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HEAVY METAL REMOVAL IN A COMBINED UASB-DFAF AND HUASB-DFAF SYSTEM REACTORS TREATING MUNICIPAL WASTEWATER

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Abstract: Heavy metal pollution has nowadays becomes a serious environmental problem. Various methods for heavy metal removal from wastewater have been extensively studied in recent years. This study is carried out to investigate the removal of heavy metals (HMs) in a combined UASB-DFAF and HUASB-DFAF systems in treating municipal wastewater. The experiment was carried out as a lab scale model involving combinations of up-flow anaerobic sludge blanket as a primary treatment system, followed by down flow aerobic filter as a secondary treatment. Performance of UASB-DFAF is compared with HUASB-DFAF system to treat the heavy metals of Cd, Pb, Al, As, Zn, Mn and Fe. The removals of heavy metals were investigated in the UASB-DFAF and HUASB-DFAF against hydraulic retention time (HRT) of 23 hours, 15 hours and 11 hours. Influent COD concentration was fed into the reactors at a constant rate of 1000 mg/l. The influent is a mixture of modified domestic wastewater with glucose, peptone and meat extract. Effluent samples were collected from the reactors and were analyzed for concentration of heavy metals. Concentration of metals decreases from 0.17 to 0.04 µg/L with time for cadmium (Cd), from 10.4 to 0.88 µg L^{-1} for (Pb), from 36.64 to 7.12 µg L^{-1} for Zinc (Zn), from 2.93 to 1.56 µg L^{-1} for Arsenic (As), from 3077 to 650.57 µg L^{-1} for Ferum (Fe), from 61.53 to 13.01 µg L^{-1} for (Al) and increase from 349.28 to 453.03 µg L^{-1} for (Mn). All heavy metals analyses were conducted using ICP-MS and AAS.

Keywords: *Heavy metals; municipal wastewater treatment; Sewerage treatment; HUASB; UASB; DFAF.*

1.0 Introduction

Wastewater is any water that has been adversely affected in quality by anthropogenic influence and comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations. Sewage is the part of wastewater that is contaminated with feces or urine. Sewage refers to wastewater from sources including domestic, municipal, or industrial liquid waste products disposed of, usually via a pipe or sewer system. Untreated sewage may contain water; nutrients, solids, pathogens, oils and greases, heavy metals and many toxic chemicals. The effluent of municipalities or industries are treated by wastewater treatment plants also contain high amounts of organic matter and pollutants including heavy metals such as Cu, Zn, Cd, Pb, etc. which contaminate the soils, ground water, sediments and surface waters.

Heavy metals pose a risk to public health because of their toxic a non-biodegradable nature and widespread occurrence in natural and human-altered environments (Mandu *et al*. 2012), and it was increased rapidly in the past few years especially in developing countries. Toxic heavy metals are considered one of the pollutants that have direct effect on man and animals. Industrial wastewater containing lead, copper, cadmium and chromium, etc. for example can contaminate groundwater resources and thus lead to a serious groundwater pollution problem (Renge *et al*. 2012). Current concern of industrialization during the last few decades has resulted in ecological unbalance and degradation of the natural resources. They are mainly introduced into the environment from point sources such as discharges from mining, metal plating, battery, and paper industries.

Many methods have been developed to address this stringent environmental regulation which necessitates removal of heavy metal compounds from wastewater. Most of these technologies, however, may be associated with high operation cost and or sludge disposal problems (Mandu *et al*. 2011; Sud *et al*. 2008). In recent years, the economical and safely methods for reduce and remove heavy metals from contaminated wastewater are developing. The use of anaerobic digestion such as UASB in term of removal heavy metals currently not widespread, In this paper a feasibility combined system UASB-DFAF and HUASB-DFAF of comparing media of Zeolite and Activated carbon for heavy metal removal from contaminated water are investigated such as Cd, Pb, Al, As, Zn, Mn and Fe.

1.1 Description of Metals

Cadmium (Cd): An Element were found in some soils, but human activities like mining and smelting released Cd into environment at higher concentrations than normal (Hamuda H.B, 2013). A maximum acceptable concentration of 0.005 mg/L (5µg/L) for cadmium in drinking water has been established on the basis of health considerations (Jarup *et al*. 1998).

