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Detection of benzene in landfill leachate from Gohagoda dumpsite and its removal using municipal solid waste derived biochar

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Abstract: Numerous landfill associated volatile organic compounds (VOCs) are emerging concern due to their potential risk of health. Benzene is one of the most common VOCs in landfill leachate. Biochar has bulged as a universal sorbent for the removal of contaminants from water and soil. Hence, this study examines the potential of biochar derived from municipal solid waste (MSW-BC) on adsorption of benzene so that MSW can be recycled to treat its own pollutants. Landfill leachate was collected from five sampling points at Gohagoda MSW dumpsite and analyzed for benzene. In order to evaluate the potential of MSW-BC for removal of benzene from water, the equilibrium adsorption was procured by using headspace GCMS. The effects of pH, contact time and sorbent (1-10 g/L), sorbate (30-300 µg/L) concentration were investigated using a batch sorption technique. Benzene was detected in landfill leachate, approximately 20 µg/L. The batch experiments indicated that benzene adsorption was dependent solution pH and percentage removal became higher above pH 7 and highest adsorption 42.7 µg/g was observed within 24 hours at pH 9. Maximum saturated sorption capacity of MSW-BC for benzene was 87.0 µg/g. Preliminary experiment data suggest a potential of MSW-BC to be utilized as a material for VOC remediation from MSW dumpsites.

Keywords: Adsorption, Benzene, Landfill leachate, MSW biochar

1. Introduction

Waste management is a serious problem faced by many countries around the world (Zurbrugg, 2002). Although open dumping is an environmental threat, many Asian countries still allow open dumps as final the disposal method due to financial constrains and operational easiness. However due to the uncontrolled solid waste management, numerous environmental and health problems simulate within the site and the adjacent area of dump. Prioritization of issues lay on landfill toxic gas emission associate air pollution, with global warming potential, and soil water contamination by landfill leachate.

Landfill leachate is formed from the degradation of waste mass by the infiltrated water. It produces organic and inorganic pollutants in a soluble form. There are four major groups of pollutants that can be observed within the leachate; dissolve organics matter, inorganic macro component, heavy metals and xenobiotics organic compounds (Christensen et al., 2001). The xenobiotics organic compounds mean organic compound that are form and emit due to the mixture of chemical products incorporate interaction in landfills. The origin of the xenobiotics belong to anthropogenic sources and include volatile organic compounds (Baun et al., 2004).

The most frequently detected VOCs in landfills are Benzene, Toluene, Ethyl benzene and Xylene (Först et al., 1989, Harkov et al., 1985, Sabel and Clark, 1984). Moreover, VOCs are found in leachate r at low concentrations (Dincer et al., 2006). Nevertheless, VOCs can pose health risks even at very low amounts; such asppb or even less (Leidinger et al., 2014). However, only a few studies in Asian countries have reported regarding

VOCs in landfill leachates although they are highly toxic pollutants.

Benzene is one of the most common VOCs detected in landfill leachates (Först et al., 1989) and it is the primary raw material for polymer production and use in several industries such printing & lithography, paint, rubber, dry cleaning, adhesives & coatings, detergents, extraction and rectification (USEPA, 2003). This may be the source of benzene in landfills. The generated benzene may volatilize and the remaining may leach to groundwater or surface water bodies. Both acute and chronic effects dominant in benzene (Cotruvo and Regelski, 1989). Therefore remediation of benzene from landfill leachate is often crucial for health and the environment. Although many different studies have shown different technologies and media for benzene removal, few studies have focused their attention on biochar for its remediation by using sorption technique. Sustainable MSW-BC utilization for remediation of heavy metal in landfill leachate were reported by Jin et al. (2014) and removal of the organic contaminant pesticide by using green waste biochar was successfully (Zheng et al., 2010). Apart from that, Bornemann et al. (2007) postulates the existence non-linear adsorption behaviour of benzene and toluene in to biochar and it showed the Langmuir isotherms fitting with indicative pore filling process. Biochars (BCs) can be produced by many different feedstocks and use of MSW would be a double benefit in terms of waste reduction and waste reuse. Hence, the objective of this research was to assess the benzene levels in the leachate from Gohagoda MSW dumpsite in Sri Lanka and produce MSW-BC to test its effectiveness on benzene removal.

2. Materials and methods

2.1. Chemicals

Commercially available EPA 524.2 analytes, analytical standards were used in 2000 µg/mL ampules (Sigma Aldrich) and Oxygen-free water was obtained by N_2 gas purging at 30 mins through milli-Q water (resistivity 18 MΩ.cm).

