



Investigating the effect of local activated carbon in the treatment of some heavy metals in spent synthetic based mud

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Abstract

The search for oil and gas is associated with drilling operations. These drilling activities are associated with many environmental issues such as heavy metal contamination in spent mud. These pose serious health issues to humans when ingested or inhaled. Spent mud contaminated with heavy metals are also toxic to marine organisms if disposed into the sea untreated. Adsorption has been investigated as a cost-effective method of removal of heavy metals from wastewater. In the present study low-cost local rice husk adsorbent was used to treat spent synthetic mud to treat four major heavy metals (Cadmium, Lead, Arsenic and Mercury). Samples of spent mud were collected from the Jubilee Field in Ghana and were digested and analysed using the Atomic Absorption Spectrometer (AAS). With local rice husk adsorbent concentrations of 10, 20 and 40 mg/l, mixing speed of 200 to 259 rpm, contact time from 20 to 30 minutes, and comparing with EPA standards, Cadmium recorded improvement from -1 168% to 59%, Lead was improved from -633% to 20%, Arsenic was improved from -4050% to -440%, Mercury recorded improvement from -200% to 80%. Metals like Cadmium, Lead and Mercury residual concentrations were able to meet global limits for effluent disposal, but Arsenic was not and may therefore require more contact time to meet global limits for effluent disposal.

Keywords: heavy metals, absorption, activated carbon, spent mud, treatment, disposal

Introduction

Petroleum accounts for over 80% of the world's energy mix (Amorin *et al.*, 2022). However, its drilling and production operations generate the highest hazardous wastes in the upstream sector of the oil and gas industry. Production operations generates produced water which is the largest generated waste and mainly contains radium isotopes, solid residues (Bakke *et al.*, 2013) [8]. Drilling operations on the other hand produce two types of wastes, drill cuttings and spent mud (Dabo, 2023) [10]. Most spent muds are disposed-off through biodegradation processes, injection into casing annulus, incineration and dumping into pits or farm lands (Ahmmed *et al.*, 2017). The spent mud may contain a wide variety of dissolved minerals, dissolved and dispersed oil compounds, salts, metal ions, Naturally Occurring Radioactive Materials (NORM) and dissolved gases (Piszuz *et al.*, 2014). Formations metals in the spent mud could be a possible source of heavy metals, and their contamination is of major concern in the environment because of their toxicity and threat to human life and the ecosystems (Purves, 1985; Ma and Rao, 1997; Al Obaidy *et al.*, 2013) [15, 11, 5]. Metal interaction in soil varies significantly with the nature of soil types. Furthermore, many environmental factors influence metals availability such as the nature of the metal species, their interaction with soil colloids, the soil characteristics and duration of contact with surface binding (Naidu *et al.*, 2003) [13]. The discharge of these contaminated fluids if not very well treated possesses many risks to both humans and other habitats. Workers in the oil and gas industry and the general public are at a risk of radiation exposure via inhalation, ingestion of groundwater, surface water and food. Ingestion of food grown in contaminated soils or seafood harvested in areas contaminated by

produced water outfalls may also result in radiation exposure increment. The basic steps for effective management of these waste include: minimisation of waste, pre-treatment, characterisation, treatment, conditioning, transport, storage and disposal (Neff, 1987) [14]. The term Activated Carbon (AC) defines a category of amorphous carbonaceous materials with high porosity and internal surface area. Activated carbon can be produced from any carbonaceous material, and until recently, anthracite and bituminous coals have been the major sources. Activated carbons are the most widely used adsorbents for the treatment of waste-waters and emissions. Adsorption has long been used as a purification and separation process on an industrial scale. Highly porous adsorbents with good selectivity such as activated carbon have shown excellent ability in the removal of organic compounds such as dyestuffs, phenolics, endocrine-disrupting compounds, pesticides, pharmaceuticals and several metal ions (Saleem *et al.*, 2019) [16].

