Sorptive removal of toluene and m-xylene by municipal solid waste biochar: Simultaneous municipal solid waste management and remediation of volatile organic compounds

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ABSTRACT

The remediation of volatile organic compounds (VOCs) from aqueous solution using Municipal solid waste biochar (MSW-BC) has been evaluated. Municipal solid waste was pyrolyzed in an onsite pyrolyzer around 450 °C with a holding time of 30 min for the production of biochar (BC). Physiochemical properties of BC were assessed based on X-Ray Fluorescence (XRF) and Fourier transform infra-red (FTIR) analysis. Adsorption capacities for the VOCs (m-xylene and toluene) were examined by batch sorption experiments. Analysis indicated high loading of m-xylene and toluene in landfill leachates from different dump sites. The FTIR analysis corroborates with the Boehm titration data whereas XRF data demonstrated negligible amounts of trace metals in MSW-BC to be a potential sorbent. Adsorption isotherm exhibited properties of both Langmuir and Freundlich which is indicative of a non-ideal monolayer adsorption process taking place. Langmuir adsorption capacities were high as 850 and 550 μg/g for toluene and m-xylene respectively. The conversion of MSW to a value added product provided a feasible means of solid waste management. The produced MSW-BC was an economical adsorbent which demonstrated a strong ability for removing VOCs. Hence, MSW-BC can be used as a landfill cover or a permeable reactive barrier material to treat MSW leachate. Thus, the conversion of MSW to BC becomes an environmentally friendly and economical means of solid waste remediation.

1. Introduction

World cities are currently generating over 1.3 billion tons of solid waste per year and the waste generation rates are predicted to be more than doubled over the next twenty years in low and middle income countries (LMICs) (Hoornweg and Bhada-Tata, 2012). Municipal solid waste (MSW) includes any refuse from households and commercial establishments including biodegradable waste, recyclable materials, electrical and electronic items, hazardous waste, biomedical waste, inert waste and toxic waste. Recent studies have shown that household wastes contribute to over two thirds of the content of MSW (Slack et al., 2005; Vithanage et al., 2016).

In most occasions, these landfills are either open dumps or poorly managed sites where the leachate and landfill gases can easily be released to the environment (Wijesekara et al., 2014). Pollutants make its way to the leachate owing to the percolation of rainwater or other external sources of water through the solid waste mass (Jayawardhana et al., 2016; Wijesekara et al., 2014). Landfill gases produced through microbial degradation in open dumps is directly emitted into the atmosphere due to the absence of capping and gas collection (Hoornweg and Bhada-Tata, 2012; Nagamori et al., 2016). A large proportion of the landfill gas is made up of methane and carbon dioxide. Additionally a significant quantity of volatile organic compounds (VOCs) such as benzene, toluene, ethylbenzene and xylene is released as well which can cause adverse health effects such as skin and sensory irritation, respiratory illnesses etc. (Hoornweg and Bhada-Tata, 2012; Kumarathilaka et al., 2016). Although VOCs are only a small fraction (1–2%) of the overall landfill gas, the impact of VOCs on the environment and on human health is far more significant (Kumarathilaka et al., 2016).

Though numerous approaches such as incineration and biogas production has been introduced for the processing of combustible and organic fractions of MSW, the complex technology and high costs associated with these techniques have made them less popular in LMICs (Hoornweg and Bhada-Tata, 2012). Municipal solid waste can be utilized as a feedstock for the production of BC (Vithanage et al., 2016). Biochar is a carbonaceous material that has been exploited in the recent past as a means of remediating heavy metal and organic pollutant contaminated waters alongside its rapidly growing utilization as an agricultural soil amendment (Peiris et al., 2017, 2019; Shaaban et al., 2018). This is thought to be effective in the control of landfill gases emitted and the leachate runoff from dumpsites. It also helps reduce the volume of MSW (Jayawardhana et al., 2016). The presence of surface functional groups and high porosity makes BC an ideal choice as an adsorbent (Ahmad et al., 2014; Peiris et al., 2017).

The emissions/discharge of VOCs into the environment is managed by facilitating the treatment of VOCs. Many physical, chemical and biological treatment methods are widely practiced for the *in situ* or *ex situ* treatment of VOCs. The currently used approaches for MSW dumps in LMICs, however, are costly owing to the chemicals and the operations used. Therefore, there is much preference towards use of sorbents such as activated carbon (AC), as it has proven to be more effective towards the adsorption of VOCs and can also be regenerated without a major loss of activity (Ncube and Su, 2012; Wang et al., 2004). It is the porosity and high surface area of AC that facilitates the good adsorption of VOCs. Due to these exemplary properties of AC, activated carbon fibers (ACFs) and carbon nanotubes (CNTs) have been wildly used to adsorb VOCs (Li et al., 2017).