Lead (Pb): Lead is among the heavy metals affecting the environment. All lead compounds are cumulative poisons. Acute lead poisoning usually affects the gastrointestinal track, the nervous system, and sometimes both. Lead causes many serious disorders like, anaemia, kidney disease, nervous disorders, and even death; it heads the toxic element list of 2008. (Karthika *et al*. 2008), the maximum acceptable concentration of lead in drinking water is 0.01 mg/L.

Zinc (Zn): Zinc is a trace element that is essential for human health. When people absorb too little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Zinc shortages can even cause birth defects. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. The maximum allowable concentration and the permissible Concentration of zinc in drinking water are 10 and 5 mg/L, respectively, according to ISI (Srinivas Raju & Naidu, 2013).

Ferum (Fe): Iron is a major constituent of the earth's crust. It occurs naturally in groundwater and surface waters. Drinking waters containing iron are not known to cause any harmful effects in humans. Iron may be removal from wastewater by oxidation of binary iron to tertiary iron. Hydrolysis subsequently causes flake formation and flake can be removed by sand filtration (El-Helece, 2012). The maximum acceptable concentration of iron in wastewater is 5 mg/L.

Arsenic (As): Arsenic occurs naturally in rocks, soil, water, air, plants, and animals. Natural activities such as volcanic action, erosion of rocks, and forest fires, can release arsenic into the environment (USEPA, 2002). Industrial products containing arsenic is present in the wastewaters producing metallurgical products, glassware and ceramic, tannery products, dye stuff, pesticides, synthetic chemicals and petroleum refinery products. The effluent allowable discharge concentration is 0.05 mg/L.

Aluminium (Al): The concentration of aluminium in natural waters can vary significantly depending on various physicochemical and mineralogical factors. Dissolved aluminium concentrations in waters with near-neutral pH values usually range from 0.001 to 0.05 mg/L but rise to 0.5–1 mg/L in more acidic waters or water rich in organic matter. At the extreme acidity of waters affected by acid mine drainage, dissolved aluminium concentrations of up to 90 mg/litre have been measured (WHO, 1997).

Manganese (Mn): Manganese is present in ground waters primarily as the divalent ion (Mn2+), due to the lack of subsurface oxygen. Waters surface may contain combinations of manganese in various oxidation states as soluble complexes, or as suspended particles. The occurrence of manganese in public water supplies presents more of an economic problem than a potential health hazard. Manganese causes dark stains in laundry and on plumbing fixtures, tends to deposit in water lines, and imparts an objectionable taste to beverages such as coffee and tea. Manganese levels in natural waters rarely exceed 1 mg/L, but levels of 0.1 mg/L are sufficient to cause the taste and staining problems. The recommended allowable manganese level in public water supplies is 0.05 mg/L. (HACH, 2011)

1.2 Effect of Heavy Metal

Heavy metals are natural components of the Earth's crust. It cannot be degraded or destroyed. Heavy metals are in the bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium and zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater (Philip *et al*, 2012).

Heavy metals are dangerous because they tend to bioaccumulate**.** Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted (Renge *et al*. 2012).

2.0 Materials and Methods

2.1 Lab Scale Description

Combination of two laboratory scale reactor Up-Flow Anaerobic Sludge blanket (UASB) with Down-Flow Aerobic filter (DFAF) are use in the experiment. One is UASB reactors R1, another two HUASB are reactors R2 and R3 were fabricated to give a working volume of 5.41L (9.0 cm diameter, 100 cm height), with six sampling ports placed at different heights. The hybrid UASB (HUASB) reactors were packed with suitable size media of 5-10 mm zeolite for R2 and coconut shell activated carbon for R3 with size ranged 2-3mm, respectively. The top of each reactor is fixed with GSS (gas-solids separators) to prevent biomass wash out. The DFAF reactors with volume 2.84 L is labelled as S1, S2 and S3. The initial concentrations and speciation of target heavy metals (Cd, Pb, Al, As, Zn, Mn and Fe) metals are taken from domestic sewerage treatment plant were screen, filtered and store in refrigerator 4^0C and the effluent concentration taken from effluent port UASB, HUASB and DFAF.

The municipal wastewater are used in this study was collected from sewerage wastewater treatment plant located in UTHM campus, Batu Pahat, Johor, Malaysia. The wastewater was collected, screened and stored at 4°C before feeding to the treatment system. The wastewater is classified as a medium strength. The wastewater was modified increase COD to 1000 mg/l COD concentration by addition of glucose, peptone and meat extract.

