also determined using a digital pH meter. The sludge was mixed with activated carbon for the purpose of treatment and left to stand for sixty minutes. Characterization was repeated on a 5g sample of treated sludge to determine the concentration of toxic substances. The pH of the treated sludge was also determined using the digital pH meter. This was adopted as a baseline concentration in the solidification and stabilization of the sludge.

Ordinary Portland Cement (OPC) which is the binder was mixed with the treated sludge using the mixing ratio of 1:4 (that is 20 percent of the binder to 80 percent of treated sludge). This is used due to its performance as the optimum binder to waste mix ratio [8]. The mixture was compacted in cylindrical molds with a height of 68mm and diameter of 100mm. After setting it was de – molded and allowed to cure at atmospheric conditions (with intermittent sprinkling of water) for 7, 14 and 28days.

The chemical testing of the samples was conducted in adherence to the Department of Petroleum Resources (DPR) / Federal Ministry of Environment (FM Env.) recommended analytical procedure as outlined in Part vii Section D of DPR guidelines and standards for the Petroleum Industry [9].

At the end of every curing interval, the solidified/stabilized sludge sample is crushed, air dried and passed through a 2mm sieve. To obtain a leachate solution, 5g of these fine particles were weighed into a 100ml beaker. 2ml HNO₃ and 6ml HCl in the ratio of 1:3 was added to the already weighed sample. The mixture was digested by heating using heating mantle ensuring that the mixture attained a state of near –dryness to enable proper leaching of the sample. More acid was thereafter added and digestion was continued for 30-40 minutes. Digestion was halted when a clear digest was obtained. The flask was cooled and the contents were transferred into a 50ml volumetric flask through a what man No. 42, 150mm filter paper, and the leachate solution were made up to the 50ml mark with de-ionized water [5].

The resulting leachate solution was analyzed for toxic substances using the Atomic Absorption Spectrophotometer. This test is based on the EPA 1311 [10]. The reduction in concentration of the toxic substances was ascertained and compared to the baseline concentration level. The reduction in concentration can be mathematically expressed as:

$$\text{Reduction in concentration (\%)} = \frac{(\text{concentration of treated sludge} - \text{concentration of leachate solution})}{(\text{concentration of treated sludge})} \times 100 \quad (1)$$

3. RESULTS AND DISCUSSION

The characterization tests results and pH values for the untreated and activated carbon treated flocculation effluent (sludge), are shown in Tables 1 and 2. The reduction in concentration (%) for the treatment of the sludge is obtained from (1).

Table 1: Characterization test results for untreated flocculation effluent (sludge)

S/No.	Toxic substances	Concentration (mg/l)	pH
1	Arsenic	0.005	4.8
2	Barium	7.0	
3	Cadmium	0.023	

4	Chromium	0.162	
5	Lead	0.18	
6	Mercury	0.98	
7	Selenium	0.12	
8	Silver	0.04	
9	Zinc	2.9	

Table 2: Characterization test results for activated carbon treated flocculation effluent (sludge)

S/No.	Toxic Substances	Concentration (mg/l)	Reduction in concentration (%)	pH
1	Arsenic	0.003	40	5.6
2	Barium	4.0	42.857	
3	Cadmium	0.017	26.087	
4	Chromium	0.14	13.580	
5	Lead	0.06	66.667	
6	Mercury	0.30	69.388	
7	Selenium	0.09	25	
8	Silver	0.02	50	
9	Zinc	1.5	48.276	

A comparison of Table 1 and Table 2 shows a remarkable reduction in concentration level of toxic substances and a slight increase of the pH of the sludge from 4.8 to 5.6; which is a decrease in the acidity. The decrease in the concentration of toxic substances influenced the pH of the sludge. This indicates a relationship between pH and the level of toxicity of a substance or material.

The reduction in the concentration of toxic substances due to the addition of activated carbon indicates that activated carbon has good potentials for removal of heavy metals and trace metals from waste effluents. In this study, the activated carbon only had the potency of reducing the concentration and not total removal of the toxic substances present due to the toxic nature of the sludge.

Table 3, table 4 and table 5 shows concentration levels of toxic substances in leachate solution obtained from solidified/stabilized treated sludge after curing for 7, 14 and 28 days.

Table 3: Concentration levels of toxic substances in leachate solution obtained from solidified/stabilized treated sludge after curing for 7 days

S/No.	Toxic Substances	Concentration (mg/l)	Reduction in concentration (%)	pH
1	Arsenic	< 0.001	< 66.67	8.9
2	Barium	3.0	25	
3	Cadmium	0.017	29.412	
4	Chromium	0.13	7.143	
5	Lead	0.003	95	
6	Mercury	0.23	23.333	
7	Selenium	0.02	77.778	
8	Silver	0.001	95	
9	Zinc	0.7	80	

Table 4: Concentration levels of toxic substances in leachate solution obtained from solidified/stabilized treated sludge after curing for 14 days

S/No.	Toxic Substances	Concentration (mg/l)	Reduction in concentration (%)	pH
1	Arsenic	<0.001	<66.667	9.2
2	Barium	2.9	27.5	
3	Cadmium	0.009	47.059	

4	Chromium	0.130	---	
5	Lead	0,002	96.667	
6	Mercury	0.21	30	
7	Selenium	0.02		
8	Silver	< 0.001	< 95	
9	Zinc	0.5	66.667	

Table 5: Concentration levels of toxic substances in leachate solution obtained from solidified/stabilized treated sludge after curing for 28 days

S/No.	Toxic Substances	Concentration (mg/l)	Reduction in concentration (%)	pH
1	Arsenic	< 0.001	66.667	9.2
2	Barium	2.19	45.250	
3	Cadmium	0.0063	62.941	
4	Chromium	0.129	7.857	
5	Lead	0.002		
6	Mercury	0.21		
7	Selenium	0.01	88.889	
8	Silver	< 0.001	< 95	
9	Zinc	0.35	76.667	

The results of the characterization of the leachate solution after 7 days of curing are taken into cognizance because it marks the onset of the stabilization process. There after actual reduction or chemical reaction within the matrix is minimal for the subsequent curing intervals as illustrated in the in Table 3, 4 and 5 respectively.

Table 6 provides an overview of the solidification and stabilization process. It contains a comparison of the concentration levels of toxic substances in the untreated sludge; activated carbon treated sludge and solidified/stabilized sludge.

Table 6: Comparison of the concentration levels of toxic substances in the untreated sludge; activated carbon treated sludge and solidified/stabilized treated sludge

S/No.	Toxic Substances	Untreated sludge (mg/l)	Activated carbon treated sludge (mg/l)	Solidified/stabilized sludge (mg/l)
1	Arsenic	0.005	0.003	<0.001
2	Barium	7.0	4.0	2.19
3	Cadmium	0.023	0.017	0.0063
4	Chromium	0.162	0.14	0.129
5	Lead	0.18	0.06	0.002
6	Mercury	0.98	0.30	0.21
7	Selenium	0.12	0.09	0.01
8	Silver	0.04	0.02	<0.001
9	Zinc	2.9	1.5	0.35

A comparison was presented in table 4.6 to show the concentration of toxic substances present in each stage. The comparison was between the untreated sludge, activated carbon treated sludge and the solidified/stabilized sludge. It can easily be deduced from the table that the treatment of the sludge using activated carbon is more potent in the reduction of the concentration of toxic substances compared to solidification and stabilization.

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