Biochar is a surrogate for AC and is produced by the slow pyrolysis of biomass at low temperature ($< 700\,°C$), in the complete absence or when exposed to a low concentration of oxygen. Compared to AC, BC is cost effective (1/6th cost of commercial AC) and this is largely due to the feedstock and the mild pyrolysis conditions applied (Alhashimi and Aktas, 2017). Past studies have examined BC's ability to adsorb both organic and inorganic pollutants from contaminated waters (Ahmad et al., 2014; Peiris et al., 2017). Among many different VOCs, toluene and m-xylene are VOC commonly observed to be associated with landfills of MSW (Kumarathilaka et al., 2016). Carbonaceous material has been incorporated for the remediation of VOCs in previous studies (Zhang et al., 2017). Biochar based sorptive removal of VOCs such as naphthalene, nitrobenzene and m-dinitrobenzene using pine needle BC has been reported in literature whereas the sorption of trichloroethylene using pine needle, peanut shell and soybean BC has also been reported (Ahmad et al., 2013a, 2013b; Chen et al., 2008). However, there is no experimental data relating to BC produced using MSW. Hence, the present study focuses on (a) an effective method to dispose MSW generated in LMICs and (b) on the uptake of VOCs on to MSW-BC. Effective solid waste management techniques and the unavailability of suitable technology makes the waste disposal in LMIC a challenge. Literature to support BC production from MSW as an effective alternative for solid waste management is inadequate, creating a research gap. To bridge this gap, MSW collected from different waste dumpsites in Sri Lanka have been incorporated in the production of BC and this BC was further investigated for its efficacy as an adsorbent. Moreover, as per our knowledge, adsorption of VOCs using MSW-BC has not been given an in depth inquiry (Jayawardhana et al., 2017). To compensate for this, the study was carried out using MSW-BC for the adsorption of m-xylene and toluene which were considered as model adsorbates in evaluating the associated chemodynamic parameters of VOC adsorption.

2. Material and methods

2.1. Reagents and standards

The analytical standard 524 of the Environmental Protection Agency (EPA VOC Mix 2, analytical standard 48777, Sigma-Aldrich, USA) was used for the quantification of VOCs in aqueous solution while purge and trap grade methanol (Methanol $\geq 99.9\%$, PESTINORM 83967.290, VWR, USA) was used for the preparation of stock solutions, primary and calibration analytical standards. Mili Q water ($0.055\,\mu S/cm$) saturated with high purity nitrogen (99.999%) for 30 min was utilized for batch sorption studies to control acidity in water. All chemicals used in characterization and batch experiments were analytical grade reagents (Sigma-Aldrich USA).

2.2. Leachate characterization

Characterization was conducted in such a way that it represented the climatic regions of the wet, intermediate and dry zones in Sri Lanka. Samples were collected from four different dump sites in the country; Dambulla, Gohagoda, Nuwara Eliya and Galle. The Dambulla dump site located in the dry zone of Sri Lanka takes up the spatial coordinates 80° 42′ 7.4″ E 7° 57′ 40.9″ N whereas the Gohagoda and the Galle dumpsites located in the wet zone took the coordinates 80° 37′ 17.9″ E 7° 18′ 47.5″ N and 80° 11′ 57.6″ E 6° 2′ 42.2″ N respectively. Both the Gohagoda and Galle dumps are located close to two of the major rivers in Sri Lanka namely the Mahaweli River and the Nilwala River. The Nuwara Eliya dumpsite is positioned within the coordinates of 80° 49′ 12.6″ E 6° 56′ 35.2″ N and is found in the intermediate zone. Fig. 1 shows the sample locations in Sri Lanka with the respective climatic zones. From each of the dumpsites in the different zones, three samples were collected to compute the deviations. Sample pre-treatment, transportation and preservation were done for all the samples according to the standard water and wastewater method (Andrew et al., 1999). Leachate samples were tested for pH, electrical conductivity (EC), oxidation reduction potential (ORP), chemical oxygen demand (COD),
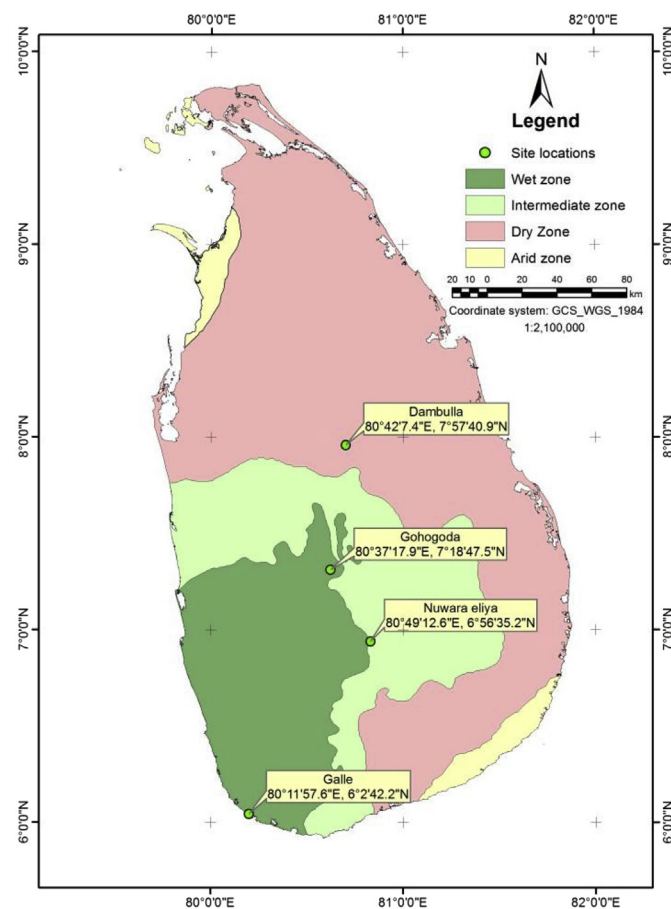