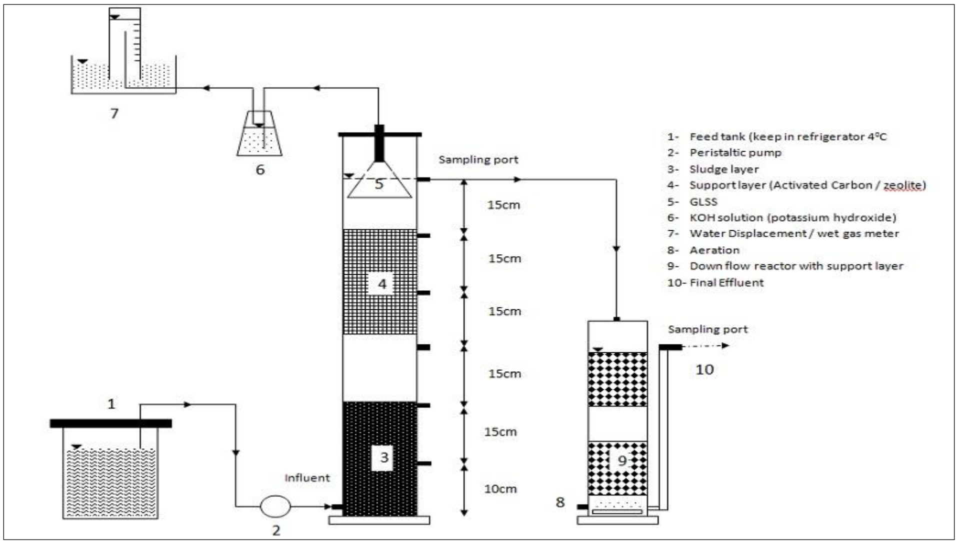

Figure.1: Schematic diagram of UASB-DFAF and HUASB-DFAF reactor

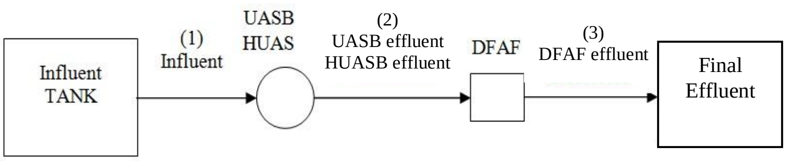

Figure 2: Schematic set up of lab scale (plan view)

2.2 *Wastewater Sampling*

The wastewater used in this study was taken from wastewater treatment plant located in UTHM campus, Batu Pahat, Johor, Malaysia. Wastewater sample were collected of the influent of the treatment plant. All samples were collected in 100 ml polyethylene bottles (PTFE) pre-cleaned with 30% nitric acids and deionized and transported in a refrigerated, where they were stored at 4^0C until analysis.

2.3 Analysis

In the determination of heavy metals content, an aliquot part of wastewater sample was filtered through 0.45µm membrane filters and acidified with 10% concentrated nitric acids. Metal concentrations were determined using inductively couple plasma mass spectrometry (ICP-MS) for Cd, Pb, Al, As, Zn and atomic adsorption spectrometer (AAS) only for Ferum (Fe). General water parameters were also measured in all wastewater samples following analytical methods described in standard methods (APHA, 2011). Besides that the allowable standard discharge of metal by Malaysian Standard are followed Department of Environmental (DOE) shown in table 1.

Table 1: Standard discharge Heavy Metals in Malaysia

Parameter	**Unit**	**Standard**	
		A	**B**
Cadmium (Cd)	mg/l	0.01	0.02
Arsenic (As)	mg/l	0.05	0.10
Lead (Pb)	mg/l	0.10	0.50
Manganese (Mn)	mg/l	0.20	1.00
Zinc (Zn)	mg/l	1.00	1.00
Iron (Fe)	mg/l	1.00	5.00

(Source: http://www.iwk.com.my/v/knowledge-arena/effluent-standards)

3.0 Results and Discussion

3.1 General Parameter of System Operation

Table 2 shows the general water quality at different changing of hydraulic retention time of reactor system of UASB-DFAF and HUASB-DFAF. Wastewater temperature is in the range of 26 ± 3^0C (ambient temperature) and pH from 4.0 to 8.0. Organic load, as indicted by the content in TSS and COD shown a good removal value. A combination of anaerobic and aerobic system produces the best removal value in all indicator parameter. In these conditions of UASB and HUASB system removed 80% of COD and 35% of TSS on average. Final effluent concentration for COD value showed up 90% removal efficiency.