Heavy Metals are metallic elements having density greater than 5 kg/m³ and atomic number greater than 20. They are encountered during drilling and production activities and are related to a variety of environmental concern (Broni-Bediako, 2022) [9]. In small concentration, some heavy metals are useful for animal and plant growth, such as iron, mangan, cobalt, molybdenum, zinc, iodine, nickel and copper. If they are not present and available in the soil at a minimum level, deficiency will occur, but excessive amount may be toxic. Due to their potential toxicity in large quantity, it is of interest to make an analytical estimation of their presence in spent drilling muds and waste water, when these materials are to be disposed by burying in the soil (Mulyono *et al.*, 1996) [12].

The Environmental Protection Agency (EPA) has a limit for the percentage for heavy metals concentration allowable in a spent drilling mud before their disposal. Preventing heavy metal pollution is critical as cleaning contaminated soils is extremely expensive and difficult (Tamulonis, 2000) [17]. Table 1 shows the typical concentration and their EPA required limits before disposal.

Table 1: Typical Concentration and EPA Requirement for Heavy Metals

Metals	Typical Concentration(mg/kg)	Threshold Limit Values (TLV)(mg/m ³)
Arsenic	7.0	0.2
Cadmium	0.35	0.05
Lead	25.0	0.15
Mercury	0.07	0.05

(Source: Broni-Bediako, 2022) [9]

This worked therefore determined the effect of using locally produced activated carbon (form rice husk) in the treatment of heavy metals in spent drilling fluid in the oil and gas industry in Ghana. The commercialisation of activated carbons production in Ghana from agro-waste would provide employment, reduce foreign exchange on importation of the product, improve upon management of biomass wastes among others (Woodland *et al.*, 2022) [18].

Methods

The experiments conducted included basic heavy metal testing, activated carbon treatment and a second heavy metal testing. First testing that was conducted to know the level of concentration of heavy metals in the spent water-based drilling mud was conducted by using Buck Model 210/211 AAS 220GF graphite Furnace and 220 AS auto sampler. After, the sample was further divided into three (3) samples labelled A-C of 20 mg/l of spent mud. Atomic Absorption Spectrometry (AAS) is an analytical technique that measures the concentrations of elements. It is so sensitive that it can measure down to parts per billion of a gram (µg dm⁻³) in a sample (Anon, 2020) [17].

Activated Carbon Testing

The adsorption of heavy metal ions by rice husk ash was evaluated under various conditions such as mixing speed and adsorbent dose through both kinetic and isotherm studies. In general, the sorption consisted of 20 mg/l of each sample at an agitation rate of 200 rpm with an adsorbent time of 30 min at room temperature (25 ± 3) °C.

Atomic Absorption Spectrometry 2nd Testing

After the adsorption of heavy metals were conducted with the risk husk ash, the samples were tested again using the Buck Model 210/211 AAS 220GF graphite Furnace and 220 AS auto sampler, to know the concentration of heavy metals left in the three samples treated

Results

Experiments were carried out on the spent mud samples to find out how best they can be treated with locally produced activated carbon.

Atomic Absorption Spectrometry 1st Testing

The heavy metal concentrations in the mud sample are shown in Table 2.

Table 2: Heavy Metal Concentration of the Untreated Spent Mud Sample

Metals	Concentration (mg/m ³)	Threshold Limit Values (TLV) (mg/m ³)	Percentage Increase Over TLV (%)
Arsenic	8.30	0.20	4150.0
Cadmium	0.160	0.05	320.0
Lead	1.10	0.15	733.3
Mercury	0.15	0.05	300.0

From Figure 1 and Table 2, it is shown that all metals tested for in the drilling mud were in higher concentration than the EPA threshold limit values. Arsenic recorded the highest value with 4 150% increase over the EPA threshold limit value. This was followed by Lead with 733.3%, Cadmium with 320% and Mercury with 300%. This therefore can be harmful to the environment, plants and animals if disposed without proper treatment.