Fig. 1. Dump site leachate characteristics sampling location map in Sri Lanka.

biological oxygen demand (BOD), Total organic carbon (TOC), available anions, available heavy metals and VOCs. The pH of the leachate was measured with ROSS Sure-Flow combination epoxy body electrode equipped with a pH meter (Orion 210 A, USA) and EC of leachate was measured by using a conductivity meter (Orion 5 star, Thermo Scientific, USA). While, ORP was measured using the portable field kit conjugated surf flow combination redox ORP probe (oyster series, Taiwan), a DO probe assigned to Orion 5 star meter (Thermo Scientific, USA) was used for DO measurements. Further, BOD and COD were measured using the DO probe method and the dichromate digestion method (HACH DRB 200) respectively following the standard protocols (Andrew et al., 1999). Total organic carbon fractionation was obtained using the TOC analyzer (Shimadzu Japan) and the available heavy metal content was determined using an Inductively coupled plasma emission spectrometer (ICP-OES 7000 Thermo, USA). Furthermore, the anions in the leachate was measured by using ion chromatography equipped with a conductivity detector (IC- Shimadzu CDD 10A vp, Japan). The determination of VOCs of the samples were carried out using the EPA 524 protocol and 10 ml aliquots were collected in to headspace gas chromatography coupled mass spectrometer (Headspace GC-MS) vials and saturated with NaCl (1.0 g) for expand partitioning coefficient. Vials were immediately crimped with the butyl/PTFE septum to minimize the volatilization and the samples were transported to the laboratory under 4 °C to minimize degradation and alteration of the extracted VOCs (Eichelberger et al., 1992). Finally, samples were placed in the static head space for equilibration and measurements were made using the gas chromatography coupled mass spectrometer (GC-MS), (GC-MS Ultra 2010, Shimadzu, Japan) using a 20 m × 0.18 mm X 1 μm 6% cyanopropylphenyl/94% dimethyl polysiloxane (Rtx-624) capillary column. The oven was programmed to heat as follows; initially at 35 °C for 2 min, then from 35 to 230 °C at 20 °C min^{-1} and hold at 230 °C for 3 min. In the headspace analyzer, the oven temperature was set to 70 °C and both the sample and transfer line temperatures were set to 150 °C. Pressurizing time was 1 min, load time was 0.5 min and the injection time was 1 min. Split injection was carried out for a split ratio of 30 at 200 °C inlet temperature. The total ion current (TIC) was scanned from 35 to 260 m/z by electron ionization mass spectrometer (EI-MS) at 70 eV. Compounds were separate based on retention time, target and qualified ion basis.

2.3. Biochar production and characterization

Segregated organic fraction of MSW was subjected to air drying process and thin pieces of material were used to obtain uniform pyrolysis. The process was followed in a batch pyrolysis reactor built in the Gohagoda dump site.

For pyrolyzing the waste, the reactor was ramped to a temperature of 450 °C during 30 min and was held at this temperature for a further 30 min. Then, reactor was switched to a water bath to bring the BC in contact with water allowing the materials to cool down and finally air dried and sifted through 2 mm sieves. The fraction of BC obtained was stored in a sealed container. The stored BC was used for further characterization and batch experiments. Proximate analysis (moisture, mobile matter, ash, and residual matter contents) and elemental composition (C,H,N,S,O) of the MSW-BC samples were carried out using standard protocols (Ahmad et al., 2013c). Briefly, crucibles were cleaned by heating in a muffle furnace (Nabertherm N 7/H, Germany) under 750 °C for 30 min prior to the proximate experiment. Afterwards, the moisture content of the MSW-BC was measured by oven drying the sample at 105 °C overnight. For acquisition of the mobile matter content, MSW-BC were heated at 450 °C for a 1 h period in a furnace. The ash content of the MSW-BC was determined by open top crucible method and the sample heated at 750 °C for a 1 h period. Finally the fixed carbon content of the MSW-BC was obtained by resident matter content remaining in the crucible. The elemental analysis was performed after pretreatment of MSW-BC with an elemental analyzer

(Vario MAX CN, Elementary, Germany) to determine the elemental composition (C, H, N, O, and S) of samples.

