MMT Nano-clay and Gasified Cinnamon Biochar Embedded Horizontal Flow Bio-Geo Filter For Treating Laboratory Wastewater

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Abstract –*Clay and activated carbon are widely used absorbents for treatment processes. Identify the presence of Montmorillonite (MMT) clay in naturally occurred clay deposits in Murunkan and scrutinize the contaminants in laboratory wastewater construct and operate an eco-friendly and efficient treatment system for laboratory wastewater. FTIR, XRD and TGA were done to verify the presence of MMT in the clay sample. Gassified cinnamon biochar by-product of syngas production, plays a key role removing pollutants from laboratory wastewater due to its distinctive physiochemical properties such as higher SSA, lower H/C & higher O/C molar ratio in CHN analysis. Operating the treatment system Horizontal Flow Constructed Wetland with gassified cinnamon biochar and MMT clay from Murunkan as a filter media gives eco-friendly and efficient solution for contaminated laboratory wastewater.*

Keywords: *MMT clay, biochar, Constructed Wetland, Laboratory wastewater*

1 INTRODUCTION

Laboratory wastewater means used water from laboratories, which contains lots of chemical, biological, pathogenic, toxic and hazardous substances. International Biochar Initiative defines biochar as a solid material obtained from thermo chemical conversion of biomass in an oxygen limited environment (IBI, 2014).

Most of the laboratories in Sri Lanka, onsite storing their hazardous wastages for a maximum period of 90 days or a maximum quantity of 10,000 kgs, permitted by the CEA. Currently National Environmental (Protection & Quality) regulation No. 01 of 2008 by the gazette notification No 1534/18 is in practice for the Management of Scheduled Waste in Sri Lanka. Collection and transportation of scheduled waste to off-site storage, treatment and /or disposal facility done by the registered and licensed persons. Ultimately these scheduled wastages can undergo Recovery Co Processing and Recycling, Treatment and Disposal process based on its category. Some laboratories are operating owned treatment and disposal systems. Meanwhile, wastewaters from few laboratories were released to the canals, rivers, sewers, municipal wastes, and other water streams without proper treatment. There are lots of hazardous and toxic chemicals in it, which causes diseases to human and pollute our environmental system (Waste Management Unit, 2008).

Soluble inorganic arsenic is acutely toxic, and ingestion of large doses leads to gastrointestinal symptoms, disturbances of cardiovascular and nervous system functions, and eventually death (Brain et al., 2014). Environmental laboratory in Nawala Campus extend its valuable services to all diploma and undergraduate students for all regional centres. This laboratory uses lots of toxic and hazardous chemicals for the experiments hence the wastewater contains harmful Heavy Metals, Toxic substances, and other pesticides. Physical and chemical pollutants from laboratory wastewater contain heavy metals such as As, Cd, Hg, Pb, Cr, etc, Soluble Organic materials, Inorganic Particles (sand, grit, metals, ceramics), Soluble inorganic materials (Ammonia, Cyanide, Hydrogen Sulfide), Toxins (Pesticide, Herbicide, Poisons), Pharmaceuticals, etc. Biological pollutants from laboratory wastewater contain pathogens.

As there is no sufficient researches and solutions found specifically in this area, it will be a good proposal to treat low flow rate and highly toxic laboratory wastewater in an eco-friendly, efficiently and environment friendly manner. To ensure the safeguard of the eco system it becomes necessity to remove the harmful elements before discharging to the natural water bodies. Solutions like conventional treatment system cannot be proposed due to its corrosiveness of pipelines, low flow rate, high toxicity, flammability, expensiveness and maintenance difficulty of chemical treatment process. Horizontal flow constructed wetlands by using bio-geo filters are well suited for this purpose.

Hence this research was focused on development of a filter media with locally available materials such as MMT clay and biochar to removes contaminants from wastewater. Generally, out of the clays in the smectite group, MMT has preferred in the synthesis of adsorbents as low-cost adsorbent due to its availability, high cation exchange capacity, high surface area non-toxicity, high biocompatibility and low-cost as an adsorbing material (Akbari et al., 2017) and porosity. Biochar is a porous solid material, which is obtained from the carbonization of biomass and it has been successfully used to adsorb a wide variety of metal contaminants. There are many characteristics of Biochar such as rich in carbon, stable solid, non-toxicity, high surface area, high cation exchange capacity and low-cost raw material as an adsorbing material (Lawrinenko, 2014).

A combination of biochar and MMT clay minerals several advantages for environmental application. Since both of these materials are low-cost and possess good adsorption capability. The objectives of this paper is to construct and operate an eco-friendly and efficient solution laboratory wastewater treatment system with MMT clay and biochar.

2 METHODOLOGY

2.1 Collection of sample

Clay samples were collected from various locations, which are distributed in the Murunkan area in Mannar district of Northern Province in Sri Lanka. Fig.1 shows clay sampling locations in Murunkan area. Table 1 lists all the location of these samples. Collection of samples was done at a depth of 0.9 m from the surface.

