Municipal solid waste-derived biochar for the removal of benzene from landfill leachate

Yohan Jayawardhana · S. S. Mayakaduwa · Prasanna Kumarathilaka · Sewwandi Gamage · Meththika Vithanage

Abstract The potential of biochar, produced from fibrous organic fractions of municipal solid waste (MSW), for remediation of benzene, one of the frequently found toxic volatile organic compounds in landfill leachate, was investigated in this study based on various environmental conditions such as varying pH, benzene concentration, temperature and time. At the same time, landfill leachate quality parameters were assessed at two different dump sites in Sri Lanka: Gohagoda and Kurunegala. MSW biochar (MSW-BC) was produced by slow temperature pyrolysis at 450 °C, and the physiochemical characteristics of the MSW-BC were characterized. All the leachate samples from the MSW dump sites exceeded the World Health Organization permissible level for benzene (5 μg/L) in water. Removal of benzene was increased with increasing pH, with the highest removal observed at ~pH 9. The maximum adsorption capacity of 576 μg/g was reported at room temperature (~25 °C). Both Freundlich and Langmuir models fitted best with the equilibrium isotherm data, suggesting the involvement of both physisorption and chemisorption mechanisms. Thermodynamic data indicated the feasibility of benzene adsorption and its high favorability at higher temperatures. The values of ΔG suggested physical interactions between sorbate and sorbent, whereas kinetic data implied a significant contribution of chemisorption. Results obtained from FTIR provided clear evidence of the involvement of functional groups in biochar for benzene adsorption. This study suggests that MSW biochar could be a possible remedy for benzene removal from landfill leachate and at the same time MSW can be a potential source to produce biochar which acts as a prospective material to remediate its pollutants while reducing the volume of waste.

Keywords Landfill leachate · Physisorption · Chemisorption · Thermodynamic · Open dumps

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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 a final disposal method due to its low cost and ease of operation (Visvanathan and Trankler 2003). However, due to uncontrolled solid waste disposal, numerous environmental and health problems can occur. A

number of issues are attributed to open dumping, including toxic gas emission associated air pollution, soil water contamination by landfill leachate. As the final stockpile for most industrial and household wastes in developing countries, open dump sites are often designated as intense sources of a wide range of trace pollutants including volatile organic compounds (VOCs) in landfill leachate and gaseous emission, which leads to appalling odors.

The environmental significance of VOCs is well known due to their potential role as carcinogenic and mutagenic compounds and in the formation of photooxidants (Srivastava and Mazumdar 2011). 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). It has been estimated that landfills in the USA emanate 10% of VOCs emitted in the entire USA (Kim et al. 2008). Apart from that, several countries Korea, USA, China have reported benzene concentrations in landfill leachate, respectively, as follows 32, 12, 0.73 μg/L (Kim et al. 2006; Wood and Porter 1987; Zou et al. 2003). Not only that, Denmark and Hawaii islands also reported 1.5 and 0.47 μg/L benzene in leachate, respectively (Mournighan et al. 2007; Scheutz et al. 2004). However, only few studies in Asian countries have reported VOCs in landfill leachates, despite their high toxicities (Abdullah and Chian 2011). One study examined drinking water in peninsular Malaysia and detected 54 different VOCs, which was attributed to improper disposal practices (Abdullah and Chian 2011). Among the different types of VOCs, 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 and lithography, paint, rubber, dry cleaning, adhesives and coatings, detergents, extraction and rectification (EPA 2003a). The generated benzene may volatilize into the atmosphere, and the remaining may leach into groundwater or surface water bodies. Both acute and chronic effects dominate in benzene (Cotruvo and Regelski 1989). Therefore, remediation of benzene from landfill leachate is often crucial for public health and the environment.

A considerable effort has been dedicated in the recent past to the removal of benzene from wastewater. Although several remediation methods have been proposed and developed, the most extensively used method is adsorption. The application of traditional methods (e.g., flocculation, sedimentation, filtration) for water treatment is likely impractical for low-level contamination of organic compounds. The application of activated carbon (AC) for adsorption has been identified as one of the most efficient technologies for removing VOCs (Abumaizar et al. 1998; Tham et al. 2011; Cal et al. 1996; Navarri et al. 2001). A dynamic-volumetric adsorption study reported high adsorption of toluene via adsorption by diffusion through the surface (Wibowo et al. 2007; Pei and Zhang 2012), whereas micropore structure has been reported to be responsible for the efficient removal of the benzene–toluene mixtures (Lillo-Ródenas et al. 2006). At the same time, number of studies have shown enhanced adsorption capacity of ACs using physical and chemical methods for more efficient VOC removal (Wibowo et al. 2007; Lillo-Ródenas et al. 2006). Although AC is one of the most important and widely used microporous adsorbents from an industrial perspective, the production of AC is expensive for developing countries. Therefore, it is necessary to develop alternatives from raw materials available locally (Daifullah and Girgis 2003).

Biochar has gained an interest as an alternative to AC due partly to its similar sorption capacities (Zhang et al. 2015; Xu et al. 2016). Biochar can be produced by any biological raw material. However, its characteristics differ based on the pyrolyzing temperature, technology and feedstock difference, among other variables (Lehmann and Joseph 2009). Only a few studies have focused on biochar for benzene remediation using sorption techniques (Yakout 2014; Xiao et al. 2014). Benzene and toluene adsorption is postulated via the existence of nonlinear adsorption behavior through Langmuir isotherms fitting with pore filling process (Bornemann et al. 2007). However, no studies are found on benzene sorption by municipal solid waste biochars.

Direct waste-to-energy processes are suitable for the production of gas, liquid and solid hydrocarbons or other valuable products to obtain energy from the municipal solid waste (MSW) via pyrolysis (Ateş et al. 2013). During such processes, biochar is produced as a byproduct (Bernardo et al. 2012), which can eventually be used as a material for landfill cover, permeable reactive barrier and in leachate treatment process. In addition to environmental remediation, biochars are beneficial for carbon sequestration, bioenergy production and agricultural benefits and are positive

interventions from water conversion. municipal solid waste-derived biochar (MSW-BC) has well-exhibited efficacy in removing heavy metals, metalloids and dyes (Agrafioti et al. 2014; Jin et al. 2014; Agarwal et al. 2015). In addition, MSW-BC has been used for soil quality improvement (Liu et al. 2015; Milla et al. 2013). Low-cost adsorbents are more popular with waste and locally available material for leachate treatment (Mor et al. 2016; Heavey 2003; Kaur et al. 2016). In that sense, using MSW to produce biochar would be effective in several ways for environmental remediation and to reduce the solid waste volume of landfill. Sustainable MSW-BC utilization for remediation of heavy metals in landfill leachate was reported (Jin et al. 2014). However, little attention has been directed to understand benzene removal by biochar (Bornemann et al. 2007). Therefore, this study reports for the first time the potential of MSW-BC for removing benzene. The objectives of this work were to assess the benzene levels in the leachate from Gohagoda MSW dumpsite in Sri Lanka and to determine the potential of MSW-BC for benzene removal as a sustainable solution for MSW.

Materials and methods

Chemicals

Commercially available EPA 524.2 analyte and analytical standards were used in 2000 µg/mL ampules (EPA VOC Mix 2, Sigma-Aldrich Co. LLC., MO, USA, Analytical grade). Oxygen-free water was obtained by N_2 gas purging for 30 min with Milli-Q water (resistivity 18 MΩ/cm). All other chemicals (Analytical grade) were obtained from Sigma-Aldrich, USA.