Table 2: Average concentration of wastewater quality parameter in the Influent wastewater, UASB/HUASB and DFAF effluents

	Influent	UASB and HUASB Effluent			DFAF Effluent		
		R1	**R2**	**R3**	**S1**	**S2**	**S3**
COD mg/L							
HRT 23 hour	925	422	245	206	228	104	87
HRT 15 hour	980	335	126	127	275	66	52
HRT 11 hour	1080	481	137	136	163	99	62
NH_3-N mg/L							
HRT 23 hour	43	66	11	37	32	10	38
HRT 15 hour	40	56	27	44	36	21	34
HRT 11 hour	42	58	23	41	15	16	39
pH							
HRT 23 hour	5.5	6.0	6.4	6.8	6.9	7.2	7.0
HRT 15 hour	4.9	6.4	6.2	6.7	6.4	7.7	7.3
HRT 11 hour	4.1	6.2	6.3	6.5	6.5	6.8	7.5
TSS mg/L							
HRT 23 hour	49.6	98.0	68.0	43.4	75.0	1.0	3.4
HRT 15 hour	47.3	81.3	43.2	23.7	50.2	2.5	2.8
HRT 11 hour	46.6	102.0	39.3	21.9	47.3	3.0	1.8
Colour							
HRT 23 hour	180	933	618	568	540	422	38
HRT 15 hour	250	825	604	574	436	382	40
HRT 11 hour	230	921	625	604	532	235	42
Turbidity							
HRT 23 hour	129	462	428	304	466	10	11
HRT 15 hour	200	309	312	280	243	8	7
HRT 11 hour	227	251	158	113	136	3	5

**R1-UASB, R2-HUASB, R3-HUASB - S1-DFAF, S2-DFAF S3-DFAF*

3.2 Heavy Metal Concentration in Influent And Effluent

Table 3 shows the concentration of heavy metals in the wastewater influent to the system. The values of Ferum (Fe) and manganese (Mn) in this study shown high value of heavy metal ranging from 381-3077 µg/L and 131.29-538.50 µg /L respectively. Cadmium (Cd) on the other hand has shown a lower value of between 0.09-0.19 µg/ L.

Table 3: Minimum and Maximum concentration of metal in the influent wastewater.

Heavy Metals	HRT 23 hours	HRT 15 hours	HRT 11 hours
Cd	0.09-0.12	0.13-0.17	0.13-0.19
Pb	4.21-4.69	4.34-10.40	2.89-5.22
Al	44.64-61.53	35.05-58.97	41.68-52.97
Mn	185.74-349.28	131.29-192.97	142.26-538.50
As	2.54-2.93	2.84-3.43	2.76-3.53
Zn	20.64-36.64	32.81-58.16	34.19-37.65
Fe	567.00-587.00	381.00-546.00	504.00-3077.00

*Concentration in $\mu g.L^{-1}$

Figure 3, 4 and 5 shows the removal percentages for the first phase of treatment process by anaerobic condition using UASB-R1, HUASB-R2 and HUASB-R3 system for Cd, Pb, Al, As and Zn in average percentages. While in the removal percentage of successive combined system treatment anaerobic-aerobic UASB-DFAF(R1), HUASB-DFAF(R2) and HUASB-DFAF(R3) are presented in figure 6, 7 and 8. Heavy metal is arranged from higher to lower heavy metal removal for overall system. According to figure 6, 7 and 8, heavy metal removal could be classified in the following range of heavy metal removal (overall combined system):

- High removal efficiency (average): Al > Pb (Ranging from 78% to 82%)
- Medium removal efficiency (average): Zn > Cd > As > Fe (Ranging from 52% to 64%)