Wet sieve analysis was done for collected samples from 63μm sieve to remove any organic and coarse particles present in the clay. Then each of the specimens was dried in the oven at 110°C-120°C. The dry specimens were grinded to make the powder and dry sieve analysis was performed from 150μm sieve. Down draft gasifier operates at 700°C used for the production of syngas to the boiler to produce steam for laundry and calorifier. By-product of this gasifier called cinnamon biochar was used as a filter media in this research.

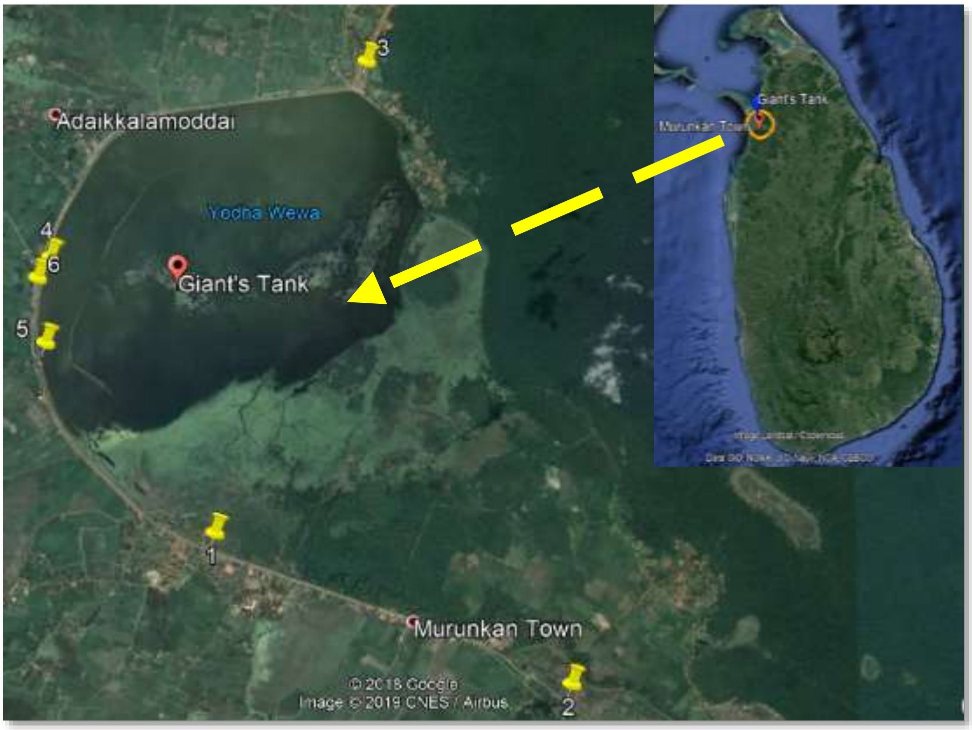

Fig.1. Clay sampling locations of Mannar district in Sri Lanka

2.2 Characterization of raw samples

After that, the initial particle size analysis was carried out for each specimen using the Laser particle size analysis technique. According to the particle size analysis results, the clay sample which is collected near the Basin of the Giant's tank was selected as the best location due to high percentage of clay fraction (beyond this the clay sample which was collected near the basin of the Giant's tank will be defined as the clay sample) and it was subjected to other analysis. To remove organic materials from the clay sample, it was heated up to 300°C for 1 hour.

Resultant powder of the clay sample was subjected to Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), and Thermal Gravimetric Analysis (TGA) to verify the presence of MMT. 20mg of the clay sample was subjected to FTIR analysis and this analysis was carried out by using Bruker Vertex80 FT-IR Spectrometer for mid-infrared frequency range, approximately 4000-400 cm^{-1} .4g of the clay sample was subjected to XRD to ensure the presence of MMT and to verify the FTIR results. XRD was carried out using Bruker D8 Focus X-Ray Diffractometer. TGA test was done using TA Instrument- SDTQ600 Thermal Gravimetric Analyser by heating the clay sample from ambient temperature to 1000°C (10°C /min). The basic principle in TGA is to measure the mass of a sample as a function of temperature.

Carbon Hydrogen and Nitrogen (CHN) analysis of biochar sample was carried out to determine the carbon, hydrogen and nitrogen elemental concentrations by using Perkin Elmer 2400 Series II CHNS Analyzer. X-Ray Fluorescence (XRF) analysis of both clay and biochar samples were carried out to identify the chemical composition by using HORIBA Scientific XGT- 5200 X-ray Analytical Microscope. All of these analyses were carried out at the Sri Lanka Institute of Nanotechnology (Pvt) Ltd, Sri Lanka.