Leachate

Leachate collection was performed in Gohagoda and Kurunegala dumpsites in Sri Lanka. Gohagoda is located in the city of Kandy in the wet zone of Sri Lanka, centralized around latitude and longitude of 7°18′47.85″N and 80°37′19.02″E, respectively (Wijesekara et al. 2014). The open dumpsite is around 2.5 ha. Solid waste generation was estimated about 152 tons by Kandy Municipal Council (KMC), with some waste segregation and application of 3R; reduce, reuse and recycle within the KMC (WACS May 2014). However, the majority of KMC waste from households, fish markets, slaughter houses and non-infectious hospital pharmaceutical wastes are dumped without any pretreatment (Wijesekara et al. 2014). The other dump site was located in Kurunegala city, Sri Lanka, with latitude and longitude of 7°30′31.7″N and 80°21′11.6″E. This dump site represents the intermediate zone of Sri Lanka. The leachate samples were collected from in fresh waste areas, old waste areas and leachate draining channels. In total, 5 samples were collected from the Gohagoda dump site and 3 from Kurunegala site. Triplicate samples were performed in each location, and 1 g of NaCl electrolyte was added as a peak-resolving agent. The leachate sample, 10 mL was filled to reach the gauge line of the vial headspace. After leachate collection, the vials were immediately crimped tightly to minimize loss of VOCs (Kolb and Ettre 2006). The container was then transferred to the laboratory under 4 °C, and samples were analyzed for benzene under the headspace using gas chromatography mass spectrometer (GCMS) (Eichelberger et al. 1989). The pH was measured in situ with a ROSS Sure-Flow combination epoxy body electrode. The temperature (T) and electrical conductivity (EC) were measured with a conductivity meter (Orion 5 star series). The dissolved oxygen (DO) was measured with a DO probe equipped with Orion 5 star meter. Leachate samples were also collected for physic-chemical characterization following the same environment regulation parameters for sample transportation. Five-day biological oxygen demand (BOD_5) was measured by the Winkler method and chemical oxygen demand (COD) using a spectrophotometer (HACH DRB 200). Phosphate was measured by the ascorbic acid method (Watanabe and Olsen 1965), whereas nitrate and nitrite were, respectively, measured by the cadmium reduction method and the diazotization method (Andrew et al. 1981).

Biochar production and characterization

The manually segregated organic fraction of the MSW obtained from Gohagoda dumpsite, Kandy, was used for producing MSW-BC. Pyrolysis was performed in a batch reactor built in Gohagoda dumpsite under slow pyrolysis conditions, with 30 min holding time and 15 °C/min ramping up to 450 °C within the reactor. After the pyrolysis, the container was automatically

transferred to a water bath and finally air-dried for experiments. The air-tight container was used to store the 2 mm sieved fraction of MSW-BC prior to analysis. 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 °C overnight. For determination of mobile matter content, BCs were heated in covered crucibles at 450 °C for 1 h in a muffle furnace. The ash content was measured by heating samples in open-top crucibles at 750 °C for 1 h. Finally, the remaining resident matter, analogous to fixed matter, was calculated from ash, mobile matter and moisture contents. To measure pH and EC, MSW-BC suspensions were prepared in deionized water with 1:10 ratios with rigorous shaking at 100 rpm for 4 h. Measurements were taken using a gel electrode equipped with a Metrohm pH meter for pH, whereas EC was collected by Orion 5 star meter. Elemental analysis was performed after pretreatment of MSW-BC. An elemental analyzer (Vario MAX CN, elementary, Germany) was used for determination of elemental composition (C, H, N, S and O) (Rajapaksha et al. 2015). Molar H/C and O/C ratios were calculated from the elemental analysis for supportive indications of aromaticity and polarity. The total available and bioavailable concentrations of heavy metals on biochar were determined by HNO_3, $CaCl_2$ and diethylenetriaminepentaacetic acid (DTPA) extraction. The processed supernatant was analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) (PerkinElmer Optima 4300 DV ICP-OES, USA). The Brunauer–Emmett–Teller (BET) specific surface area, total pore volume and pore diameter were determined using an N_2 gas sorption analyzer (NOVA-1200; Quantachrome Corp., Boynton Beach, FL, USA).

Batch experiments

The solutions used in batch adsorption were prepared by using analytical-grade benzene to reduce interferences of other constituents (Ilhan et al. 2008). Leachate has many other chemical compounds. Due to that, the other constituents can be interfered with the benzene adsorption and mislead the optimal adsorption parameters and modeling data which are taken through the batch adsorption experiments. Leachate from landfill was characterized in order to determine the actual conditions and compare with the optimal adsorption parameters resulted from the batch adsorption experiments. Batch experiments were performed with 1 g/L of MSW-BC at 4 different pH values (3, 5, 7 and 9) in order to encompass the pH range typically found in the environment. Before the addition of benzene, MSW-BC solution was hydrated for 4 h at 100 rpm after initial pH adjustment. A 10 mL sample was filled to reach the gauge line of headspace vial, and consequently, 25 µL of a benzene primary dilution standard was spiked into the headspace vial. The samples were shaken overnight at 100 rpm. During the measurements of the pH adsorption edge, temperature (25 °C), initial concentration of sorbate (50 µg/L), sorbent dosages (1 g/L) were taken as fixed parameters for optimizing the adsorption potential. Kinetic experiments were performed under controlled laboratory conditions at different time intervals, 0.5, 1, 2, 4, 12, 18 and 24 h. For the isotherm of MSW-BC, the sorbate concentration (30–300 µg/L) at 24 h duration was investigated using batch experiments. For all sorption tests, oxygen-free water was used for the preparation of samples. In addition, headspace vials were crimped tightly to minimize loss of benzene. The measurement of remaining concentrations of all the pH kinetics and isotherm samples followed the EPA 524 method and are further discussed in "Analytical method" section. Data were collected with a GCMS instrument (Safarova et al. 2004; Kolb and Ettre 2006). The equilibrium sorption capacity of MSW-BCs was calculated following Eq. 1 (Ok et al. 2007):

$$q_e = \frac{C_0 - C_e \times V}{m} \quad (1)$$

where q_e represents the equilibrium benzene solid phase concentration (µg/g), C_0 and C_e represent the benzene concentrations of the initial and equilibrium aqueous phases (µg/L), respectively, V represents the volume of solution (L), and m represents the mass of adsorbent (g). Nonlinear curve fitting was performed using Origin 6.0 software. Two parameter-based equilibrium isotherm models, Langmuir and Freundlich, were applied to model benzene adsorption on MSW-BCs. For the sorption kinetics, benzene sorption to MSW-BC was evaluated by nonlinear curve fitting with pseudo-second-order rate approximations, with Elovich and power functions.

Thermodynamics studies

The variable temperature of incubation and corresponding adsorption studies were performed to identify the thermodynamic behavior of benzene sorption. Three different temperatures 25 (room temperature), 35 and 45 °C were adopted for the isotherm experiments. All isotherms were managed in an incubation shaker for temperature equilibration. The same concentration range (30–300 µg/L) was introduced to the MSW-BC suspension and a 24-h reaction period was used. Benzene concentrations in the equilibrium aqueous phase were measured by GC–MS. Highest initial benzene concentration and equilibrium data were used for thermodynamics calculation. The thermodynamic parameters, namely, the Gibbs free change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) were calculated using the following equations (Salman et al. 2011).

$$\ln K_{\mathrm{d}} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{2}$$

$$\Delta G = \Delta H^0 - T\Delta S^0 \tag{3}$$

where T represents the temperature (K), and R represents the universal gas constant (8.314 J/K mol), respectively. The equilibrium distribution coefficient is indicated by K_{d} obtained from Eq. 4 as expressed below.

$$K_{\mathrm{d}} = \frac{[C_0 - C_{\mathrm{e}}]V}{C_{\mathrm{e}}m} \tag{4}$$

FTIR investigations

Infrared spectra of both the bare and the benzene-adsorbed MSW-BCs were obtained using a Fourier transform infrared spectrometer (FTIR Nicolet, model 6700, USA) in the range of 400–4000 cm^{-1} with 64 resolutions of background and 128 scans per sample.

Analytical method

Quantitative analysis of the benzene standards and samples were performed using gas chromatograph (GC, Shimadzu QP 2010 plus, Japan) equipped with amass detector (QP 2010 ultra-MS) and a Shimadzu HS-20 head space auto-sampler. Chromatographic separations were performed with a 20 m Rtx-624 column with 0.18 mm internal diameter and 0.001 mm film thickness (Restek Scientific Inc.) using injections in the split mode (1/30). The oven temperature was held at 35 °C for two min and then increased up to 230 °C with a gradient of 20 °C/min holding for three min at the final level. The temperatures of the injector and detector were both 200 °C. Ultra-high-purity helium was used as the carrier gas at a flow of 24.7 mL/min at a constant rate (Eichelberger et al. 1989; Restek 2000).