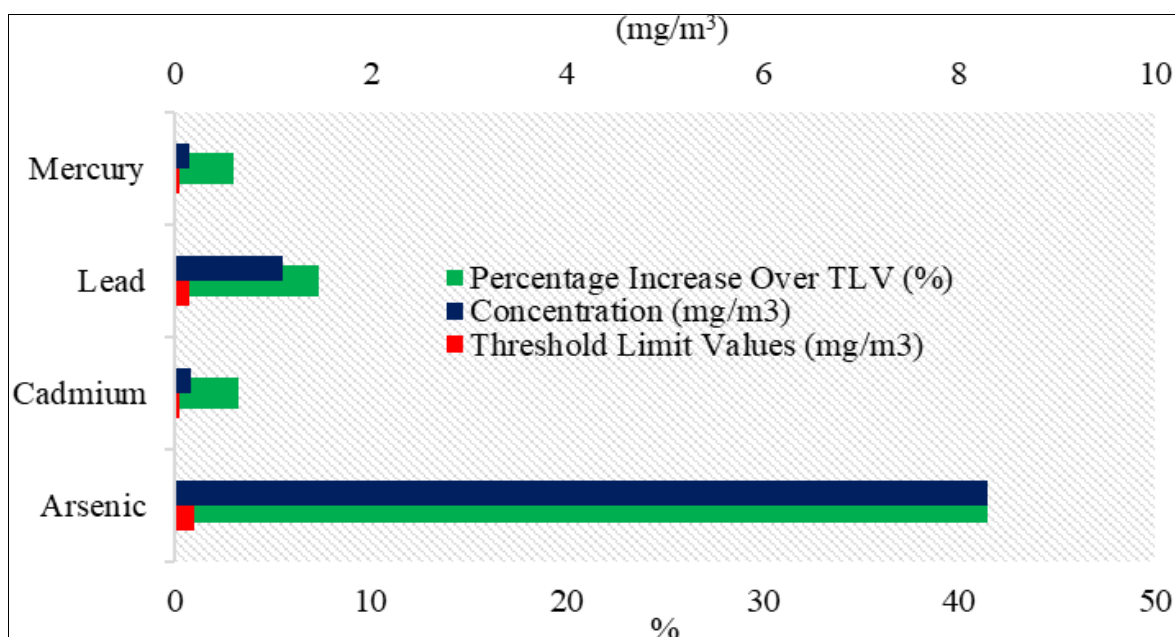


Fig 1: Concentration of Heavy Metals in Spent Water Based Mud

Activated Carbon Treatment

After the first Atomic Absorption Test was performed, the mud was divided into three samples according to Table 3 with varying adsorption dose of the AC, using different mixing speeds and contact time to obtain the optimal method for metal reduction in the various mud samples, using EPA Standards as a bench mark. Table 3 shows the Revolutions Per Minute (RPM), contact time and adsorption dose of the mud samples with the local activated carbon at room temperature.

Table 3: Activated Carbon Treatment

Samples	Mixing Speed (rpm)	Contact Time (min)	Adsorption Dose (g/l)
A	200	30	10
B	250	30	20
C	200	20	40

Atomic Absorption Spectrometry 2nd Testing

Tables 4 to 6 show the results of the AC on each sample after the treatments were carried out. Tables 7 to 9 show the results of each metal treated with varying dose of AC.

Table 4: Heavy Metal Concentration of Sample A, B, C after Treatment

Metals	Sample A after Treatment		Sample B after Treatment		Sample C after Treatment	
	Concentration (mg/m ³)	Threshold Limit Values (mg/m ³)	Concentration (mg/m ³)	Threshold Limit Values (mg/m ³)	Concentration (mg/m ³)	Threshold Limit Values (mg/m ³)
Arsenic	2.077	0.20	1.66	0.20	1.079	0.20
Cadmium	0.028	0.05	0.0224	0.05	0.0206	0.05
Lead	0.86	0.15	0.63	0.15	0.12	0.15
Mercury	0.112	0.05	0.0125	0.05	0.021	0.05