The wastewater sample was undergone some physical and chemical tests for characterization. 200ml sample from each wastewater container was collected; properly mix those together to prepare the composite sample. A 10ml sample was collected from this composite sample and then diluted with 1000ml distilled water. Model No: DR 900 colorimeter is used to measure Dissolved phosphate and TKN content in the wastewater. Model No: FOC 225 incubator used to measure BOD value in the barometric method. Model No 3510 pH meter used to measure pH value. After filtration, effluent from the treatment system underwent physical and chemical characterization of wastewater. This effluent quality is analysed with CEA inland surface discharge standards.

2.3 Preparation of treatment unit

Treatment unit was constructed with bio materials such as macrophytes and geo materials such as biochar, calicut tile, MMT clay and aggregates. There were 4 tanks in the treatment system. Tank no 1,2 & 3 planted with cannas while tank no 4 is with cattail. These wetland plants collected from Kelaniya wetland areas. These plants up take pollutants in soluble format and deposit in its roots, stem and leaf.

Laboratory wastewaters are small quantity and highly contaminated, composite sample of laboratory wastewater collected and then diluted to 1:70000 volume batches finally allowed to pass through the treatment system. Effluent quality from each tank was tested for each batch of samples.

3 RESULTS AND DISCUSSIONS

3.1 Characterization of clay sample

3.1.1 Laser Particle Size Analysis for Clay Samples

According to the laser particle size results shows in Fig.2, the clay sample (sample no 5) had a high percentage of clay fractions which has fallen below 2 μm size when comparing with the other five samples and that sample was selected to perform other analyses.

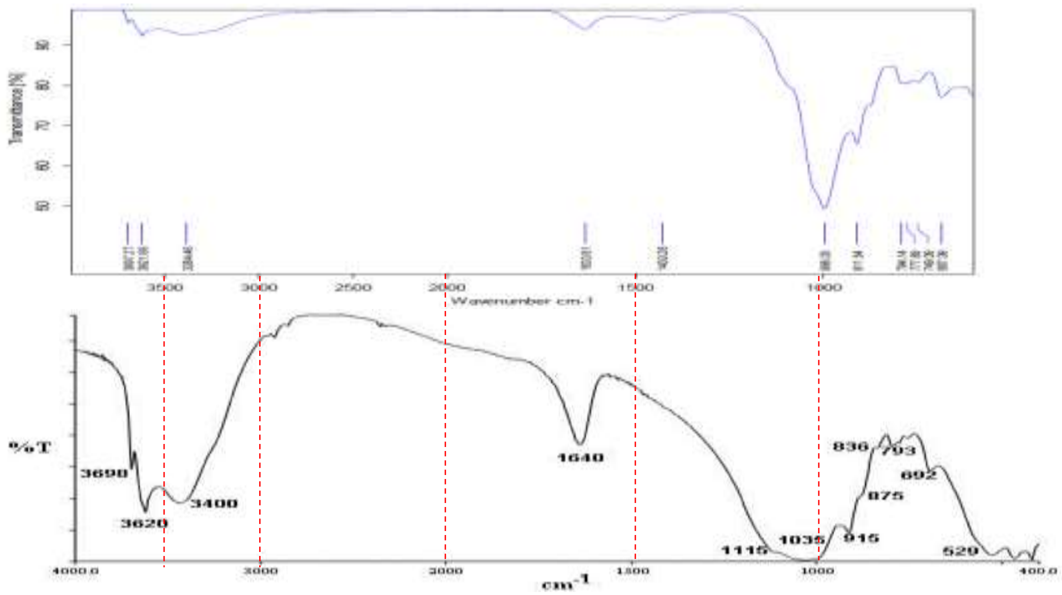

Fig.3. FTIR results for samples (a) clay sample; (b) pure MMT (Patel et al.,2006)

3.1.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis for Clay

The clay sample, which was considered the FTIR results, has shown in Fig.3 and Table 1 summarizes the adsorption bands found in the spectrum.