The point of zero charge (PZC) of MSW-BC was determined by potentiometric titration methods (Kosmulski, 1997). Three titration cycles were carried out utilizing electrolyte concentrations of NaNO$_3$ (0.1, 0.01, 0.001 M). At each titration point the pH value and titrant volume was recorded using a KEM auto titrator, (KEM AT-610, Japan). General parameter of pH and EC of the MSW-BC was measured by following the method of Herath et al. (2015). The Fourier-transform infrared spectroscopy of the MSW-BC were obtained by mixing the air dried, crushed and homogeneous sample with fused KBr (FTIR grade, Sigma Aldrich, USA) pellets. The spectrometer was operated at 4 cm^{-1} resolution, measuring the transmittance window from 400 to 4000 cm^{-1} and by obtaining 128 scans (FTIR Nicolet, model 6700, USA) for qualitative functional group identification. Base line correction, noise reduction and peak assignment were evaluated using the OMNIC software (Version 6 Thermo, USA). In addition, quantification of functional groups in biochar were determined by the modified Boehm titration method (Fidel et al., 2013). Scanning electron microscopic (SEM) images were taken of the BC for the identification of porous structure development (ZEISS EVO LS15 Germany). The XRF spectrums were taken from samples of MSW-BC for molecular identification (Rigaku NEX CG, USA). In addition, the cation exchange capacity (CEC) was measured in a 1: 5 suspension of BC in ammonium acetate with the exchangeable potassium, sodium, calcium, and magnesium been excreted from the material (Sumner and Miller, 1996). Concentrations of metals were analyzed using the atomic absorption spectrometer (AAS Shimadzu AA-7000, Japan).

2.4. Batch sorption experiments

A sorbent dose of 1 g/L was used for all sorption experiments carried out under different conditions. Equilibrium kinetics was evaluated at initial concentration of toluene and m-xylene (50 μg/L) over different time intervals (0.5, 1, 2, 4, 12, 18 and 24 h) under controlled laboratory conditions. Effect of pH on sorption of toluene and m-xylene was evaluated with 50 μg/L adsorbate under different pH (3, 5, 7, 8.3 and 9) conditions. Batch isotherm experiments were carried out at pH ~ 8. Initial toluene and m-xylene concentrations were set to 25–600 μg/L. In addition, different temperatures (25, 35 and 45 °C) were used for isotherm experiments to obtain thermodynamic parameters of toluene and m-xylene for the adsorption process. Sorption data was modelled using Langmuir, Freundlich and Hill iostherms to calculate sorption parameters (Foo and Hameed, 2010). For the prediction of sorption mechanisms, the results were fitted to pseudo first order (PFO), pseudo second order (PSO) and Elovich kinetic models (Qiu et al., 2009).

2.5. Analytical separation and quantification

Quantitative analysis of toluene and m-xylene were performed using static headspace equipped GS-MS (Shimadzu QP 2010). Chromatographic separations were achieved by fused silica Rtx-624 (internal diameter 0.18 mm, film thickness 1.00 μm and length 20 m, Restek Scientific Inc.) capillary column. The EPA 524 method was adopted for sample analysis. The detection limit was managed within the range of 0.1–0.01 μg/L (Kavcar et al., 2006; Safarova et al., 2004). The auto sampler (HS-20 Shimadzu, Japan) was used for sample injection and the oven temperature was controlled at 70 °C for 20 min for equilibration. The GC temperature programme of the analyzer was compiled from 35 °C to 230 °C with a ramping of 20 °C min^{-1}, and the total cycle time was managed within 14 min for optimum separation. High purity He (99.9996%) was used as a carrier gas and the flow rate was 24.7 ml/min in the method (Eichelberger et al., 1989; Restek, 2000). The toluene and m-xylene in the aqueous solutions were quantified on the basis of their retention times, target and qualifier ions.

Table 1
General leachate characteristics in four different dumpsites in Sri Lanka ($n = 3$).

Parameters	Dambulla	Nuwara Eliya	Gohagoda	Galle	Typical Range[a]
pH	8.02 ± 0.61	8.24 ± 0.59	7.69 ± 0.96	8.24 ± 1.05	5.3–8.5
EC (mS/cm)	9.23 ± 3.59	8.88 ± 2.06	23.04 ± 2.53	13.78 ± 0.79	–
Temperature (°C)	26.9 ± 1.1	22.1 ± 1.2	33.6 ± 0.8	32.4 ± 0.6	–
VOCs					
Toluene (μg/L)	545.27 ± 16.89	12.87 ± 5.43	9.02 ± 2.41	2.10 ± 0.15	–
m-xylene (μg/L)	24.14 ± 8.55	89.22 ± 15.96	1.58 ± 0.87	4.32 ± 1.09	–
Heavy Metals					
Pb (μg/L)	22.5 ± 4.4	8.9 ± 3.5	107.1 ± 55.2	115.9 ± 54.9	–
As (μg/L)	nm	7.52 ± 1.63	nm	30.40 ± 9.65	–
Cd (μg/L)	2.13 ± 0.95	0.75 ± 0.29	2.13 ± 0.94	1.50 ± 0.50	–
Cu (μg/L)	64.7 ± 26.9	74.2 ± 37.5	109.1 ± 39.7	54.2 ± 14.0	–
Nutrients					
Phosphate (mg/L)	3.62 ± 0.71	10.14 ± 4.31	28.65 ± 4.42	66.45 ± 58.06	1–70
Nitrate-N (mg/L)	111.2 ± 21.1	207.9 ± 32.9	64.1 ± 19.2	17.9 ± 3.9	–
Nitrite-N (mg/L)	0.21 ± 0.11	6.34 ± 2.24	0.18 ± 0.08	nd	5–40
Pollution Parameters					
DO (mg/L)	2.14 ± 0.69	0.99 ± 0.42	0.97 ± 0.31	0.63 ± 0.11	–
COD (mg/L)	1103 ± 340	583 ± 303	7020 ± 280	5453 ± 1850	3000 -45,000
BOD (mg/L)	2422.4 ± 508.1	474.3 ± 17.7	976.5 ± 37.4	1084.2 ± 19.5	2000–30,000
TOC (mg/L)	954 ± 184	421 ± 184	nm	963 ± 39	1500-20,000
ORP (mV)	nm	162 ± 12	nm	−146 ± 92	–

nm = not measured nd = not detected.