Results and discussion

Characteristics of leachate

All the leachate samples exceeded the maximum concentration level (MCL) (0.005 mg/L) of benzene in water except for the Kurunegala dumpsite samples. The obtained values are summarized in Table 1. Characteristics of the leachate in the two sites were demarcated by a wide range due to differences in the climatic region of wet and intermediate zones, respectively, in Gohagoda and Kurunegala. The measurements show that the pollutant loading from the landfill leaches to the environment. Detailed investigations were conducted by Wijesekara et al. (2014) and revealed that other parameters such as COD, BOD and heavy metals in surface and

Table 1 Characteristics of leachate recorded with standard deviation from two different sites in Sri Lanka

Parameters	Gohagoda	Kurunegala	Unit
pH	7.39 ± 0.09	8.49 ± 0.08	
EC	23.04 ± 2.48	18.8 ± 3.97	mS/cm
T	33.4 ± 0.5	33.9 ± 0.7	°C
DO	1.12 ± 0.80	0.98 ± 0.95	mg/L
COD	950 ± 80	3230 ± 120	mg/L
BOD	4423 ± 212	1020 ± 108	mg/L
Phosphate	2.67 ± 1.02	38 ± 4.57	mg/L
Nitrate–N	67.2 ± 12.1	2445 ± 197.5	mg/L
Nitrite–N	0.276 ± 0.10	2.14 ± 0.08	mg/L
Benzene	12.12 ± 1.76	1.3 ± 0.16	µg/L

subsurface surroundings were significantly high and contaminated the environment around the Gohagoda dump site. The regulation of COD, BOD and other physico-chemical parameters with biological materials were tested and reported for leachate in tropical countries. These parameters are critical to examine before discharging into surface waters due to pollution of drinking water sources (Mor et al. 2016; Kaur et al. 2016). Heavy metal contamination mainly Fe, Mn and Zn can be attributed largely to the disposal of batteries, paints, Fe scraps, chemicals for photograph processing and petroleum by-products from vehicle service stations (Wijesekara et al. 2014; Mor et al. 2006). Furthermore, considerable VOC contamination in addition to benzene in Gohagoda landfill was recorded by previous studies, which was also observed in our work (Kumarathilaka et al. 2016). Although the leachate directly flows to surface water bodies in the surroundings, e.g., Mahaweli River, which provides water to the general public, the data indicate that the leachate must not discharge directly to the environment. Leachate characteristics are often considered as stabilized and therefore physical and chemical treatment would be more effective than biological treatments (Li et al. 2010).

Characteristics of the MSW-BC

The analytical results for the MSW-BC are presented in Table 2. As expected, the pH remained within the alkaline range of 9, which can be due to the separation of alkali salts from the organic materials in the feedstock as well as with increases in ash content and loss of acidic functional groups during pyrolysis (Ahmad et al. 2013; Cantrell et al. 2012). In addition, MSW-BC has less volatile matter in favor of more resident matter. Removal of volatile material led to a substantial enhancement in ash content. The MSW-BC surface area, as well as average pore size, shows that the material is lower in surface area compared to AC. The surface area of MSW-BC is much higher than the organic MSW and that may be the fact for enhanced adsorption capacity in MSW-BC (Wu et al. 2001; Su et al. 2010). As shown in the Fig. 1 in raw biochar, the majority of pores is observed to be mesopores. However, scanning electron micrograph (SEM) of raw and benzene-loaded MSW-BC showed that a large amount of pores exist in MSW-BC (Fig. 1). However, chemical analysis indicated that the low molar O/C ratio is due to high pyrolytic temperature. Atomic ratios of the H/C and [(O + N)/C] are

Table 2 Physico-chemical characteristics of MSW-BC

pH	EC (mS/cm)	Moisture (%)	Mobile matter (%)	Ash (%)	Resident matter (%)
Proximate analysis					
9.7 ± 0.05	0.31 ± 2	6.3 ± 0.1	31.6 ± 2.2	15.6 ± 3.3	46.5 ± 4.0

C (%)	H (%)	O (%)	N (%)	S (%)	Molar H/C	Molar O/C	Molar [(O + N)/C]
Ultimate analysis							
60.8 ± 0.12	2.79 ± 0.05	14.6 ± 0.02	1.33 ± 0.01	0.16 ± 0.03	0.04 ± 0.01	0.24 ± 0.02	0.26 ± 0.002

Element (mg/kg)	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	V	Zn
Elemental parameters												
Total	ND	ND	ND	9.27	10.90	1810.00	305.00	1.81	2.48	ND	ND	82.80
$CaCl_2$ extract	ND	ND	ND	0.08	1.40	11.94	3.50	ND	2.04	ND	ND	14.26
DTPA extract	ND	ND	ND	ND	1.96	18.44	6.61	ND	4.69	ND	ND	9.08

BET surface area (m^2/g)	Langmuir surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Surface characteristics			
108.47 ± 0.04	212.95 ± 0.41	0.013 ± 0.008	13.57 ± 0.06

ND not detected

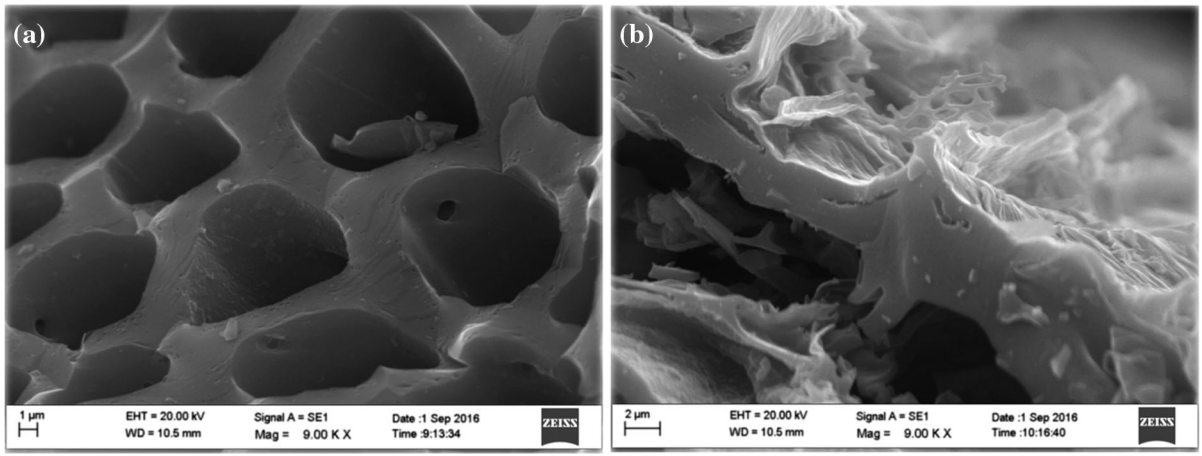

Fig. 1 SEM images in **a** raw MSW-BC and **b** benzene loaded

recognized as an indicator for aromaticity and polarity of BC, respectively (Sizirici and Tansel 2010; Florez Menendez et al. 2004). Also, 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, implying a highly aromatic structure. However, the decrease in polar functional groups on the MSW-BC is consistent with a decrease in water molecule adsorption, and thus productive for benzene adsorption (Xiao et al. 2014). Lower polarity index and H/C ratios contribute to intermolecular attraction with aromatic and aliphatic groups. Therefore, non-polar benzene can be potentially sorbed by MSW-BC (Costa et al. 2012; Daifullah and Girgis 2003). The reduction of O/C and H/C ratios can be explained by dehydration, decarboxylation and decarbonylation, which is due to pyrolysis process at higher temperatures and has been observed previously Edil (2003). Finally, the heavy metal content of MSW-BC is very low. Therefore, MSW-BC can be potentially implemented as a sorbent without any constrain on the environment.