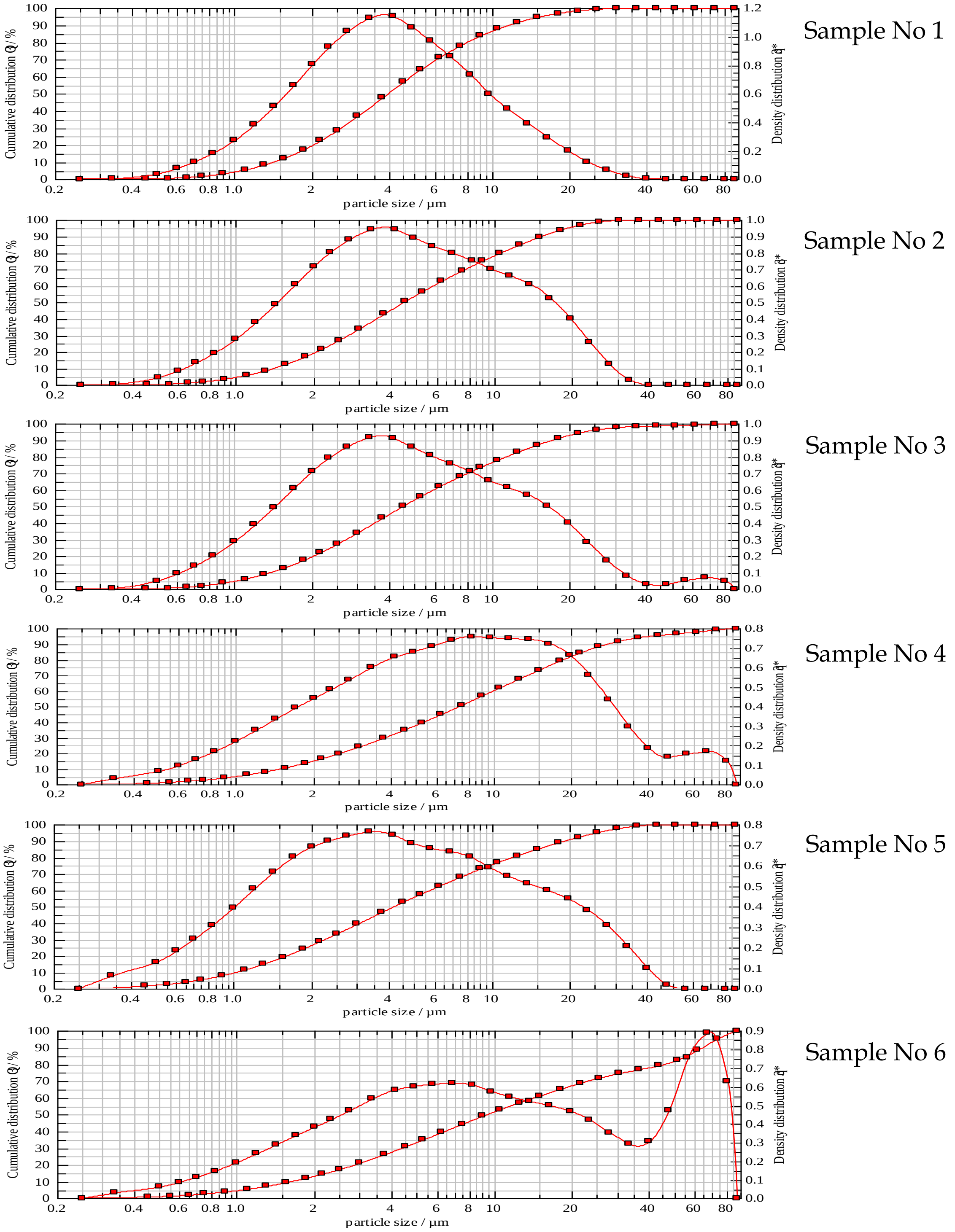

Fig. 2. Particle size analysis results of clay samples

Table 1 Adsorption bands in the FTIR spectrum

Absorption Bands	Pure Montmorillonite (Patel et al.,2006)	Clay sample
1	3698	3697.27
2	3620	3621.66
3	3400	3384.46
4	-	1633.81
5	1640	1430.28
6	-	-
7	1115	-
8	1035	998.03
9	-	-
10	915	911.54
11	875	794.14
12	836	777.89
13	793	749.09
14	692	687.09
15	529	-

According to the results of the FTIR analysis for the clay sample, FTIR absorption peaks of MMT clay mineral was identified. Most important bands which are needed to identify the MMT clay mineral in the test range are 3620.66, 3384.46, 998.03, 911.54, & 529 which are present in the test specimen.

When comparing the FTIR analysis of pure MMT with the FTIR analysis of clay sample, FTIR adsorption peak values of MMT of clay sample shows similar value to the Literature values of MMT clay mineral. This verifies that the clay sample consists of MMT clay mineral. Hence, it helps to remove heavy metals from laboratory wastewater.

3.1.3 X-Ray Diffraction (XRD) Analysis for Clay

Variation of intensity was obtained against the changing angle on a strip chart and obtained the result shown in Fig.4. The intensity of each peak in XRD analysis is proportional to the amount present in each mineral and the intensities of other peaks change when the intensity of the main peak varies. Due to this reason, some peaks may not be visible and difficult to detect in the XRD analysis.

According to the XRD analysis, the maximum intensity peak was recorded for MMT and there is considerable amount of peak values are indicated for MMT on this graph than other minerals. This verifies that the clay sample consists of MMT clay mineral.

3.1.4 Thermal Gravimetric (TGA) Analysis for Clay

The result of the thermos gravimetric analysis for the clay sample is shown in Fig.5. Exothermic peaks that occur due to the presence of MMT clay mineral and quartz will be present after 1000 ^{0}C. So that the data obtained from this experiment, also confirm the presence of MMT clay mineral. The values in the range of 650 - 700 °C are as a results of loss of hydroxyl in MMT (Adikary and Wanasinghe, 2012). According to this pattern, it can be verified that the clay sample consists of MMT clay mineral.