Table 5: Removal with Varying Adsorption Dose for sample 1, 2, 3

Sample	Arsenic		Cadmium		Lead		Mercury	
	Adsorption Dose (mg/l)	Concentration (mg/m ³)	Adsorption Dose (mg/l)	Concentration (mg/m ³)	Adsorption Dose (mg/l)	Concentration (mg/m ³)	Adsorption Dose (mg/l)	Concentration (mg/m ³)
1	10	2.077	10	0.028	10	0.86	10	0.12
2	20	1.66	20	0.0224	20	0.63	20	0.0125
3	40	1.07	40	0.0206	40	0.12	40	0.01

Arsenic (As) Removal by Different Weights of Adsorbents

According to Figure 2, as AC concentration was increased from 10, 20, to 40 mg/l, the rate of Arsenic removal increased from 75.0% to 87.0%. Increasing the adsorption dose of the AC in the third sample removed most of the Arsenic metal even with low contact time. It was able to

reduce the Arsenic concentration from 8.3 mg/m³ to 1.079 mg/m³ (87% improvement over the initial spent mud). This also represented a reduction from the initial -4050% to -440% compared to the EPA standard. This however did not meet the EPA Standard of 0.20 mg/m³ according to Table 4. This may be due to the contact time used possibly being shorter (Table 3).