pH-dependent sorption of benzene on MSW-BC

Adsorption capacities were evaluated under different pH conditions, and it is clear that the amount of adsorbate uptake via the adsorbent slightly depends on the solution pH ($r = 0.9915$) (Fig. 2). Adsorption of benzene on MSW-BCs was favored at alkaline pH. The highest removal capacity of 39.6 µg/g was observed at pH 9. The negatively charged surface of

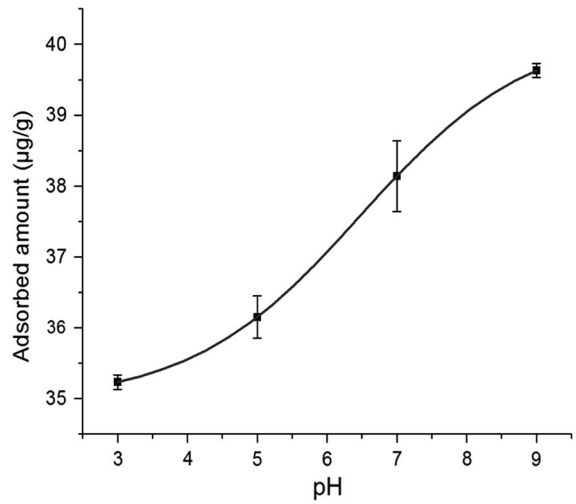

Fig. 2 Effect of solution pH on benzene adsorption onto MSW-BC

MSW-BC at higher pH contributes to polar π interactions, which is just an electrostatic interaction. However, the positively charge species of metallic ions at the biochar surface would help to polarize the p-electron cloud and lead to the formation of weak electrostatic interactions, and thus to higher sorption at higher pH (Steed and Atwood 2013; Lehmann and Joseph 2015). Previous studies have also shown that benzene adsorption prefers high pH conditions (Wibowo et al. 2007). Since pH values of both MSW-BCs and landfill leachate have a similar pH range, pH adjustments may not be required in practical applications.

Adsorption isotherm for MSW-BC

The data indicate high sorption capacity of benzene on MSW-BC and, as expected, sorption rate decreased with increase in the benzene concentration, which may be due to the reduction in available sites for adsorption. Adsorption isotherm models describe the relationship between the amount of benzene adsorbed by a unit weight of MSW-BC and the remaining amount of substance in the solution at equilibrium. Table 3 shows the regression coefficients and isotherm parameters obtained from isotherm adsorption modeling. It is evident that the equilibrium sorption data fitted both Langmuir and Freundlich models with high regression coefficients ($R^2 > 0.9$) (Fig. 3). The Freundlich isotherm modeled data suggest that benzene adsorption is a multilayer physical type of adsorption onto heterogeneous surfaces of MSW-BC, which have different adsorption energies (Ho et al. 2002; Mohan et al. 2011). The n values obtained from the Freundlich equation are <1 indicating the heterogeneity of the surface of the MSW-BCs. Benzene adsorption data were also well described by the Langmuir model, suggesting that benzene adsorption can also be governed by chemisorption mechanisms. The maximum adsorption amount determined from the Langmuir equation was 576 μg/g at room temperature. Moreover, the best-fitted models seemed to vary depending on the temperature of the isotherm experiment. At room temperature, the adsorption data were more inclined toward Langmuir behavior, which indicates monolayer adsorption. However, with increases in temperature, both models seemed to be well fitted to adsorption data. The goodness of fit for both Freundlich and Langmuir isotherms was reported by previous studies and demarcate the contrasting effect of chemisorption and physisorption processes (Mor et al. 2007). This adsorption behavior can be explained by monolayer chemisorption processes becoming increasingly heterogeneous with physisorption favored at increasing in temperature. Therefore, the mechanisms of both chemisorption and

Table 3 Isotherm and kinetic parameters for benzene adsorption onto MSW-BC (pH 8.7)

	Name	Nonlinear equation	Description	Parameters	Values		
					25 °C	35 °C	45 °C
Isotherm models	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}	576	148	517
				K_L	0.006	0.056	0.012
			q_{max} (μg/g) is the maximum adsorption capacity	R^2	0.932	0.917	0.920
			K_L (L/mg) is the Langmuir affinity parameter				
			C_e (μg/L) is the equilibrium adsorbate aqueous phase concentration				
	Freundlich	$q_{ads} = K_F C_e^n$	K_F is the (μg/g)/(μg/L)^n) is the Freundlich affinity—capacity parameter	K_F	0.475	7.90	11
				n	0.875	0.76	0.79
			n is the Freundlich exponent	R^2	0.945	0.969	0.954
Kinetic models	Pseudo-second order	$q_t = \frac{q_e^2 k_2 t}{1+k_2 t q_e}$	k_2—the rate constant (g/μg/min)	k_2	0.027		
			q_e, q_t—sorption capacity at equilibrium and	q_e	44.210		
			at time t, respectively (μg/g)	R^2	0.993		
	Elovich	$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t)$	q_t—sorption capacity at time t (μg/g)	a	263.782		
			a—initial sorption rate (μg/g/μin)	b	0.152		
			b—desorption constant (g/μg)	R^2	0.932		
	Power function	$q_t = b\left(t^{kf}\right)$	q_t—sorption capacity at time t (μg/g)	b	24.905		
			b—power function constant	k_f	0.189		
			k_p—power function rate constant	R^2	0.879		

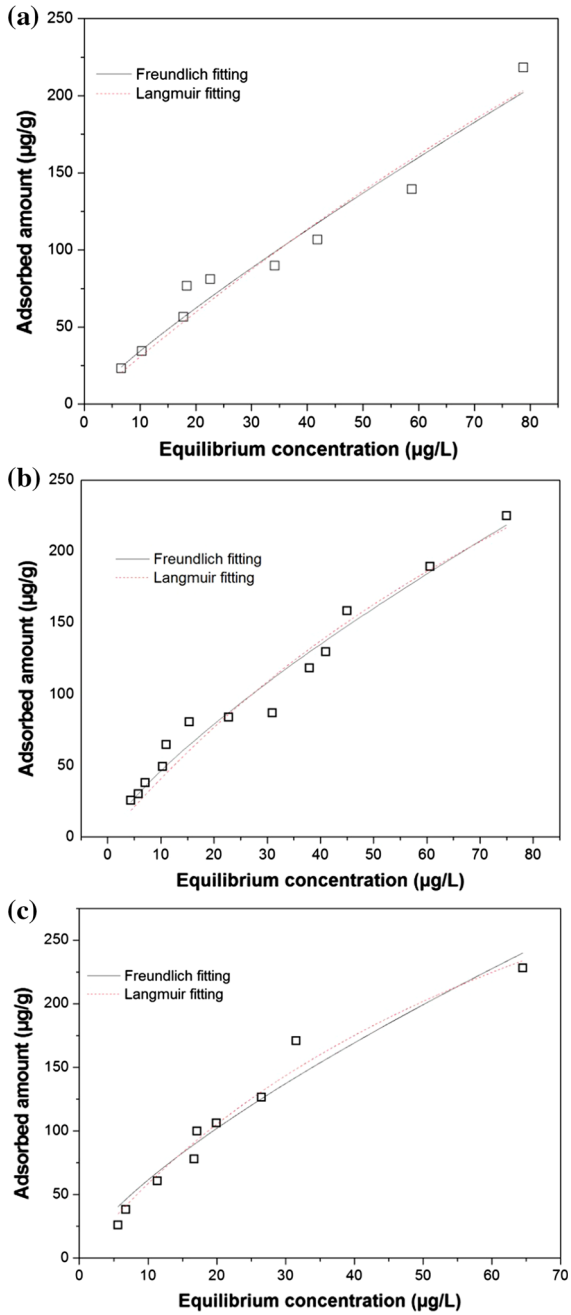

Fig. 3 Isotherm fitting for benzene by MSW-BC at **a** 25 °C, **b** 35 °C and **c** 45 °C. The symbols represent experimental results and lines show the model predicted data fittings

physisorption may be involved in benzene removal (Horsfall et al. 2004). Chemisorption can be further explained through the electrostatic attractions between benzene and the polarized π-electron cloud on biochar surface resulted from positive charge species of