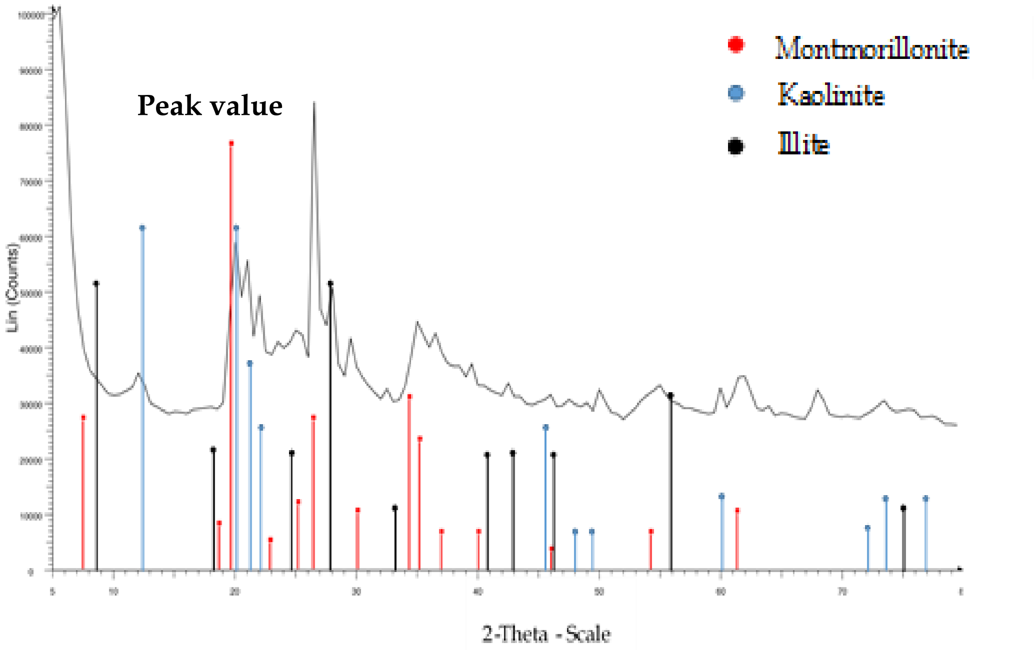

Fig.4. XRD Analysis for clay sample

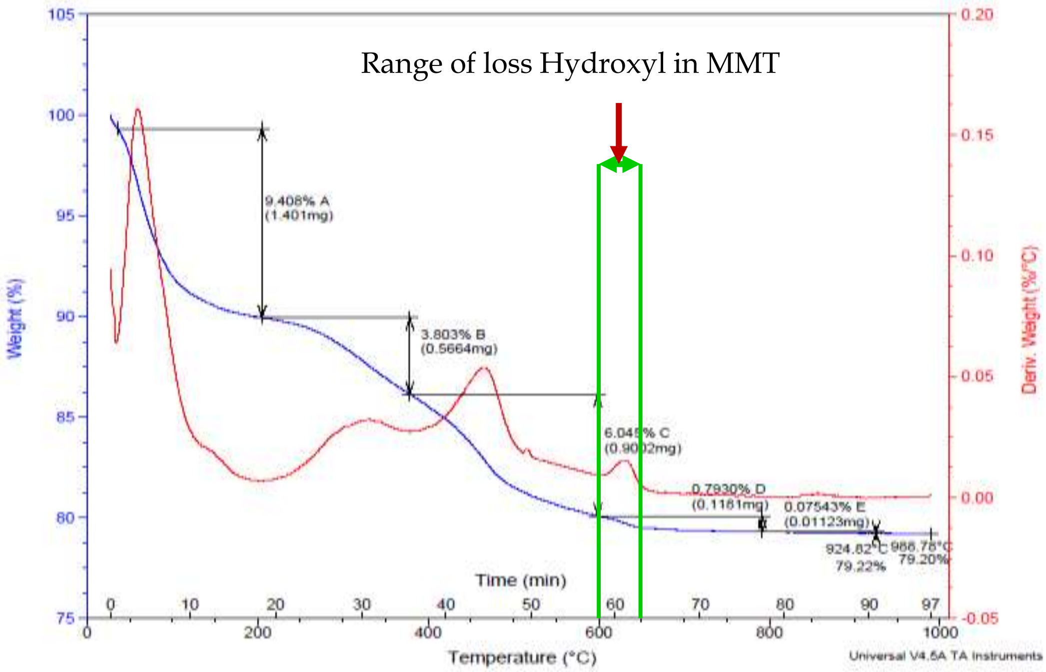

Fig.5. Thermal Analysis for clay sample

3.1.5 X-Ray Florescence (XRF) Analysis for Clay

The results of this analysis for raw samples are denoted in Table 2 and this table indicates the most prominent elements that are present in the adsorbent on a mass percentage basis. MMT clay minerals have structures of Fe^{2+}, Fe^{3+} and Mn^{2+} ions in octahedral sheets embedded with metal cations like Si^{4+} and Al^{3+} in the tetrahedral layers (Muriithi et al., 2012). Therefore, this clay sample signified presence of MMT clay minerals.