[a] Solid Waste Association of Northern America (1991).

3. Results and discussion

3.1. Leachate characterization

Climatically originated leachates are different in each zone. Dilution effects are more in wet zone dumps and ion concentrated leachates can be found mostly in the dry zone. Therefore, the selected leachates were different from one another according to the climatic factors. Volatile organic compounds fluctuate over a vast concentration range. For toluene it ranged between 2.10–545 μg/L and m – xylene concentration varied in between 1.58 and 89.22 μg/L. The temperature of the dump area and leachate had an effect on the VOCs with high concentrations observed in low temperature areas, such as in the Nuwara Eliya dumpsite.

All leachates were of basic pH (7.6–8.3). Lead content was as high as 115.9 μg/L and the copper content was as 109.1 μg/L. Phosphates and nitrates have been detected in levels as high as 66 and 207 mg/L respectively. The water quality parameters, COD and BOD, ranged from 583-7020 and 474–2422 mg/L respectively. The results are presented in Table 1. The typical ranges of several leachate parameters as defined by the Solid Waste Association of Northern America (SWANA) is included in the table for comparison (Azim et al., 2011). Most of the parameters of the tested leachates fall within the range stated by SWANA implying high contamination. However, deviations in the nitrate, COD and BOD values were observed in some dumpsites.

3.2. Biochar characteristics

The proximate characteristics and the elemental composition of the MSW-BC are reported in Table 2. The yield of the MSW-BC was 36% in the reactor under pyrolysis temperature. The indication of aromaticity and polarity of the BC can be identified by respective atomic ratios of H/C and [(O + N)/C] (Florez Menendez et al., 2004; Sizirici and Tansel, 2010). Furthermore, lower values of H/C and polarity index ratios of MSW-BC recognize highly carbonized and high temperature derived BC. The PZC of the MSW-BC was 6.7 and closer to the neutral condition, which could facilitate removal of positive as well as negatively charged species. The main absorption bands in the FTIR spectrum at 3442 and 1034 cm^{-1} were assigned to −OH stretching and aliphatic C−O−C stretching respectively. The total acidity calculated by Boehm titrations was 791.20 μmoL/g whereas the lactonic, phenolic and carboxylic groups were 528.03, 238.28 and 24.88 μmoL/g respectively. The total basic groups were quite high (1329.27 μmoL/g) for MSW-BC. A SEM image showing the porous surface morphology of BC is shown in Fig. 2. The total CEC was 36.7 ± 2.37 cmoL/kg (n = 3).

3.3. Edge sorption

The pH dependency in aqueous media of toluene and m-xylene can be considered as a prominent factor. A dynamic adsorption pattern was recorded with the same sample at different pH. Adsorption was favored at pH 8.3 for toluene and pH 9 for m-xylene. Relatively high adsorption was recorded for toluene and Fig. 3A shows the pH dependence of VOC sorption on MSW-BC.

3.4. Isotherm and kinetics

Toluene sorption is higher than m-xylene sorption at room

Table 2
Physico-chemical characteristics of MSW-BC ($n = 3$).

Proximate analysis					
pH	EC	Moisture (%)	Mobile matter (%)	Ash (%)	Resident matter (%)
9.76 ± 0.05	0.31 ± 0.02	6.3 ± 0.1	31.6 ± 2.2	15.6 ± 3.3	46.5 ± 4.0

Ultimate analysis								
C (%)	H (%)	O (%)	N (%)	S (%)		Molar H/C	Molar O/C	Molar [(O + N)/C]
60.83 ± 0.12	2.79 ± 0.05	14.62 ± 0.02	1.33 ± 0.01	0.16 ± 0.03		0.04 ± 0.01	0.24 ± 0.02	0.26 ± 0.01

Surface functional groups				
Total basic		Total acidic	Carboxylic	Lactone	phenol
1329.27 ± 58.23		791.20 ± 44.93	24.88 ± 1.83	528.03 ± 30.37	238.28 ± 16.85
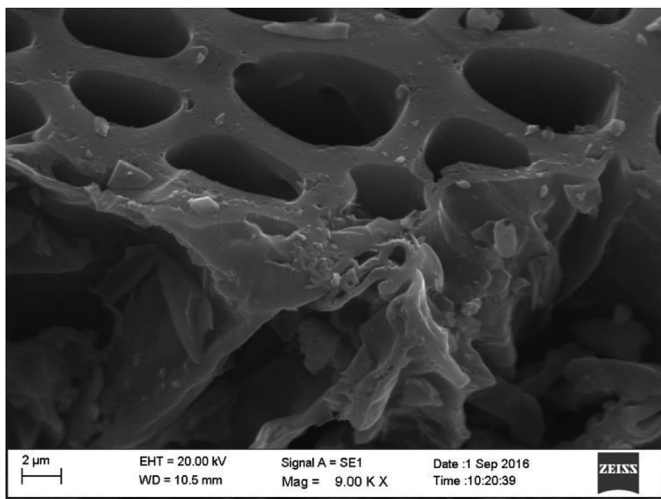
Fig. 2. Developed pore structure visualization in a SEM image of MSW-BC.