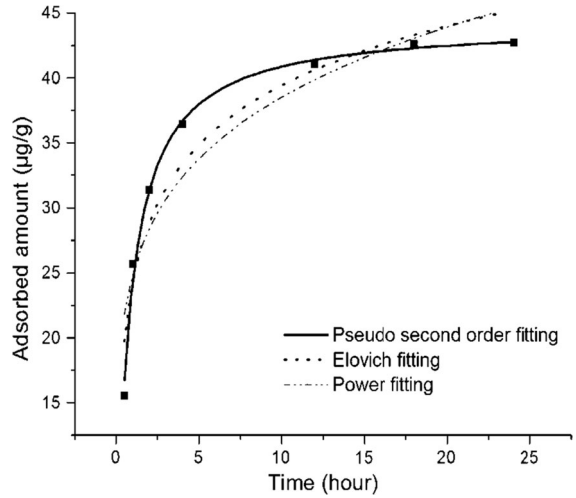

Fig. 4 Pseudo-second-order, power and Elovich models on kinetic data. The symbols represent experimental results and lines show the model predicted data fittings

metallic ions in biochar surface through the pH dependencies.

Kinetics of benzene adsorption

The adsorption kinetics of benzene exhibited two stages, a very rapid adsorption step in the initial stage followed by a slow adsorption step (Ahmad et al. 2012). Rapid sorption of benzene was observed within the first 5.5 h of contact time resulting in an adsorption of almost 40 mg/g (73.0%), which was followed by a slow adsorption rate reaching equilibrium (Fig. 4). This multistage sorption can be attributed to the fact that the available active sites on MSW-BCs tend to be progressively saturated with time, thereby resulting in a slow adsorption of the benzene to the bulk of MSW-BCs. The estimated values of kinetic model parameters together with the correlation coefficient (R^2) values are summarized in Table 3. It can be noted that the best fitting kinetic model order is pseudo-second-order $\gg$ Elovich $>$ power function. Best fitting to pseudo-second-order model may indicate that the rate-controlling step is chemisorption.

Thermodynamics studies

The values of the thermodynamic parameters are considered as indications of the type of adsorption force (Table 4). The values obtained for ΔG^0 were

Table 4 Thermodynamic parameters of benzene adsorption onto MSW-BCs

Parameter	Value
ΔH^0 (kJ/mol)	−24.40
ΔS^0 (J/mol K)	135.10
ΔG^0 (kJ/mol)	
25 °C	−64.66
35 °C	−66.01
45 °C	−67.36

negative for all three considered temperatures implying the spontaneous nature of the adsorption reaction at a given temperature (Hercigonja et al. 2012). The ΔG^0 values for MSW-BCs at 25, 35 and 45 °C were −64.66, −66.01 and −67.36 kJ/mol, respectively. Thus, physisorptive adsorption processes are suggested based on the general guidelines: $-400 < \Delta G^0 < -80$ kJ/mol for chemical adsorption and $-20 < \Delta G^0 < 0$ kJ/mol for physical adsorption. Furthermore, the negative ΔG^0 values increased with increasing temperature, indicating that benzene adsorbs favorably at higher temperatures. This property can be explained by the enlargement of pore size in MSW-BCs and enhancement of the molecular velocity of benzene toward the interior of the MSW-BCs (Memon et al. 2009). The negative value of ΔH^0 (−24.40 kJ/mol) which is close to 20.00 kJ/mol further confirms that the adsorption process is governed by physical interactions and is exothermic (Dula et al. 2014). Based on previous literature, negative values of free energy inversion for the removal of benzene with montmorillonite showed that the process is thermodynamically feasible and spontaneous (Nourmoradi et al. 2012). In addition, competitive adsorption of model oil and benzene on granular AC was deemed a spontaneous and exothermic adsorption process (Wang et al. 2016). The results of Table 4 show the sorption capacities of MSW-BC for benzene at various temperatures also verified this fact. The positive value of ΔS^0 of 135.10 J/K mol confirms the randomness of benzene molecules at the solid–solution interface during the adsorption process, indicating high affinity of benzene for MSW-BC.

FTIR interpretation

The FTIR spectra (Fig. 5) illustrate changes in MSW-BC surface functional groups following interactions with benzene. Though benzene is symmetric, the appearance of new stretching bands in benzene-sorbed MSW-BC surface can be attributed to changing resonances over the reaction period with overtones and combinations of the near-infrared region (Workman and Weyer 2012). However, visualization of intense peaks closer to the fingerprint area may explain the sorption of aromatics (1615–1495 cm^{-1}) and the plainer C–H bending vibration of moderate absorption at 1150–950 cm^{-1} confirmed the aromaticity of MSW-BC (Coates 2000). The stretching of the band at 1118 cm^{-1} may be due to the phenolic OH group, which disappeared in the spectrum of benzene-adsorbed MSW-BC (Daifullah and Girgis 2003). This disappearance may be due to the interaction of the resonance electron cloud of the benzene ring with the positive charge of phenolic hydrogen. The new band at 1618 cm^{-1} can be attributed to the presence of asymmetric –COOH (Gebelein et al. 1991) or a shifting of the band at 1614 cm^{-1} representing C=C dissociation. Also, π–π donor interactions can be the possible output of such peak shifting (Wolbach and Anders 1989; Xiao et al. 2014). The spectrum of benzene-adsorbed MSW-BCs exhibited an intense band at 1617 cm^{-1}, indicating the accumulation of COO aromatics (Gómez-Serrano et al. 1994; Van der Mass 1969). Furthermore, the splitting of the broad peak near 3000–3500 cm^{-1} can be due to changes in the chemical interaction between the position and nature of substances on the ring and MSW-BC (Coates 2000). However, all the normal CH stretching patterns of benzene spectrum are deficient in current graph, further explaining the dissociation of parent molecules.(Larkin 2011; Workman and Weyer 2012). In addition, only some of the substituent can provide structural vibration information with a mechanical coupling (Larkin 2011). Hence, the substitution of one substituent results in significant increments of vibration and, therefore, lead to a spectrum with complex vibrations (Colthup et al. 1990). Apart from that, the wave number of 886.9 cm^{-1} can be a possible vibration from mono-substituted benzene present in the matrix (Colthup 1976). The occurrence of different mono-substituted bands within the region suggests the formation of different complexes, including di- and tri-substituted forms (Workman and Weyer 2012). Furthermore, several studies suggested the chemisorption of benzene under the presence of catalyst at ambient temperature, which implies by several sorbents (i.e., porous carbon, AC, zeolite,