Table 2 Chemical composition of clay

Element	Biochar mass %
Al	-
Si	7.47
P	2.74
S	2.01
K	86.61
Ca	-
Ti	0.85
Mn	0.61
Fe	2.64

3.2 Characterization of biochar sample

3.2.1 X-Ray Florescence (XRF) Analysis for biochar

Biochar sample were subjected to XRF analysis to determine the elemental composition of materials. The results of this analysis for raw samples are denoted in Table 3 and this table indicates the most prominent elements that are present in the adsorbent on a mass percentage basis. The extractable cations from the biochar consisted of mostly Ca, K and Mg, with lesser amount of Na, Mn, Ba, Fe and Sr (Brewer et al., 2012).

Table 3 Chemical composition of biochar

Element	Clay mass %
Al	17.10
Si	57.89
P	-
S	0.37
K	4.25
Ca	4.31
Ti	2.39
Mn	0.38
Fe	19.40

3.2.2 Carbon Hydrogen Nitrogen Analysis for biochar

The CHN analysis results for biochar sample was represented in Table 4. Generally, biochar consists of rich in carbon. According to the results cinnamon biochar has high carbon percentage. And other elements such as Hydrogen and Nitrogen percentages are more less when considering carbon percentage.

Table 4 CHN results of biochar

Sample weight	Element	Mass %
1.982 mg	Carbon (C)	79.88
	Hydrogen (H)	1.46
	Nitrogen (N)	0.84

Biochar produced at higher temperature facilitated the release of volatile materials and created more pores, resulting in larger surface area (Vithanage et al., 2016). By compared with other materials cinnamon biochar shows higher BET specific surface area of $563m^2/g$ via BET analysis. Hence, it shows more affinity for adsorption and enable to separate various heavy metals from laboratory wastewater. According to elemental analysis data, carbon content in gasified cinnamon biochar was 79.88%. Breaking of weaker bonds in biochar structure and removal of water, hydrocarbons, H_2, CO and CO_2 during pyrolysis at high temperature may cause lowering in O and H contents in tea waste biochar pyrolysis at 700°C and rice husk biochar pyrolysis at 700°C than those biochar produced at <700 ^{0}C (Ahmad et al., 2014).

Moreover, molar ratio values of O/C cinnamon biochar was 0.30. As molar ratio of O/C is indicative of the polarity, biochar may express more hydrophilic (Kuhlbusch, 1995). The raw wood sawdust had relatively high H/C atomic ratio, reflecting low aromaticity compared to that of the biochar samples. The C/N ratio obtained for biochar produced at 450°C and 550°C were greater than 20.

3.3 Characterization of laboratory wastewater

Laboratory wastewater key parameters against the CEA's standard "tolerance limits for the discharge of industrial wastewater in to inland surface waters" were tested and tabulated. Important parameters of the influent tabulated in Table 5. All the parameters are really high especially; heavy metal concentration in the laboratory wastewater is extremely high. The EC values give measure of the total water soluble ions (salinity).

Table 5 Important parameters of the influent wastewater

Parameter	Unit	Results
Ph @ ambient temperature		2.05
Electric Conductivity	ms/cm	3212
Biochemical Oxygen Demand (BOD5 in five days at 200C)	mg/l	12500
Dissolved Oxygen	mg/l	226

Total Dissolved Solids	g/l	1020
Resistivity	MΩ	-100
Turbidity	NTU	820
Fluorite	mg/l	106
COD	mg/l	22,500

Further analysis was done to identify the existing elements in the laboratory wastewater. Fig.6 illustrates the elements of OUSL environmental laboratory wastewater. As according to the available elements' removal mechanism should be identified.