2.2. Leachate

Leachate collection was performed in Gohagoda dumpsite that is located in Kandy centralized around latitude and longitude of 7º 18′ 47.85″ N and 80º 37′ 19.02″ E, respectively (Wijesekara et al., 2014). The open dumpsite spatial distribution is extent up to 2.5 ha. Recent investigation of solid waste generation in Kandy municipal council (KMC) was 152 tons, while few of places are located for waste segregation and application of 3R within the KMC (WACS, 2014). However, the majority of KMC waste from households, fish market, slaughter house and non-infectious hospital pharmaceutical waste are daily dumped without any pre-treatment (Wijesekara et al., 2014).

The leachate samples were collected from points of GS-9, GS-8, GS-7, GS-5 and GS-1 (Figure 1). Triplicate samples were performed in each location and 1 g of NaCl electrolyte stabilization as a peak resolving agent was added into headspace vials. The leachate sample, 10 mL, was filled to reach the gauge line of headspace vial. After the leachate collection, immediately, the vials were crimped tightly to minimize loss of VOCs. Then container transferred to laboratory environment under 4 ºC and samples were analysed for benzene under the headspace GCMS.

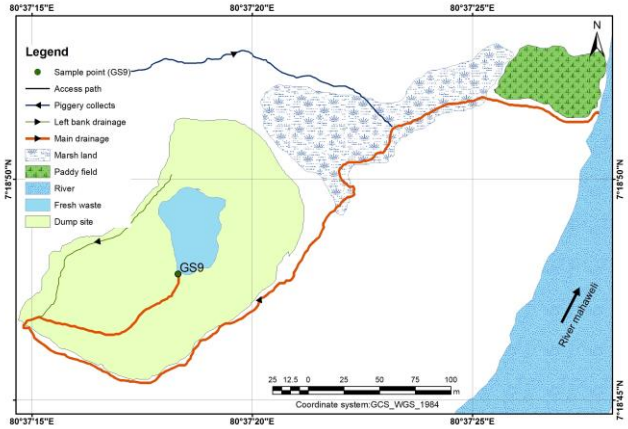

Figure 1: Sampling points in a Gohagoda dumpsite

2.3. Biochar

Segregated organic fraction of the MSW has been used for producing MSW-BC and pyrolysis was performed in batch reactor built in Gohagoda dumpsite under slow pyrolysis. Proximate analysis was conducted based on the experimental procedure described by Ahmad et al. (2013). The moisture content of MSW-BC was determined by drying samples at 105 ºC overnight. For determination of mobile matter content, BCs were heated in covered crucibles at 450 ºC for 1 hr in muffle furnace. Meanwhile ash content was measured by heating samples in open top crucibles at 750 ºC for 1 hr. Finally rest of the resident matter, analogous to fixed matter was calculated from ash, mobile matter and moisture contents. In order to measure pH and electrical conductivity (EC), MSW-BC was dilluted ⋯ . Elemental analysis was performed after oretreatment using microwave (⋯, ⋯) .

The elemental analyzer (Vario MAX CN, elementar, Germany) was used for determination of elemental composition (C,H,N,S and O). Molar H/C and O/C ratios were calculated from the elemental analysis for supportive indications of aromaticity and polarity. Concentrations of heavy metals on biochar were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 4300 DV ICP-OES, US).

2.4. Batch experiments

Batch experiments were performed for MSW-BC and identification of suitable pH to conduct sorption experiment. The 1 g/L of biochar with initial and 4 different pHs (3, 5, 7 and 9) were tested to determine suitable pH. Prior to the addition of benzene the biochar solution was hydrated for 4 hours at shaker in 100 rpm after initial pH adjustment. The sample of 10 mL was filled to reach the gauge line of headspace vial and consequently 25 µL of benzene primary dilution standard amount were spiked into the headspace vial. The samples were shaking overnight at 100 rpm. The kinetic experiment was performed in controlled laboratory conditions and at different time intervals, 0.5, 1, 2, 4, 12, 18 and 24 hr. The isotherm, sorbate (30-90 µg/L) concentration at 24 hrs length was investigated using a batch experiment. For all sorption tests, oxygen free water were used to preparation of samples, immediately headspace vials was crimped tightly to minimize loss of benzene, remaining concentrations data were collected by using GCMS. Non linear curve fitting were performed for identification of possible mechanisms of MSW-BC with Benzene.

2.5. Analytical method

Quantitative analyses of the Benzene standards and samples were performed using gas chromatograph (GC, Shimadzu QP 2010 plus, Japan) equipped with mass detector (QP 2010 ultra-MS), and a Shimadzu HS-20 head space auto-sampler. Chromatographic separations were accomplished with a 20 m Rtx-624 column in 0.18 mm i.d. and 0.001 mm film thickness (Restek Scientific Inc.) using injections in the split mode (1/30). The oven temperature was held at 35 ºC for 2 mins and then increased up to 230 ºC with a gradient of 20 ºC min^{-1} holding for 3 mins at final level. The temperatures of the injector and detector were 200 ºC and 200 ºC, respectively. Ultra high purity helium was used as the carrier gas at a flow of 24.7 mL/min with a constant rate.