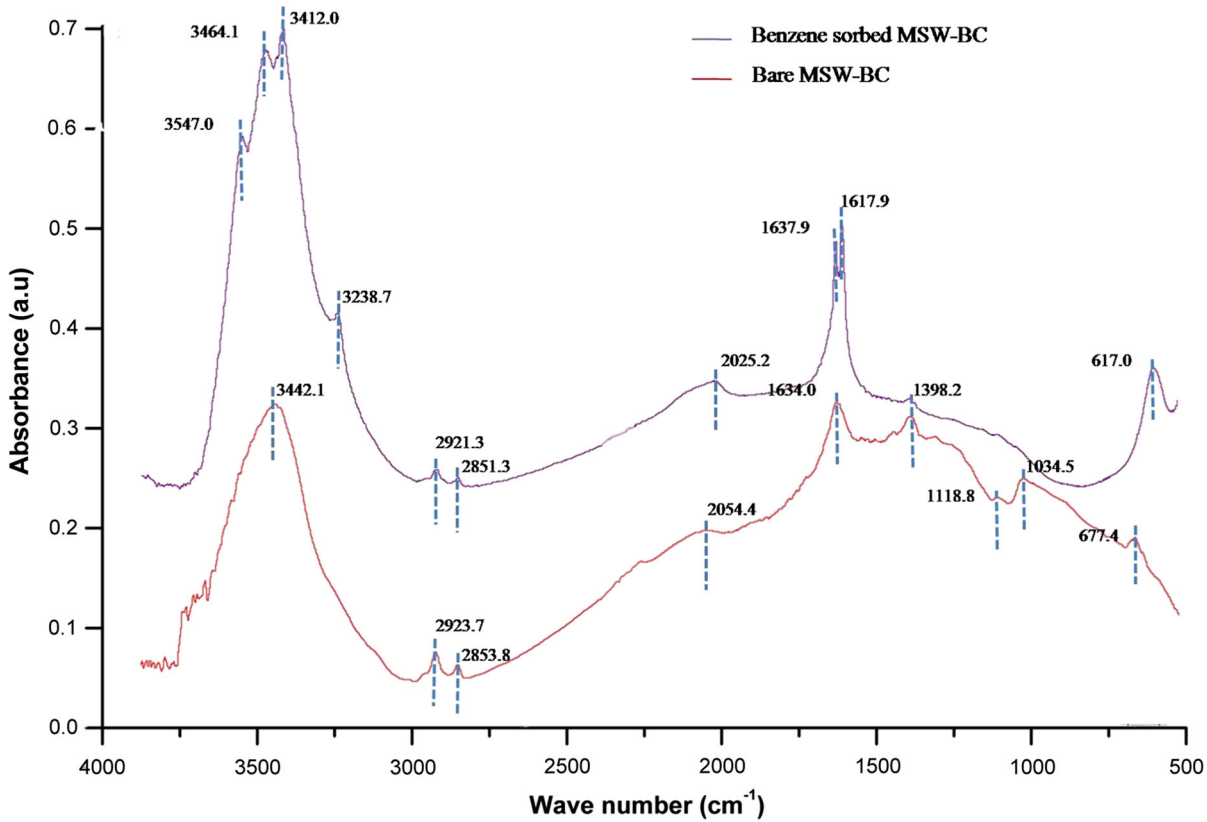

Fig. 5 FTIR spectrum for bare (*bottom spectrum*) and benzene-adsorbed MSW-BCs (*top spectrum*)

montmorillonite) with Zn and Ti catalyst. (Chun et al. 2004; Huang et al. 2008; Slovetskaya et al. 1970; Hinedi et al. 1993). MSW-BC contains both Zn and Ti, which can act as a catalyst within the media and which inhibit the energy gap of resonance structures. Therefore, new assignments of stretches in the spectrum might be due to chemical interactions with the benzene ring. It is suggested that the observed high intensity of FTIR bands can be attributed to weak chemical interaction with the benzene ring.

Conclusions

The present study was conducted to investigate for the first time the remediation of benzene in leachate draining from MSW dumpsites using biochar derived from the MSW itself. In summary, all the leachate samples obtained from Gohagoda dumpsite exceeded the MCL for benzene. The low availability of heavy metals in MSW-BC confirms the possibility of MSW-BC for potential use to remove benzene from leachate. The adsorption of benzene onto MSW-BCs was highly pH dependent, and the maximum adsorption was recorded under alkaline pH conditions (pH $\sim$ 9). Both Freundlich and Langmuir models fitted best the equilibrium isotherm data suggesting physisorption as well as chemisorption mechanisms governed benzene adsorption. The kinetics of the adsorption process was explained well by the pseudo-second-order model, indicating that benzene adsorption onto MSW-BC occurs more likely through chemisorption mechanism. Nevertheless, thermodynamic parameters indicated the spontaneous and feasible nature of benzene adsorption and showed great favorability at higher temperatures, and important physical interactions. Analysis of FTIR spectra demonstrated the involvement of different physiochemical interactions in benzene adsorption on heterogeneous MSW-BC. Overall, our results showed that MSW-BC is highly effective in removing benzene from aqueous solution in conditions representative of the environmental (e.g.,

circum neutral). Therefore, it is essential that this green technology be transferred from the laboratory phase to the field to remediate leachate, which will reduce the quantity and volume of MSW in part by using the MSW as the source for the BC to control its own contaminants.

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References

Abdullah, M. P., & Chian, S. S. (2011). Chlorinated and nonchlorinated-volatile organic compounds (VOCs) in drinking water of peninsular Malaysia. *Sains Malaysiana, 40*(11), 1255–1261.

Abumaizar, R. J., Kocher, W., & Smith, E. H. (1998). Biofiltration of BTEX contaminated air streams using compost-activated carbon filter media. *Journal of Hazardous Materials, 60*(2), 111–126.

Agarwal, M., Tardio, J., & Mohan, S. V. (2015). Pyrolysis biochar from cellulosic municipal solid waste as adsorbent for azo dye removal: Equilibrium isotherms and kinetics analysis. *International Journal of Environmental Science and Development, 6*(1), 67.

Agrafioti, E., Kalderis, D., & Diamadopoulos, E. (2014). Arsenic and chromium removal from water using biochars derived from rice husk, organic solid wastes and sewage sludge. *Journal of Environmental Management, 133,* 309–314.

Ahmad, M., Lee, S. S., Dou, X., Mohan, D., Sung, J.-K., Yang, J. E., et al. (2012). Effects of pyrolysis temperature on soybean stover-and peanut shell-derived biochar properties and TCE adsorption in water. *Bioresource Technology, 118,* 536–544.

Ahmad, M., Lee, S. S., Rajapaksha, A. U., Vithanage, M., Zhang, M., Cho, J. S., et al. (2013). Trichloroethylene adsorption by pine needle biochars produced at various pyrolysis temperatures. *Bioresource Technology, 143,* 615–622. doi:10.1016/j.biortech.2013.06.033.

Andrew, D., Lenore, S., Eugene, W., & Arnold, E. (1981). *Standard methods for the examination of water and wastewater: Selected analytical methods approved and cited by the United States Environmental Protection Agency*. Washington, DC: American Public Health Association.

Ateş, F., Miskolczi, N., & Borsodi, N. (2013). Comparision of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part I: Product yields, gas and pyrolysis oil properties. *Bioresource Technology, 133*, 443–454.

Bernardo, M., Lapa, N., Gonçalves, M., Mendes, B., Pinto, F., Fonseca, I., & Lopes, H. (2012). Physico-chemical properties of chars obtained in the co-pyrolysis of waste mixtures. *Journal of Hazardous Materials, 219–220*, 196–202.

Bornemann, L. C., Kookana, R. S., & Welp, G. (2007). Differential sorption behaviour of aromatic hydrocarbons on charcoals prepared at different temperatures from grass and wood. *Chemosphere, 67*(5), 1033–1042.

Cal, M. P., Rood, M. J., & Larson, S. M. (1996). Removal of VOCs from humidified gas streams using activated carbon cloth. *Gas Separation and Purification, 10*(2), 117–121.

Cantrell, K. B., Hunt, P. G., Uchimiya, M., Novak, J. M., & Ro, K. S. (2012). Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Bioresource Technology, 107,* 419–428. doi:10.1016/j.biortech.2011.11.084.

Chun, Y., Sheng, G., Chiou, C. T., & Xing, B. (2004). Compositions and sorptive properties of crop residue-derived chars. *Environmental Science and Technology, 38*(17), 4649–4655.

Coates, J. (2000). Interpretation of infrared spectra, a practical approach. In *Encyclopedia of analytical chemistry*. Chichester: Wiley.

Colthup, N. B. (1976). The calculation of some CH wag group frequencies in substituted benzenes, naphthalenes, and acetylenes. *Applied Spectroscopy, 30*(6), 589–593.

Colthup, N. B., Daly, L. H., & Wiberley, S. E. (1990). *Introduction to infrared and Raman spectroscopy* (3rd ed.). San Diego: Academic Press.

Costa, A. S., Romão, L., Araújo, B., Lucas, S., Maciel, S., Wisniewski, A., et al. (2012). Environmental strategies to remove volatile aromatic fractions (BTEX) from petroleum industry wastewater using biomass. *Bioresource Technology, 105,* 31–39.