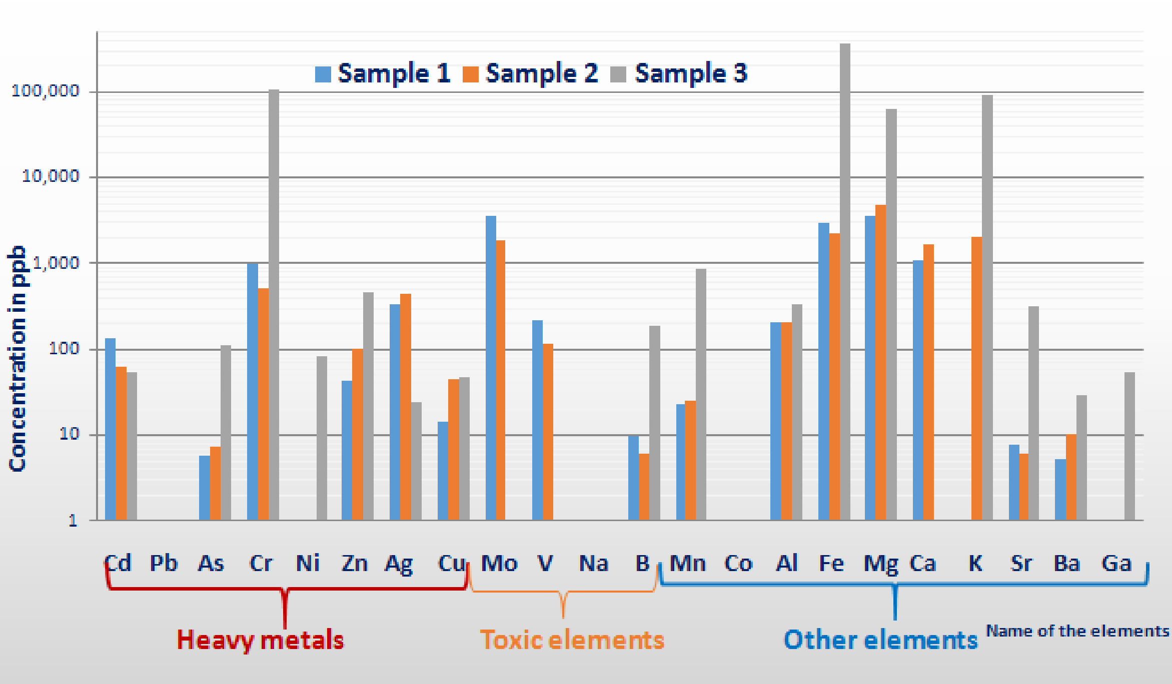

Fig.6. Elements of OUSL Environmental laboratory wastewater

3.4 Subsurface Flow (SSF) Constructed Wetland System

The laboratory wastewater was allowed to pass through the prototype model then the effluent quality from each tank was recorded. For this purpose, previously used abandoned horizontal flow subsurface constructed wetland treatment system for this purpose with locally available materials.

Constructed wetland is selected due to its simplicity, inexpensiveness, eco-friendly and efficient treatment for heavy metals. Typically, filter media for wetlands include laterite soil, sand, gravel, etc. Gravel is used as the filter media as it provides a large surface area for biochemical processes. It provides high conductivity which is required to stabilize hydraulic retention time of wetland. Sand is considered as the most suitable filter media in relation to hydraulic and organic loading. In this research biochar, 20mm aggregates and Calicut tile are selected as filter media.

Sand and coir mixed layer followed by 24mm thick laterite layer was designed to facilitate the vegetation roots growth and water supply for plants. Fig.7 illustrates cross section of the treatment system. Further, Fig.8 shows the plan view of the treatment unit. Laboratory wastewater sample contains lots of pollutants at high concentrations, especially heavy metals. Sand and gravel cannot treat the wastewater in an effective manner. Calicut tile and 20mm coarse aggregates used as filter media helps to increase the permeability of wastewater treatment system. Influent BOD value was taken from the composite sample collected from the environmental laboratory's onsite storage tank and diluted to 1:70000 volume ratio.