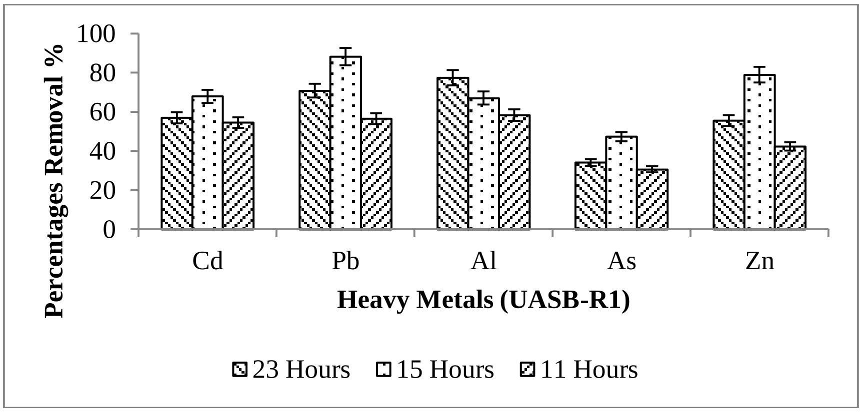

Figure 3: Removal percantages of heavy metals in UASB-R1 reactors at different HRT

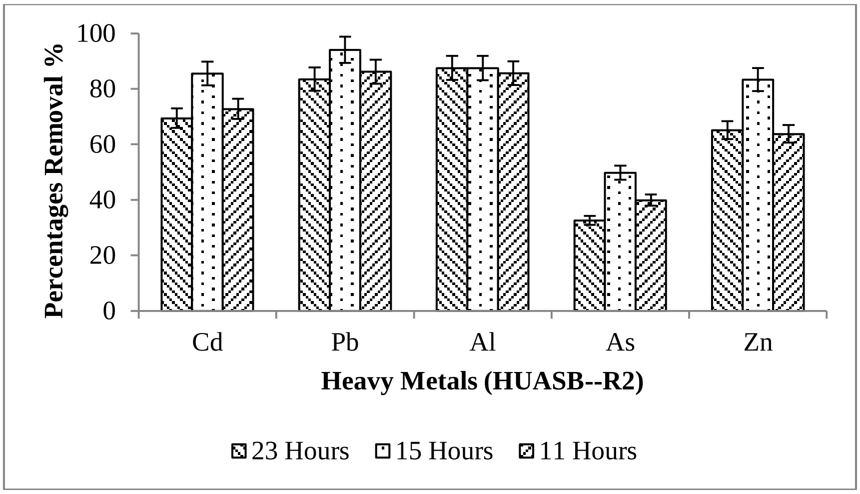

Figure 4: Removal percentages of heavy metals in HUASB-R2 reactors at different HRT

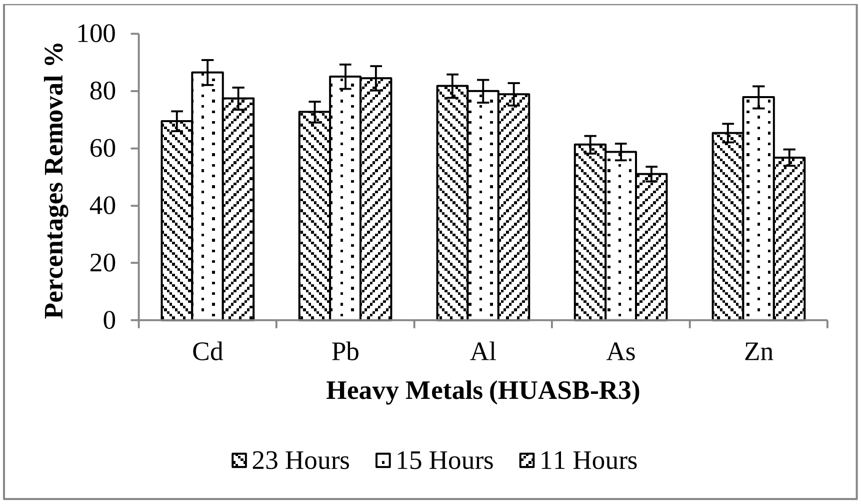

Figure 5: Removal percantages of heavy metals in HUASB-R3 reactors at different HRT

Removal of heavy metals in all reactors took place mainly in the UASB and HUASB shown in figure 3, 4 and 5. The pattern of removal of heavy metal in anaerobic condition has shown removal percentages over 50% for, Al, Pb, Zn and Cd, but for As removal percentages is below than 50% for UASB-R1 and HUASB-R2. For Zinc the average removal in UASB-R1 is 58.95%, while in HUASB-R2 and HUASB-R3 average percentage removal of heavy metal is 70.73% and 66.63% respectively where the HRT 15 hours shown the best removal for zinc. For Arsenic, the average percentage removal increases from 37.35% in reactor UASB-R1 to 40.76% in reactor HUASB-R2 and 57.01% in reactor HUASB-R3 respectively. Similar removals of heavy metal were registered for Al, Pb, and Cd from average percentages removal from 67.59% to 86.92% for Al, from 71.82% to 87.93% for Pb, and from 59.77% to 75.91% for Cd.