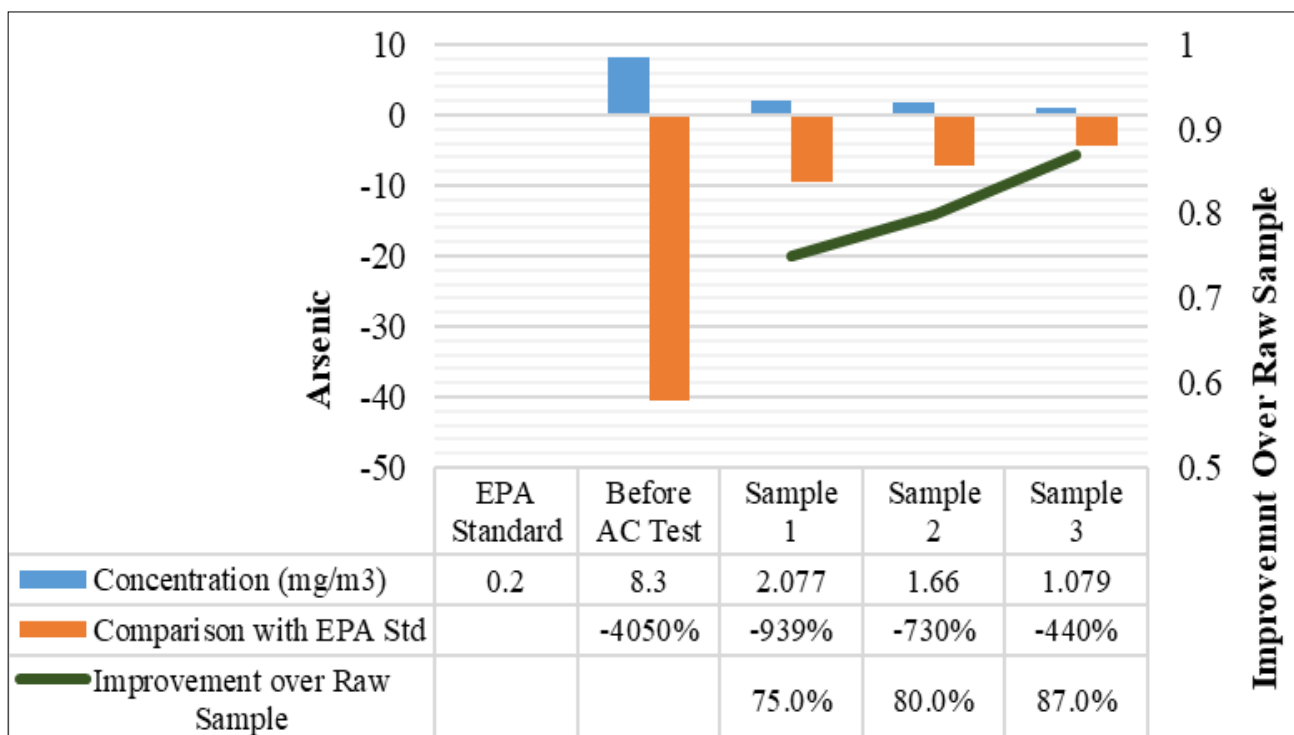


Fig 2: Arsenic Removal with AC

Cadmium (Cd) Removal by Different Weights of Absorbents

According to Figure 3, as AC concentration was increased from 10, 20, to 40 mg/l, the rate of Cadmium removal increased from 95.6% to 96.8%. It was able to reduce the

Cadmium concentration from 0.634 mg/m³ to 0.0206 mg/m³ (-1168% to 59% over the EPA standard). An improvement from 95.5% to 96.8% over the raw sample. From Figure 3, increasing the adsorption dose of the AC in the third sample removed most of the Cadmium metal even with low contact time.

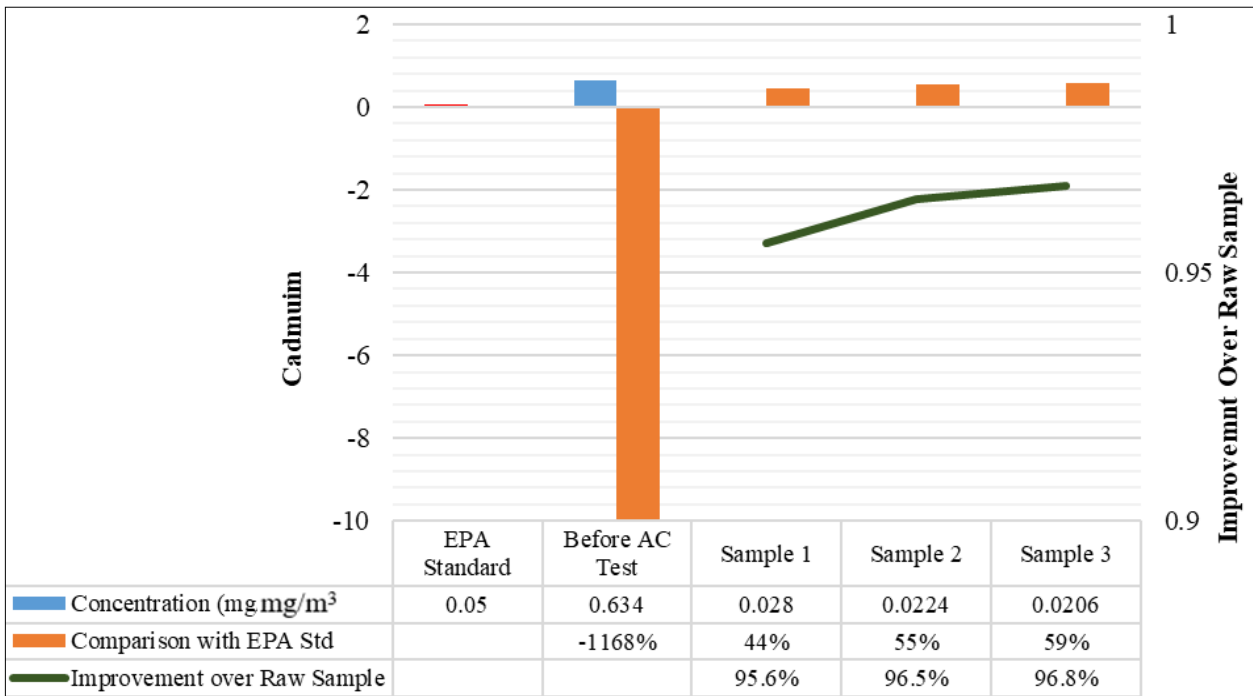


Fig 3: Cadmium Removal by AC

Lead (Pb) Removal by Different Weights of Absorbents

According to Figure 4, as AC concentration was increased from 10, 20, to 40 mg/l, the rate of Lead removal increased from 21.8% to 89.1%. It was able to reduce the Lead concentration from 1.1 mg/m³ to 0.12 mg/m³ (-633% to 20%