3. Result and discussion

3.1. Characteristics of leachate

All the leachate samples of exceed MCL (0.005 mg/L) of benzene in water. The obtained values are summarized in Table 1.

Table 1: Benzene concentration in Gohagoda leachate

Sample point	Benzene concentration µg/L
GS-1	18.3 ± 1.9
GS-5	11.4 ± 5.2
GS-7	21.5 ± 1.3
GS-8	18.4 ± 2.5
GS-9	21.7 ± 3.1

3.2. Characteristics of the biochar

The analytical results for the MSW-BC are presented in Table 2. However, ultimate analyses indicated that the low molar O/C ratio is due to high pyrolytic temperature. Pyrolysis temperature on benzene adsorption can be distinguish according to the (Bornemann et al. (2007) and it shows the high temperature derived biochar favourable for benzene adsorption. Atomic ratios of the H/C and [(O+N)/C] are recognized as indicator for aromaticity and polarity of BC, respectively (Sizirici and Tansel, 2010, Florez Menendez et al., 2004). In addition, lower values of both H/C and the polarity index [(O+N)/C] ratios of the MSW-BC indicated that the high temperature-derived BC are highly carbonized, visualizing a highly aromatic structure. The reduction of O/C and H/C ratios further explain by Edil (2003) and processes of dehydratation, decarboxylation, and decarbonylation exhibit due to pyrolysis process at higher temperatures.

Table 2: Analytical data for the MSW- BC

Proximate analysis		
pH	9.7	± 0.05
EC (mS/m)	31	± 2
Moisture (%)	6.3	± 0.1
Mobile matter (%)	31.6	± 2.2
Ash (%)	15.6	± 3.3
Resident matter (%)	46.5	± 4.0
Ultimate analysis		
C (%)	60.8	± 0.12
H (%)	2.79	± 0.05
O (%)	14.6	± 0.02
N (%)	1.33	± 0.01
S (%)	0.16	± 0.03
Molar H/C	0.04	± 0.01
Molar O/C	0.24	± 0.02
Molar [(O+N)/C]	0.26	± 0.002

Table 3 shows concentration of heavy metal on the MSW-BC and municipal sewage sludge biochar (Liu et al., 2014). Compared to the sewage sludge derived biochar, the amount of heavy metals are very low in MSW-BC. Therefore potential utilization of MSW-BC as sorbent can be implemented without any constrain on environment. The Table 3 shows concentration of heavy metal on the municipal sewage sludge biochar and MSW-BC.

Table 3: Elemental analysis data for the MSW- BC

Element	Average concentration (mg/kg)	(Liu et al., 2014)	Element	Average concentration (mg/kg)	(Liu et al., 2014)
As	Nd	Nm	Mo	Nd	Nm
Be	Nd	Nm	Ni	1.81	Nm
Ca	5920	Nm	Pb	2.48	67.5
Cd	Nd	4.12	Sb	Nd	Nm
Co	Nd	Nm	Se	Nd	Nm
Cr	9.27	92.2	Sr	14.3	Nm
Cu	10.9	125	Ti	15.8	Nm
Fe	1810	Nm	Tl	Nd	Nm
Li	Nd	Nm	V	Nd	Nm
Mg	2320	Nm	Zn	82.8	749
Mn	305	Nm			

Nd- not detected , Nm- not measured

3.3. pH dependent sorption of benzene on MSW-BC

The effect of solution pH on benzene adsorption onto biochar is shown in Figure 2. The highest removal was at pH 9 where as maximum adsorption (39.6 µg/g) of benzene was observed for MSW-BC. High pH has shown also higher removal than the lower pH values (Wibowo et al., 2007). In addition to that, lower interaction effect of the field level biochar application into leachate can be expected from aqueous phase due to the similar pH potential in both leachate and biochar solution (Wijesekara et al., 2014).