Fe and Mn were observed to increase in concentration after treatment. (Varga et. al. 2013) mentioned that behaviour of Fe could be attributed to high solubility of iron oxides in the anoxi/anaerobic conditions which prevailed in all the units of treatment sample, and it was shown in this UASB reactor, but for both HUASB reactor R2 and R3 shown the increasing of removal efficiency for Fe because of presence of media zeolite and coconut activated carbon help the process of metal absorption. (Bernad E. et. al 2013) reported that the removal efficiency of Fe by using coconut activated carbon over 75% with pH value 2 to 6. A decreased percentage removal of Mn supported with (Kröpfelová *et al*., 2009) finding, the higher solubility of Mn oxides species in anaerobic conditions and the fact that Mn does not readily form an insoluble sulphide phase may explain the wash out of this metal from the system.

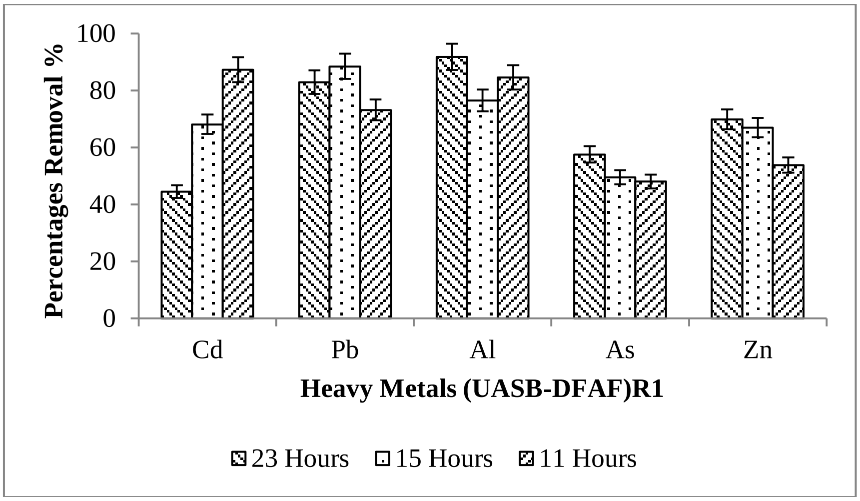

Figure 6: Removal percantages of heavy metals on combined UASB-DFAF(R1) reactors at different HRT

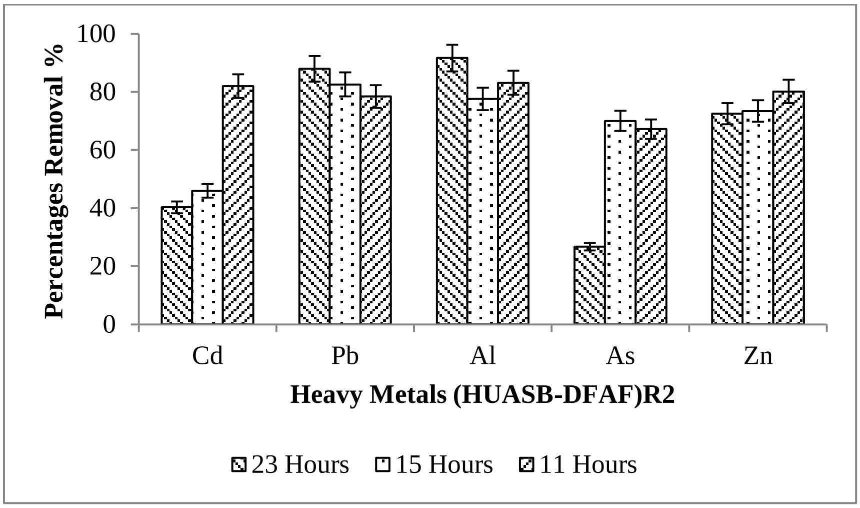

Figure 7: Removal percantages of heavy metals on combined HUASB-DFAF(R2) reactor at different HRT