suggested that the mechanism of m-xylene and toluene adsorption is a mix, which does not follow an ideal monolayer adsorption. Adsorption capacity of Langmuir expression is slightly higher in toluene than that of the m-xylene. According to the Langmuir adsorption isotherm model fitting at 25 °C, toluene has the highest maximum adsorption capacity of 1090 $\mu g\,g^{-1}$ than that of m-Xylene (555 $\mu g\,g^{-1}$). Experimental data also shows the contrasting increment of adsorption with the temperature as well as the type of sorbate system in xylene and toluene. The correlation coefficient (R^2) of toluene and m-xylene at room temperature for the Langmuir, Redlich-Peterson and Hill models are given in Table 3. The correlation coefficients and theoretical maximum adsorption capacities imply a good adsorption process representation. As a result, toluene and m-xylene adsorption can be suggested as favoring adsorption on a heterogeneous surface with corporative binding (Cattoni et al., 2016). The relevant parameters of each isotherm model are given in Table 3.

The rate limiting factor of the reaction provided a compatible correlation of the experimental data to the PFO chemical reaction (Fig. 3B). Hence, the first order rate constant (k_1) depends on the initial concentration of the adsorbate (toluene, m-xylene) and varies significantly depending on the adsorption system (Yuh-Shan, 2004). However, the adsorption phenomenon in the PFO model is supposed to be a non-dissociate molecular adsorption. The best fitting order of kinetic models were PFO $\gg$ PSO > Elovich. The relevant parameters of each kinetic model are given Table 4.

temperature. Fitting of Langmuir, Redlich-Peterson and Hill models denotes a good correlation, which indicates that the mechanism behind VOCs removal is a mix of the Langmuir and Freundlich isotherms. The data fitting to the Redlich-Peterson isotherm model, which incorporates three parameters and combines elements from both Langmuir and Freundlich equations was found to be the best correlated. Hence, it is
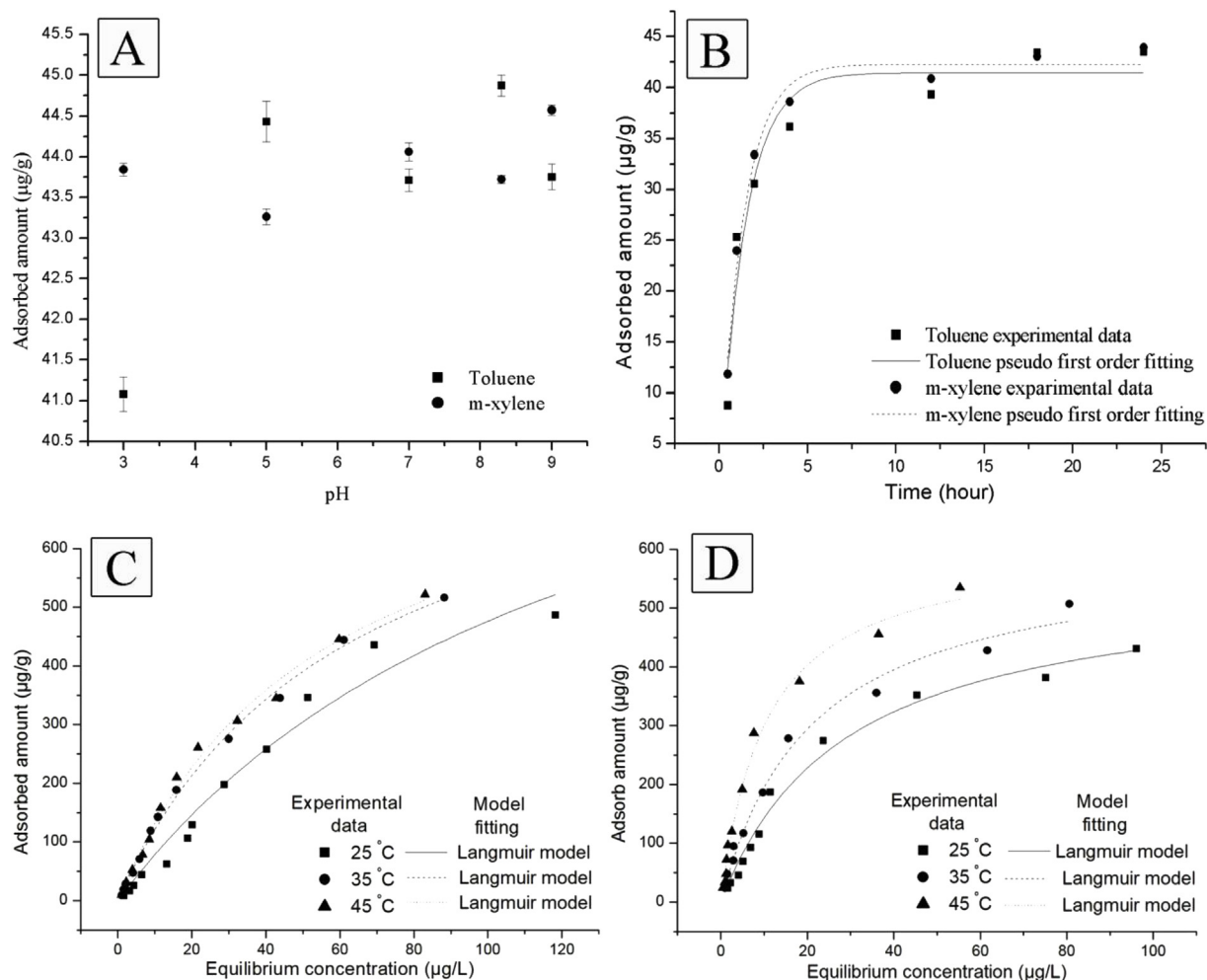