Cotruvo, J. A., & Regelski, M. (1989). National primary drinking water regulations for volatile organic chemicals. In E. J. Calabrese (Ed.), *Safe drinking water act: Amendments, regulations, and standards* (pp. 29–34). Chelsea, MI: Lewis Publishers.

Daifullah, A., & Girgis, B. (2003). Impact of surface characteristics of activated carbon on adsorption of BTEX. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 214*(1), 181–193.

Dula, T., Siraj, K., & Kitte, S. A. (2014). Adsorption of hexavalent chromium from aqueous solution using chemically activated carbon prepared from locally available waste of bamboo (*Oxytenanthera abyssinica*). *ISRN Environmental Chemistry*. doi:10.1155/2014/438245.

Edil, T. B. (2003). A review of aqueous-phase VOC transport in modern landfill liners. *Waste Management, 23*(7), 561–571. doi:10.1016/S0956-053X(03)00101-6.

Eichelberger, J., Budde-Revision, W., Munch, J., & Bellar-Revision, T. (1989). Method 524.2 measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry. In J. W. Munch (Ed.), *Environmental monitoring systems laboratory office of research and development* (p. 45268). Cincinnati, OH: US EPA.

EPA. (2003). *Integrated risk information system (IRIS) technical factsheet on: Benzene*. Washington, DC: United States Environmental Protection Agency.

Florez Menendez, J. C., Fernandez Sanchez, M. L., Fernandez Martiinez, E., Sanchez Uriia, J. E., & Sanz-Medel, A. (2004). Static headspace versus head space solid-phase microextraction (HS-SPME) for the determination of volatile organochlorine compounds in landfill leachates by gas chromatography. *Talanta, 63*(4), 809–814. doi:10.1016/j.talanta.2003.12.044.

Först, C., Stieglitz, L., Roth, W., & Kuhnmünch, S. (1989). Quantitative analysis of volatile organic compounds in landfill leachates. *International Journal of Environmental Analytical Chemistry, 37*(4), 287–293.

Gebelein, C., Cheng, T., & Yang, V. C. (1991). *Cosmetic and pharmaceutical applications of polymers*. New York: Springer, Plenum Press.

Gómez-Serrano, V., Acedo-Ramos, M., López-Peinado, A. J., & Valenzuela-Calahorro, C. (1994). Oxidation of activated carbon by hydrogen peroxide. Study of surface functional groups by FT-ir. *Fuel, 73*(3), 387–395.

Harkov, R., Gianti, S. J., Jr., Bozzelli, J. W., & LaRegina, J. E. (1985). Monitoring volatile organic compounds at hazardous and sanitary landfills in New Jersey. *Journal of Environmental Science and Health Part A, 20*(5), 491–501.

Heavey, M. (2003). Low-cost treatment of landfill leachate using peat. *Waste Management, 23*(5), 447–454.

Hercigonja, R., Rac, V., Rakic, V., & Auroux, A. (2012). Enthalpy–entropy compensation for n-hexane adsorption on HZSM-5 containing transition metal ions. *The Journal of Chemical Thermodynamics, 48,* 112–117.

Hinedi, Z., Johnston, C., & Erickson, C. (1993). Chemisorption of benzene on Cu-montmorillonite as characterized by FTIR and^ 1^ 3C MAS NMR. *Clays and Clay Minerals, 41,* 87.

Ho, Y. S., Porter, J. F., & McKay, G. (2002). Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component systems. *Water, Air, and Soil Pollution, 141*(1–4), 1–33. doi:10.1023/a:1021304828010.

Horsfall, M., Spiff, A. I., & Abia, A. (2004). Studies on the influence of mercaptoacetic acid (MAA) modification of cassava (Manihot sculenta cranz) waste Biomass on the adsorption of Cu^{2+} and Cd^{2+} from aqueous solution. *Bulletin of the Korean Chemical Society, 25*(7), 969–976.

Huang, J., Wang, X., Hou, Y., Chen, X., Wu, L., & Fu, X. (2008). Degradation of benzene over a zinc germanate photocatalyst under ambient conditions. *Environmental Science and Technology, 42*(19), 7387–7391.

Ilhan, F., Kurt, U., Apaydin, O., & Gonullu, M. T. (2008). Treatment of leachate by electrocoagulation using aluminum and iron electrodes. *Journal of Hazardous Materials, 154*(1), 381–389.

Jin, H., Capareda, S., Chang, Z., Gao, J., Xu, Y., & Zhang, J. (2014). Biochar pyrolytically produced from municipal solid wastes for aqueous As (V) removal: Adsorption property and its improvement with KOH activation. *Bioresource Technology, 169,* 622–629.

Kaur, K., Mor, S., & Ravindra, K. (2016). Removal of chemical oxygen demand from landfill leachate using cow-dung ash as a low-cost adsorbent. *Journal of Colloid and Interface Science, 469,* 338–343.

Kim, K.-H., Baek, S. O., Choi, Y.-J., Sunwoo, Y., Jeon, E.-C., & Hong, J. (2006). The emissions of major aromatic VOC as landfill gas from urban landfill sites in Korea. *Environmental Monitoring and Assessment, 118*(1–3), 407–422.

Kim, K.-H., Shon, Z.-H., Kim, M.-Y., Sunwoo, Y., Jeon, E.-C., & Hong, J.-H. (2008). Major aromatic VOC in the ambient air in the proximity of an urban landfill facility. *Journal of Hazardous Materials, 150*(3), 754–764.

Kolb, B., & Ettre, L. S. (2006). *Static headspace-gas chromatography: theory and practice*. Hoboken, NJ: Wiley.

Kumarathilaka, P., Jayawardhana, Y., Basnayake, B., Mowjood, M., Nagamori, M., Saito, T., et al. (2016). Characterizing volatile organic compounds in leachate from Gohagoda municipal solid waste dumpsite, Sri Lanka. *Groundwater for Sustainable Development, 2,* 1–6.

Larkin, P. (2011). *Infrared and Raman spectroscopy; principles and spectral interpretation*. Oxford: Elsevier.

Lehmann, J., & Joseph, S. (Eds.). (2009). *Biochar for environmental management: Science and technology* (416 p). London & Sterling, VA: Earthscan.

Lehmann, J., & Joseph, S. (2015). Biochar for environmental management: Science, technology and implementation (2nd ed., pp. 563–594). Routledge.

Li, W., Hua, T., Zhou, Q., Zhang, S., & Li, F. (2010). Treatment of stabilized landfill leachate by the combined process of coagulation/flocculation and powder activated carbon adsorption. *Desalination, 264*(1), 56–62.

Lillo-Ródenas, M., Fletcher, A., Thomas, K., Cazorla-Amorós, D., & Linares-Solano, A. (2006). Competitive adsorption of a benzene–toluene mixture on activated carbons at low concentration. *Carbon, 44*(8), 1455–1463.

Liu, G., Xie, M., & Zhang, S. (2015). Effect of organic fraction of municipal solid waste (OFMSW)-based biochar on organic carbon mineralization in a dry land soil. *Journal of Material Cycles and Waste Management*, 1–10.

Memon, G. Z., Bhanger, M., Memon, J. R., & Akhtar, M. (2009). Adsorption of methyl parathion from aqueous solutions using mango kernels: Equilibrium, kinetic and thermodynamic studies. *Bioremediation Journal, 13*(2), 102–106.

Milla, O. V., Wang, H.-H., & Huang, W.-J. (2013). Feasibility study using municipal solid waste incineration bottom ash and biochar from binary mixtures of organic waste as agronomic materials. *Journal of Hazardous Toxic and Radioactive Waste, 17*(3), 187–195.

Mohan, D., Rajput, S., Singh, V. K., Steele, P. H., & Pittman, C. U., Jr. (2011). Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent. *Journal of Hazardous Materials, 188*(1–3), 319–333. doi:10.1016/j.jhazmat.2011.01.127.

Mor, S., Ravindra, K., Dahiya, R., & Chandra, A. (2006). Leachate characterization and assessment of groundwater pollution near municipal solid waste landfill site. *Environmental Monitoring and Assessment, 118*(1–3), 435–456.