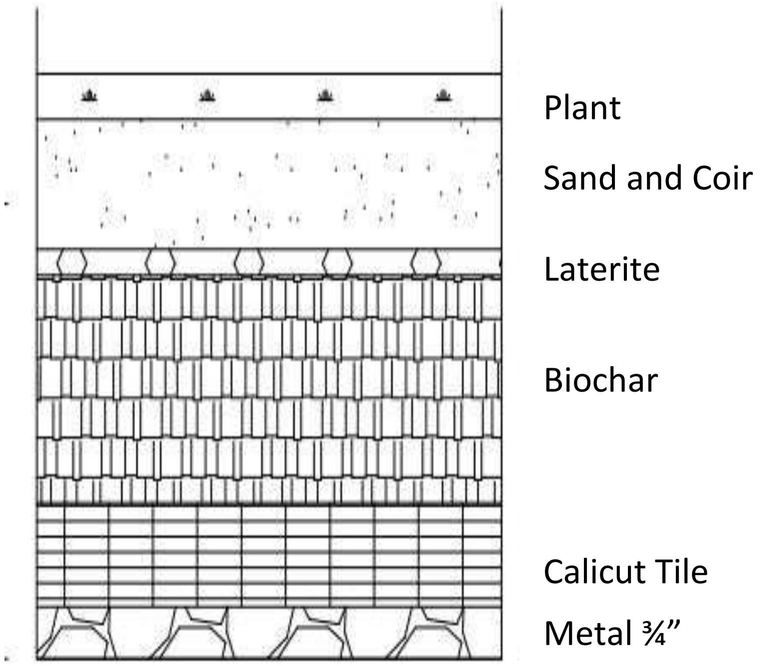

Fig.7. Cross section of the treatment System

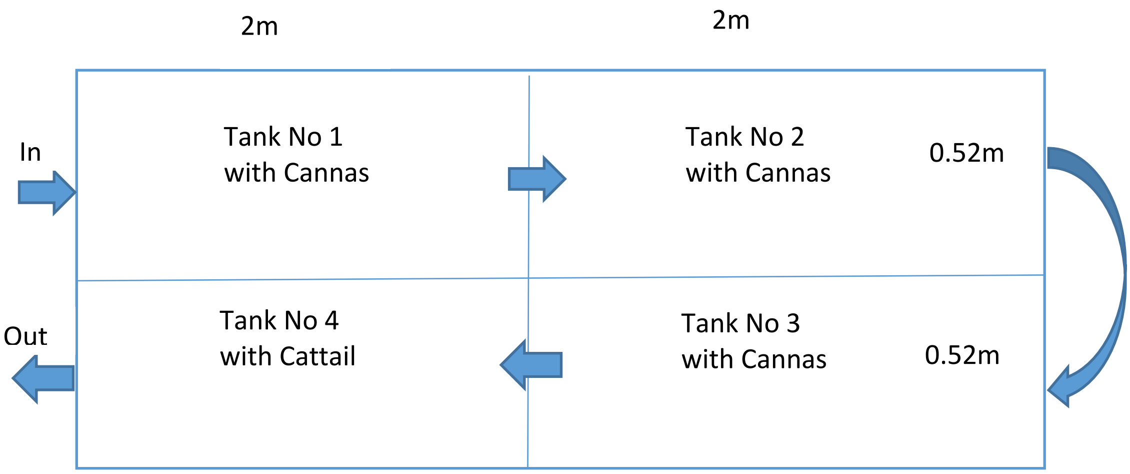

Fig.8. Plan view of the treatment system

Table 6 Characterization of effluent laboratory wastewater

Testing Parameter	Unit	Influent	Effluent	Removal %
Turbidity	NTU	2.5	1.02	59
pH at ambient temperature		6.9	7.4	
Biochemical oxygen demand (BOD_5 in five days at 20^0C)	mg/1, max.	90	30	67
Chemical oxygen demand (COD)	mg/1, max.	810	242	70
Dissolved phosphates (as P)	mg/1, max.	1.73	1.2	31
Total Kjeldahl nitrogen (as N)	mg/1, max.	1.7	1.1	35
Electrical Conductivity	µS/cm	725	425	41
Total Dissolved Solids	mg/l	225	106	53
Salinity	g/l	0.9	0.4	56
Resistivity	MΩ	-1	-1	
Temperature	° C	29.1	28.2	

Key parameters such as electric conductivity, Total Kjedahl nitrogen (as N), Biochemical Oxygen Demand (BOD_5 in five days at 20^0C), Dissolved phosphates (as P), turbidity, total dissolved solid and Chemical Oxygen Demand (COD) were reduced and effluent satisfies the discharge standard of tolerance limits for the discharge of industrial wastewater in to inland surface waters. Table 6 shows the physical and chemical parameters in the treatment unit. When considering results, Variation in all parameters were gradually decreased from tank no 1 to 4 and satisfies the CEA's discharge standard.

The biomass has the capability to reduce the concentration of total dissolved solids (TDS), turbidity and electric conductivity, when the biomass was pyrolysed under oxygen limited condition, biomass is transformed into biochar, which is a carbon rich, porous, high surface area with high adsorption capacity (Vijayaraghavan, 2019; Wu et al., 2019) and an average COD reduction of 73% for biochar columns when treating raw wastewater with an anaerobic biofilter (Kätzl, K et al., 2014). In aqueous environment, some antibiotic compound, cations tent to be adsorbed by MMT clay mineral due to it has large surface area and high surface capacity (Wu. Q et.al.,2010; Li Z et.al., 2010). Therefore, it can be concluded that concentration of all parameters were reduced due to the filter media of gasified cinnamon biochar and MMT clay mineral.

4. CONCLUSION

All of the initial analysis of the specimen such as Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), and Thermal Gravimetric Analysis (TGA) are revealed that there is significantly presence of MMT clay in Murunkan area in Sri Lanka. Hence Murunkan clay deposit can be used to extract MMT clay and used in the wastewater treatment unit forth tank in order to remove pollutant. This extracted MMT give great removal efficiency for pollutants in the laboratory wastewater. BET specific surface area of $563m^2/g$ increases water retention capacity. Hence, remove the heavy metals from wastewater through adsorption, precipitation, CEC, ion exchange, complexation etc. Molar ratio of O/C is 0.3 indicative of the polarity, biochar may express more hydrophilic. Thus biochar plays the major role in removing contaminants especially the heavy metals from the laboratory wastewater. Due to the intrinsic properties of clay and biochar this proto type model gives over all good removal efficiency for physical and chemical parameters of laboratory wastewater.

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