Fig. 3. (A) Edge sorption of toluene and m-xylene in to MSW-BC, (B) Nonlinear kinetic model fitting of toluene and m-xylene in to MSW-BC, (C) Langmuir adsorption isotherm for toluene in to MSW-BC, at 25,35 and 45 °C, (D) Langmuir adsorption isotherm for m-xylene in to MSW-BC, at 25,35 and 45 °C.

Table 3
Isotherm parameters for toluene, m-xylene adsorption onto MSW-BC (pH 8.3).

Isotherm	Non-linear equation	Description	Parameters		Values		
					25 °C	35 °C	45 °C
Langmuir	$q_{ads} = \frac{q_{max}K_L C_e}{1+K_L C_e}$	q_{ads} (µg/g) is the amount of adsorbate adsorbed per unit weight of adsorbent q_{max} (µg/g) is the maximum adsorption capacity K_L (L/mg) is the Langmuir affinity parameter C_e (µg/L) is the equilibrium adsorbate aqueous phase concentration	Toluene	q_{max}	1090	876	850
				K_L	0.007	0.016	0.018
				R^2	0.972	0.997	0.993
			m-xylene	q_{max}	555	601	612
				K_L	0.03	0.04	0.09
				R^2	0.985	0.990	0.991
Redlich–Peterson		K_R is the constant (L mg^{-1}) a_R is empirical coefficient (mg^{-1}) β is the exponent lies between o and 1	Toluene	K_R	−0.002	−1.157	−0.234
				a_R	0.05	6.14	4.26
				β	0.99	0.51	0.08
				R^2	0.937	0.921	0.932
			m-xylene	K_R	1.25	0.83	0.94
				a_R	16.41	36.10	62.66
				β	0.009	0.127	0.125
				R^2	0.989	0.992	0.991
Hill	$q_{ads} = \frac{q_{SH}C_e^{nH}}{K_D + C_e^{nH}}$	K_D is the Hill constant, n_H is the Hill cooperatively coefficient of the binding interaction q_{SH} (µg g^{-1}) refers to the Hill isotherm maximum uptake saturation.	Toluene	K_D	0.02	0.01	0.01
				n_H	1.76	0.95	0.98
				q_{SH}	578	954	874
				R^2	0.992	0.997	0.993
			m-xylene	K_D	0.05	0.03	0.09
				n_H	1.37	0.88	1.01
				q_{SH}	452	674	606
				R^2	0.993	0.991	0.991

Table 4
Non-linear kinetic parameters for toluene, m-xylene adsorption onto MSW-BC (pH 8.3).

Kinetic model	Description		Toluene	m-xylene
Pseudo first order	q_e, q_t - sorption capacity at equilibrium and at time t, respectively (µg/g) K_1 is the pseudo first order rate constant (min^{-1}).	q_e	41.4	42.3
		K_1	0.69	0.75
		R^2	0.942	0.985
Elovich	q_t - sorption capacity at time t (µg/g) a – initial sorption rate (µg/g/min) b - desorption constant (g/µg)	q_e	121.73	167.40
		K_2	0.12	0.13
		R^2	0.883	0.877
Pseudo second order	k_2 - the rate constant (g/µg/min) q_e, q_t - sorption capacity at equilibrium and at time t, respectively (µg/g)	q_e	50.73	45.91
		K_2	0.01	0.02
		R^2	0.852	0.968

3.5. Thermodynamics of toluene and m-xylene

Three different temperatures and respective adsorption fittings were visualized in Fig. 3C and D to identify the behavior of toluene and m-xylene sorption. Obtained values (Table 5) for ΔG^O were negative for all three considered temperatures. Both toluene and m-xylene implied the spontaneous nature of the adsorption reaction at experimental temperature (Hercigonja et al., 2012). The physisorptive adsorption behavior can be explained by the general literature of thermodynamic parameters for two components. Increasing negative ΔG^O value with the increasing temperature indicates that the sorption process was

Table 5
Thermodynamic parameters of toluene and m-xylene adsorption onto MSW-BCs.