over the EPA standard). An improvement from 21.8% to 89.1% over the raw sample. From the graph, increasing the adsorption dose of the AC in the third sample removed most of the Lead metal even with low contact time.

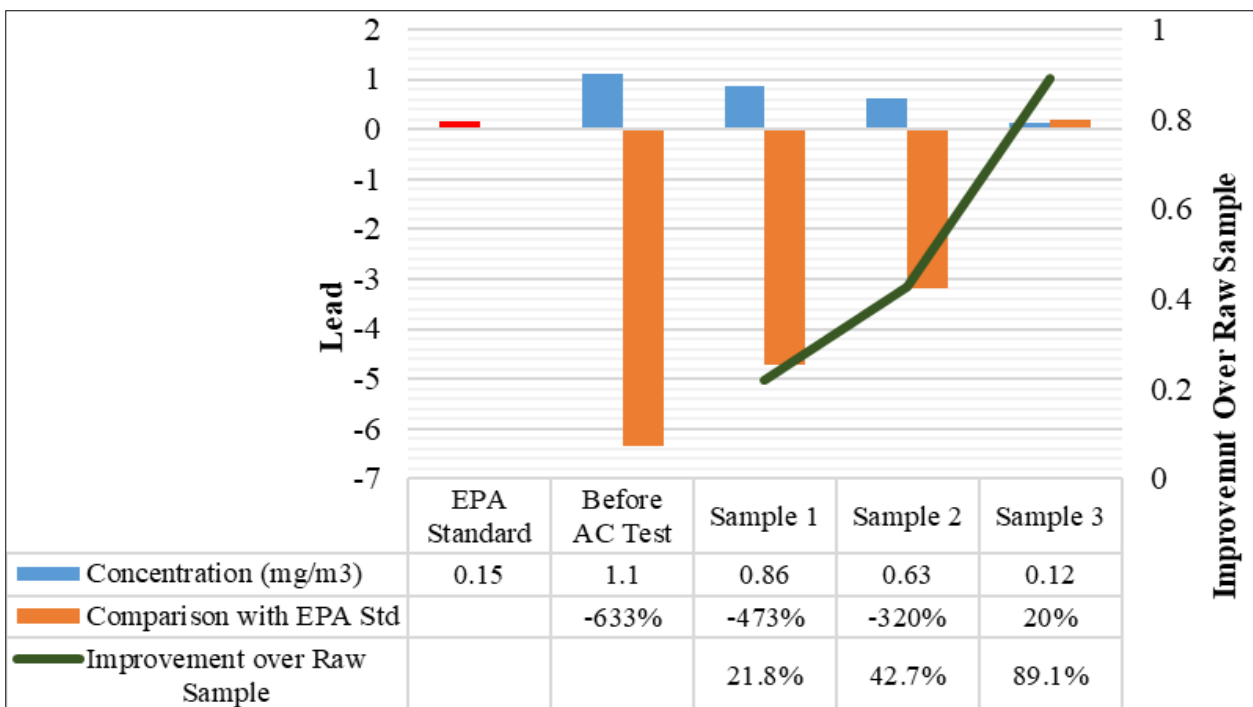


Fig 4: Lead Removal by AC

Mercury (Hg) removal by Different Weights of Absorbents

According to Figure 5, as AC concentration was increased from 10, 20, to 40 mg/l, the rate of Mercury removal increased from 25.3% to 93.3% It was able to reduce the Mercury concentration from 0.15 mg/m³ to 0.010 mg/m³

(- 200% to 80% over the EPA standard). An improvement from 25.3% to 93.3% over the raw sample. From the graph, increasing the adsorption dose of the AC in the third sample removed most of the Mercury metal even with low contact time.