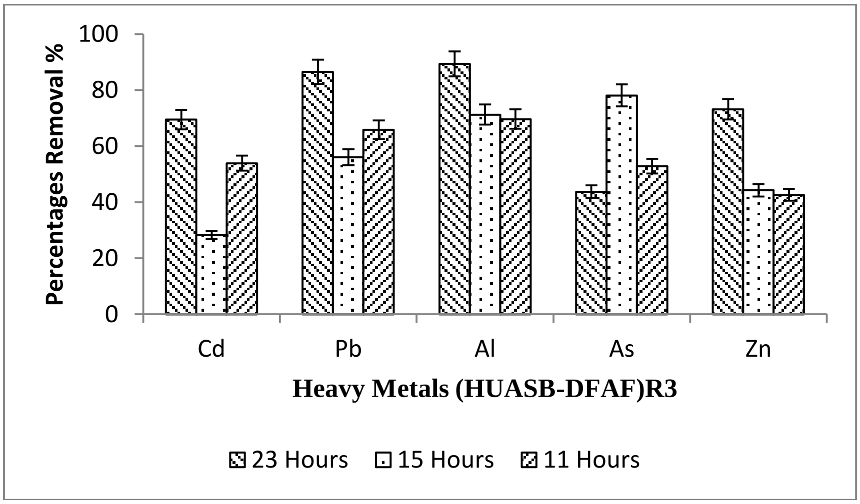

Figure 8: Removal percantages of heavy metals on combined HUASB-DFAF(R3) reactor at different HRT

Figure 8 shown a high efficiency in removal of most heavy metal, in particular of Cd, Pb, Al, As and Zn with average percentage removal 51.70% to 84.48% for UASB-DFAF (R1) and in HUASB-DFAF (R2) the removal efficiency of Cd, Pb, Al, As and Zn was maintained from 54.65% to 84.13% and 53.35 % to 76.73% for reactor HUASB-DFAF (R3). The average removal efficiency for Fe in all combined reactor is around 36.73%. (Lesage et. al. 2007) reported exportation of particulate Fe under anaerobic condition lead a negative value of removal efficiency. As indicated by (Lesage et. al. 2007) and (Kröpfelová *et al*., 2009), reduced manganese compounds are very soluble and therefore they are washed out under anaerobic condition and was fed into the second phase of treatment DFAF.

3.3 Comparison between Combined Reactors with Element of Heavy Metal

The results of these studies have been compared to determine the best reactor to removed metal from domestic wastewater. Figure 9, 10, 11, 12, and 13 shows the removal percentages of Cd, Pb, Al, As Zn, and Fe respectively. For Cd, reactor R1 and R2 had shown removal percentages of 87.27% (R^2=0.99) and 82% (R^2=0.85) respectively for HRT of 11 hours. While for R3, best removal shown was at HRT 23 hours. As for Pb, the pattern of higher removal were shown in reactor R2 and R3 with 87.91% (R^2=0.99) and 86.47% (R^2=0.44) at 23 hours HRT, but in R1 has shown the best removal was at 15 hours HRT.

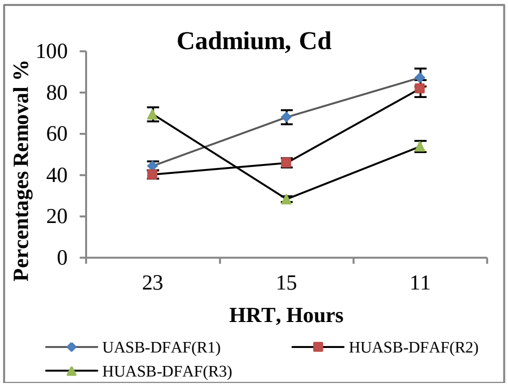

Figure 9: Comparison removal percentages of Cadmium between combined system and HRT.