Mor, S., Ravindra, K., & Bishnoi, N. (2007). Adsorption of chromium from aqueous solution by activated alumina and activated charcoal. *Bioresource Technology, 98*(4), 954–957.

Mor, S., Chhoden, K., & Ravindra, K. (2016). Application of agro-waste rice husk ash for the removal of phosphate from the wastewater. *Journal of Cleaner Production, 129,* 673–680.

Mournighan, R., Dudzinska, M. R., Barich, J., Gonzalez, M. A., & Black, R. K. (2007). *Chemistry for the protection of the environment 4* (Vol. 59). New York: Springer.

Navarri, P., Marchal, D., & Ginestet, A. (2001). Activated carbon fibre materials for VOC removal. *Filtration & Separation, 38*(1), 33–40.

Nourmoradi, H., Khiadani, M., & Nikaeen, M. (2012). Multicomponent adsorption of benzene, toluene, ethylbenzene, and xylene from aqueous solutions by montmorillonite modified with tetradecyl trimethyl ammonium bromide. *Journal of Chemistry*. doi:10.1155/2013/589354.

Ok, Y. S., Yang, J. E., Zhang, Y. S., Kim, S. J., & Chung, D. Y. (2007). Heavy metal adsorption by a formulated zeolite-Portland cement mixture. *Journal of Hazardous Materials, 147*(1–2), 91–96. doi:10.1016/j.jhazmat.2006.12.046.

Pei, J., & Zhang, J. S. (2012). Determination of adsorption isotherm and diffusion coefficient of toluene on activated carbon at low concentrations. *Building and Environment, 48,* 66–76.

Rajapaksha, A. U., Ahmad, M., Vithanage, M., Kim, K.-R., Chang, J. Y., Lee, S. S., et al. (2015). The role of biochar, natural iron oxides, and nanomaterials as soil amendments for immobilizing metals in shooting range soil. *Environmental Geochemistry and Health, 37*(6), 931–942.

Restek, A. (2000). *Technical guide for static headspace analysis using GC* (pp. 11–12). Bellefonte: Restek Corp.

Sabel, G. V., & Clark, T. P. (1984). Volatile organic compounds as indicators of municipal solid waste leachate contamination. *Waste Management and Research, 2*(1), 119–130.

Safarova, V., Sapelnikova, S., Djazhenko, E., Teplova, G., Shajdulina, G., & Kudasheva, F. K. (2004). Gas chromatography–mass spectrometry with headspace for the analysis of volatile organic compounds in waste water. *Journal of Chromatography B, 800*(1), 325–330.

Salman, J., Njoku, V., & Hameed, B. (2011). Adsorption of pesticides from aqueous solution onto banana stalk activated carbon. *Chemical Engineering Journal, 174*(1), 41–48.

Scheutz, C., Mosbæk, H., & Kjeldsen, P. (2004). Attenuation of methane and volatile organic compounds in landfill soil covers. *Journal of Environmental Quality, 33*(1), 61–71.

Sizirici, B., & Tansel, B. (2010). Projection of landfill stabilization period by time series analysis of leachate quality and transformation trends of VOCs. *Waste Management, 30*(1), 82–91. doi:10.1016/j.wasman.2009.09.006.

Slovetskaya, K., Zlotina, N., Kiperman, S., & Rubinshtein, A. (1970). Adsorption of benzene on a nickel-zinc oxide catalyst. *Russian Chemical Bulletin, 19*(5), 1014–1019.

Srivastava, A., & Mazumdar, D. (2011). *Monitoring and Reporting VOCs in Ambient Air*. Rijeka: INTECH Open Access Publisher.

Steed, J. W., & Atwood, J. L. (2013). *Supramolecular chemistry* (2nd ed.). Chichester: Wiley.

Su, F., Lu, C., & Hu, S. (2010). Adsorption of benzene, toluene, ethylbenzene and p-xylene by NaOCl-oxidized carbon nanotubes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 353*(1), 83–91.

Tham, Y., Latif, P. A., Abdullah, A. M., Shamala-Devi, A., & Taufiq-Yap, Y. (2011). Performances of toluene removal by activated carbon derived from durian shell. *Bioresource Technology, 102*(2), 724–728.

Van der Mass, J. H. (1969). *Basic infrared spectroscopy*. London: Hyden & son Ltd.

Visvanathan, C., & Trankler, J. (2003). Municipal solid waste management in Asia: A comparative analysis. In *workshop on sustainable landfill management* (pp. 3–5). Citeseer.

WACS (May 2014). Source: Waste amount and composition surveys (WACS) implemented in the Central and Southern Provinces of Sri Lanka, SATREPS report.

Wang, J., Liu, H., Yang, H., Qiao, C., & Li, Q. (2016). Competition adsorption, equilibrium, kinetic, and thermodynamic studied over La (III)-loaded active carbons for dibenzothiophene removal. *Journal of Chemical and Engineering Data, 61,* 3533.

Watanabe, F., & Olsen, S. (1965). Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soil. *Soil Science Society of America Journal, 29*(6), 677–678.

Wibowo, N., Setyadhi, L., Wibowo, D., Setiawan, J., & Ismadji, S. (2007). Adsorption of benzene and toluene from aqueous solutions onto activated carbon and its acid and heat treated forms: influence of surface chemistry on adsorption. *Journal of Hazardous Materials, 146*(1), 237–242.

Wijesekara, S. S. R. M. D. H. R., Mayakaduwa, S., Siriwardana, A. R., de Silva, N., Basnayake, B. F. A., Kawamoto, K., et al. (2014). Fate and transport of pollutants through a municipal solid waste landfill leachate in Sri Lanka. *Environmental Earth Sciences, 72*(5), 1707–1719. doi:10.1007/s12665-014-3075-2.

Wolbach, W. S., & Anders, E. (1989). Elemental carbon in sediments: determination and isotopic analysis in the presence of kerogen. *Geochimica et Cosmochimica Acta, 53*(7), 1637–1647.

Wood, J. A., & Porter, M. L. (1987). Hazardous pollutants in class II landfills. *JAPCA, 37*(5), 609–615.

Workman, J., Jr., & Weyer, L. (2012). *Practical guide and spectral atlas for interpretive near-infrared spectroscopy*. Boca Raton, FL: CRC Press.

Wu, B., Taylor, C. M., Knappe, D. R., Nanny, M. A., & Barlaz, M. A. (2001). Factors controlling alkylbenzene sorption to municipal solid waste. *Environmental Science and Technology, 35*(22), 4569–4576.

Xiao, L., Bi, E., Du, B., Zhao, X., & Xing, C. (2014). Surface characterization of maize-straw-derived biochars and their sorption performance for MTBE and benzene. *Environmental Earth Sciences, 71*(12), 5195–5205.

Xu, X., Schierz, A., Xu, N., & Cao, X. (2016). Comparison of the characteristics and mechanisms of Hg(II) sorption by biochars and activated carbon. *Journal of Colloid and Interface Science, 463,* 55–60.

Yakout, S. M. (2014). Removal of the hazardous, volatile, and organic compound benzene from aqueous solution using phosphoric acid activated carbon from rice husk. *Chemistry Central Journal, 8*(1), 1–7. doi:10.1186/s13065-014-0052-5.

Zhang, M., Ahmad, M., Al-Wabel, M. I., Vithanage, M., Rajapaksha, A. U., Kim, H. S., et al. (2015). Adsorptive removal of trichloroethylene in water by crop residue biochars pyrolyzed at contrasting temperatures:

Continuous fixed-bed experiments. *Journal of Chemistry*. doi:10.1155/2015/647072.

Zou, S., Lee, S., Chan, C., Ho, K., Wang, X., Chan, L., et al. (2003). Characterization of ambient volatile organic compounds at a landfill site in Guangzhou. *South China. Chemosphere, 51*(9), 1015–1022.

Zurbrugg, C. (2002). Urban solid waste management in low-income countries of Asia how to cope with the garbage crisis. In *presented for: scientific committee on problems of the environment* (*SCOPE*) *urban solid waste management review session* (pp. 1–13). Durban.