Parameter	Toluene	m-xylene
ΔH^O (kJ mol^{-1})	−16.82	−19.71
ΔS^O (J mol^{-} K^{-1})	68.60	79.07
ΔG^O (kJ mol^{-1})		
25 °C	−37.26	−43.28
35 °C	−37.95	−44.07
45 °C	−38.64	−44.86

favorable at higher temperatures for both compounds. Data presented by Qiu et al. (2012) shows that upon increasing the temperature the adsorption of Xylene is enhanced by the same amount as in the present study. The acceleration of molecular velocity with temperature could be the reason for higher adsorption at higher temperatures for toluene and m-xylene (Memon et al., 2009).

3.6. FTIR interpretation of sorbent-sorbate interactions

The image in Fig. 4 represents the bare spectrum of BC and the nature of IR activity in MSW-BC. Boehm data reveals the presence of phenolic, carboxylic groups within the MSW-BC. (Chern and Chien, 2002). The stretching around 1150 cm^{-1} depicts the lactonic groups and the results from Boehm provides justification for this (Laleh et al., 2011). The oscillation of carboxylic groups is represented by 1600 and 1800 cm^{-1} (Byrd, 1998; Guo and Rockstraw, 2007; Jiang et al., 2008). Moreover, the presence of oxygen containing groups quantified from modified Boehm titration can contribute to donor interaction adsorption. Upon the adsorption of toluene and m-xylene to the MSW-BC, an intense peak of aromatic C—H stretching at 3000-3100 cm^{-1} and
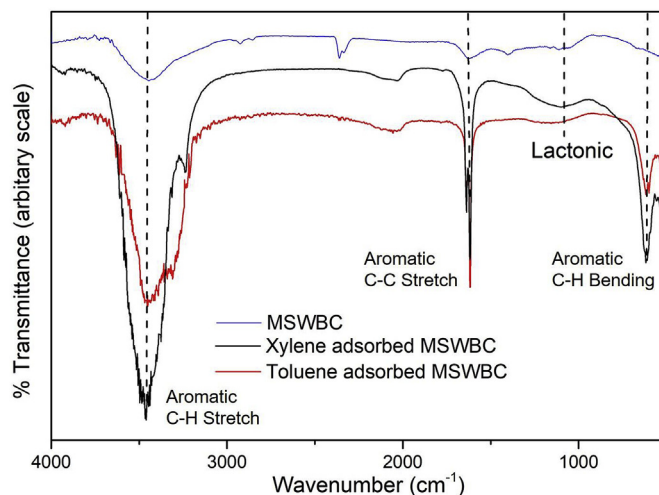

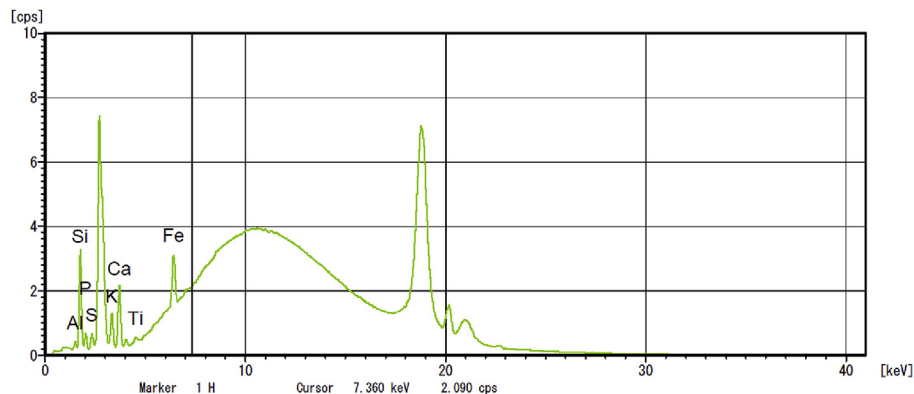**Fig. 4.** FTIR spectra for toluene and xylene adsorption in to MSW-BC.

Fig. 5. Presence of Ti in X-ray fluorescence spectra of MSW-BC.

aromatic C−C stretching at 1500 cm^{-1} appeared in the FTIR spectra. At 730 cm-1, a peak corresponding to a C−H bending is also evident. The XRF confirms the presence of Ti (Fig. 5) in the sample matrix and the catalytic effect of ZnO and TiO$_2$ in toluene and xylene, adsorption in to BC can be considered as the primary mechanism in chemisorption.

4. Conclusions

The four different leachates tested had COD values ranging from 583 to 7020 mg/L and BOD ranging from 474 to 2422 mg/L indicating high contamination due to organic matter. The organic fraction was successfully used for the BC production and used for the sorption of m-xylene and toluene. Toluene adsorption capacity was higher than that of the m-xylene for MSW-BC and over 80% removal was obtained for elevated concentrations. Hill and Langmuir were the best fitted isotherm models suggesting a corporative heterogeneous adsorption process onto MSW-BC. Kinetic modeling postulated that the rate-controlling step was a physisorption. It can be concluded that the MSW-BC can be potentially used for the removal of VOCs such as toluene and m-xylene from aqueous media. However, with a change in the environmental conditions the VOCs can be desorbed as the sorption is via physical attraction. Overall MSW-BC will address two existing environmental issues i.e. reduce the volume of waste and remove VOCs from aqueous media. However, field studies should be conducted to demonstrate practical applicability of MSW-BC for removing VOCs. The BC that is produced from MSW can become a value added product which can be used to increase the efficacy of solid waste management procedures in LMICs.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2019.02.097.

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