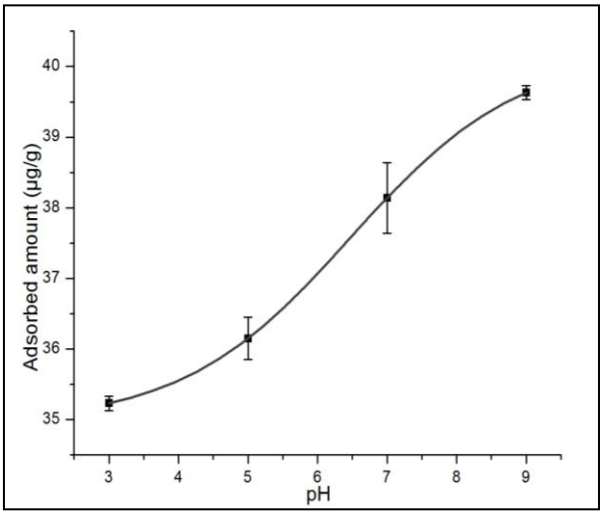

Figure 2: Effect of solution pH on benzene adsorption onto MSW-BC

3.4. Adsorption isotherm for MSW-BC

An adsorption isotherm relates the sorbent/sorbate interactions. The maximum adsorption capacity in the experiment was recorded as 87.0 µg/g of benzene. The model of best fit was Dubinin Raduskevich (DR) which is applied to isotherm data (Figure 3) and respective free energy of adsorption (E) per molecule of the adsorbate is 266.4 $KJmol^{-1}$. Physisorption process can be explained by E value and E <8 $KJmol^{-1}$ denotes the possible physisorption process. Therefore, the mechanism of benzene adsorption is not a physisorption process and it could be chemisorption or another process (Horsfall et al., 2004). The data goodness of fit were R^2 of 0.86 and 0.93 for Freundlich and Temkin models, respectively. This suggests the fit can be attributed tp heterogeneous adsorption with chemisorption process (Mohan et al., 2011).

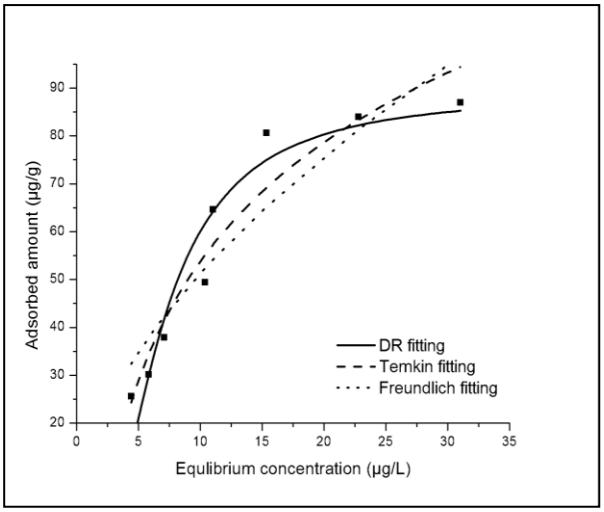

Figure 3: Freundlich, Temkin and DR adsorption isotherms of benzene by MSW-BC. The symbols represent experimental results and lines show the model predicted data fittings

3.5. Kinetics of benzene adsorption

The experimental runs were done for the effect of contact time on the batch adsorption of benzene. Result under condition at initial pH of 9 and an initial concentration of 50 µg/L is shown in Figure 4. Data modeling provided the best correlation (R^2 = 0.99) of the experimental data to pseudo-second order chemical reaction and it can be postulated that the rate-controlling step is chemisorption. The best fitting order of kinetic model is determined to be pseudo second order >> Elovich > power function.

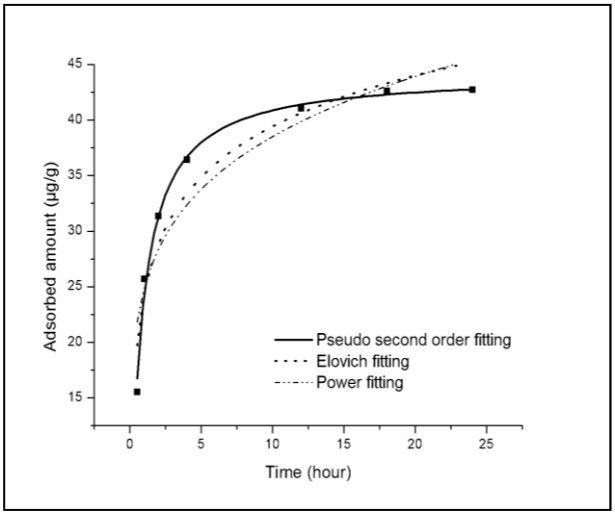

Figure 4: Pseudo-second order, Power and Elovich models on kinetic data. The symbols represent experimental results and lines show the model predicted data fittings.

4. Conclusions

In summary, all the leachate samples obtained from Gohagoda dumpsite exceeded the MCL. The adsorption isotherm, rejection of physisorption process by higher value of free energy of adsorption (E) per molecule, mechanism skewed towards chemical interaction. Therefore chemisorption can be suggested as the mechanism behind benzene removal process. The low availability of heavy metals in MSW-BC and the pH of maximum adsorption bearable with leachate environment explain the possibility of potential use of MSW-BC for Benzene removal from leachate. Hence, this study showed the possibility of VOCs removal from landfill leachate using its own biochars. More studies will be undertaken to test other VOCs.

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