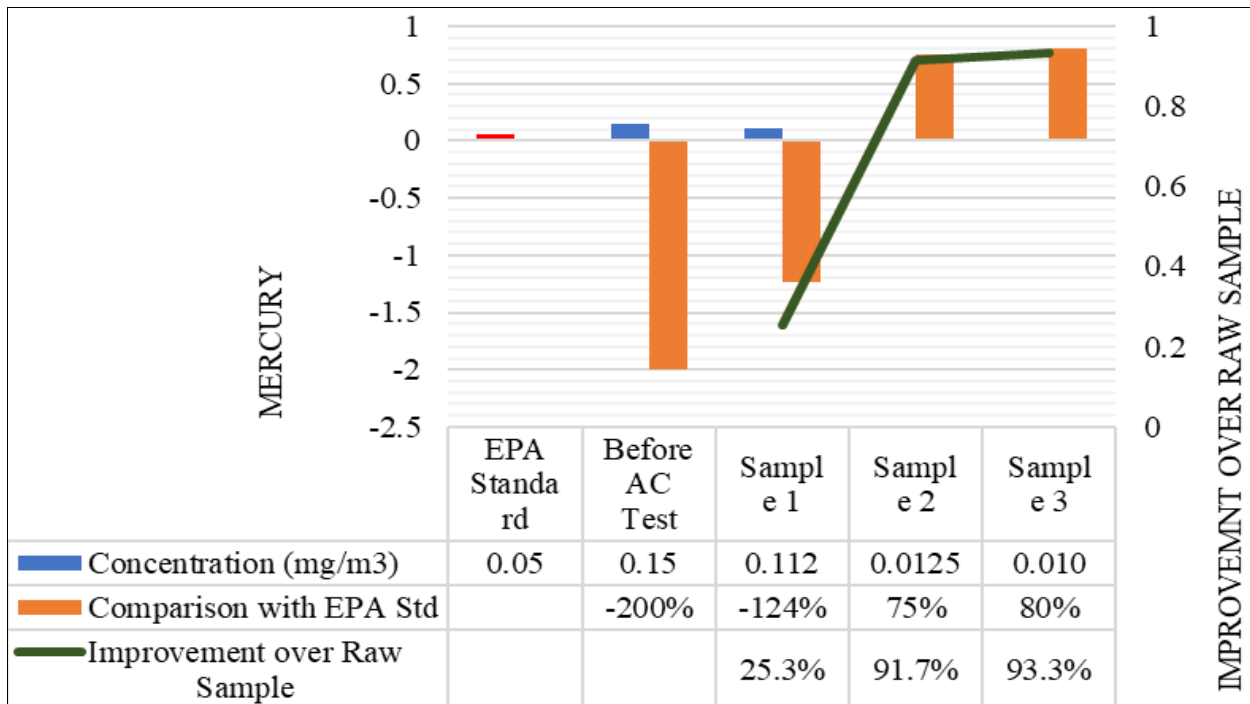


Fig 5: Mercury Removal by AC

Conclusions

Based on the results, the following conclusions were made:

1. With local rice husk adsorbent concentrations of 10, 20 and 40 mg/l, comparing with EPA standards, Cadmium recorded improvement from -1 168% to 59%, Lead was improved from -633% to 20%, Arsenic was improved from -4050% to -440%, Mercury recorded improvement from -200% to 80% showing that it is effective in the simultaneous removal of the heavy metals; and
2. It was found that the percentage removal of heavy metals was dependent on the dose of local adsorbent and contact time.

Based on the results gathered, it is recommended that the exposure or contact time could be prolonged to improve upon the effect on the local AC on the removal of Arsenic.

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