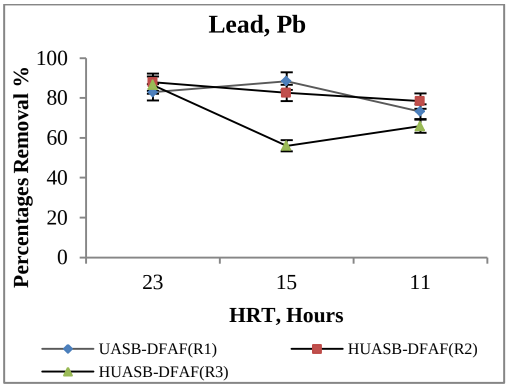

Figure 10: Comparison removal percentages of Lead between combined system and HRT.

Figure 11, 12 and 13 represent heavy metal Al, As and Zn respectively. Aluminum in figure 11 has shown the best removal percentages for reactor R1, R2 and R3 with HRT 23 hours, whereas R1 at 91.73% (R^2=0.22), R2 at 91.68% (R^2=0.36) and R3 at 89.34% (R^2=0.81). Meanwhile, Arsenic R2 at 70% (R^2=0.70) and R3 at 78.09% (R^2=0.07) shown a removal percentages higher than with HRT 15 hours but R1 at 57.53% (R^2=0.87) with HRT 23 hours. Removal percentages for Zinc showed R1 at 69.85% (R^2=0.88), R3 at 73.19% (R^2=0.79) in HRT 23 hours while R2 was at 80.16% (R^2=0.84) with HRT 11 hours.

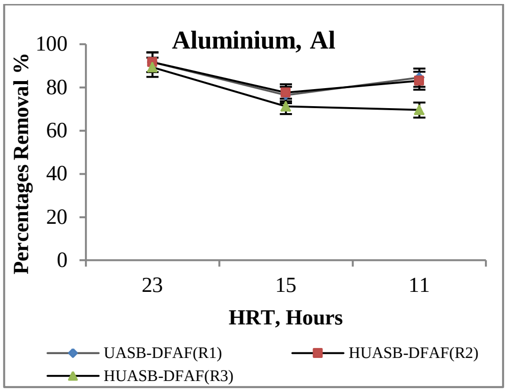

Figure 11: Comparison removal percentages of Aluminium between combined system and HRT.

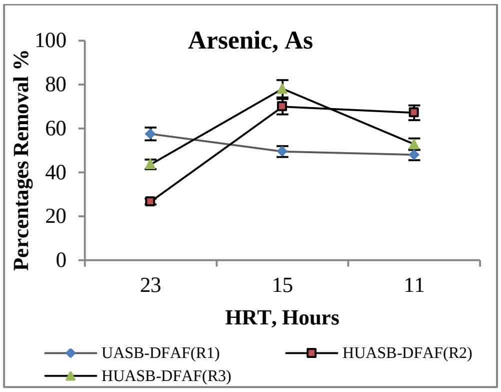

Figure 12: Comparison removal percentages of Arsenic between combined system and HRT.

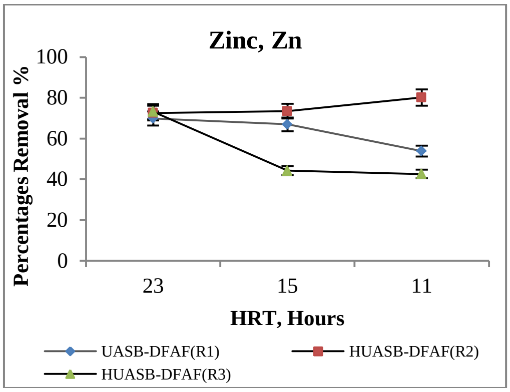

Figure 13: Comparison removal percentages of Zinc between combined system and HRT.

4.0 Conclusion

This paper has highlighted the removal efficiency of heavy metals by using anaerobic and aerobic reactor. The zeolite and activated carbon are waste substances and has been proven very efficient in removing heavy metals. The UASB-DFAF and HUASB-DFAF system treating municipal wastewater showed a potential treatment system to remove heavy metal as reported in previous studies. The high removal efficiency was found for some metal in following order: High removal efficiency (average): Al > Pb (Ranging from 78% to 82%). Medium removal efficiency (average): Zn > Cd > As > Fe (Ranging from 52% to 64%). Negative removal efficiency (average). Removal efficiency of total

HMs was very similar in UASB/HUASB and DFAF reactors, when expressed with respect to the influent to the respective treatment system. The removal of heavy metals took place in both reactors. The operation of reactor performance will be continuously researched to determine the long term removal behaviour.

5.0 Acknowledgement

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