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Equilibrium and kinetic mechanisms of woody biochar on aqueous glyphosate removal

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HIGHLIGHTS

- A waste byproduct of a bioenergy industry was used for glyphosate remediation.
- \bullet Maximum glyphosate removal at pH 5–6 due to electron donor–acceptor interactions.
- Rate limiting step may be chemisorption through sharing or exchange of electrons.
- Phenolic, amine, and carboxylic functional groups were involved in adsorption.

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ABSTRACT

We investigated the removal of aqueous glyphosate using woody (dendro) biochar obtained as a waste by product from bioenergy industry. Equilibrium isotherms and kinetics data were obtained by adsorption experiments. Glyphosate adsorption was strongly pH dependent occurring maximum in the pH range of 5–6. The protonated amino moiety of the glyphosate molecule at this pH may interact with π electron rich biochar surface via π – π electron donor–acceptor interactions. Isotherm data were best fitted to the Freundlich and Temkin models indicating multilayer sorption of glyphosate. The maximum adsorption capacity of dendro biochar for glyphosate was determined by the isotherm modeling to be as 44 mg/g. Adsorption seemed to be quite fast, reaching the equilibrium <1 h. Pseudo-second order model was found to be the most effective in describing kinetics whereas the rate limiting step possibly be chemical adsorption involving valence forces through sharing or exchanging electrons between the adsorbent and sorbate. The FTIR spectral analysis indicated the involvement of functional groups such as phenolic, amine, carboxylic and phosphate in adsorption. Hence, a heterogeneous chemisorption process between adsorbate molecules and functional groups on biochar surface can be suggested as the mechanisms involved in glyphosate removal.

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1. Introduction

Increasing use of pesticides and herbicides has led to ubiquitous contamination of water resources. Leaching, run-offs from agricultural lands, deposition from aerial applications and indiscriminate discharge from industrial wastewater are responsible for water contamination by pesticides and herbicides (Arias-Estévez et al., 2008). Glyphosate [N-(phosphonomethyl)-glycine] is a broad-spectrum, non-selective, post emergence type of organophosphorous herbicide, widely used to control annual and perennial weeds (Waiman et al., 2012). According to the recent findings, around 650,000 tons of glyphosate has been used worldwide (Ke, 2013). In addition, glyphosate is highly water soluble and could be mobile in aquatic systems (Veiga et al., 2001). Water contamination with glyphosate has recently been reported. For example, glyphosate was detected in maximum concentration of

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0.476 mg L^{-1} in natural water of United States (Battaglin et al., 2014). Similarly, 1.26–1.48 mg L^{-1} concentration range of glyphosate was reported in natural waters of Brazil (Tzaskos et al., 2012). Although there is no specific guideline value for glyphosate, the European Union limits 0.1 μ g L⁻¹ for any herbicide in drinking water (Hu et al., 2011). While glyphosate is generally believed to be an environmentally safe herbicide due to microbial degradation and short half-life, recently its biosafety is questioned (Hagner et al., 2013). Depending on soil structure and environmental conditions such as rainfall, glyphosate is prone to leaching and contaminating groundwater thereafter (Borggaard and Gimsing, 2008). Glyphosate is responsible for cardiac and respiratory problems, allergic reactions and many other acute toxic effects (Hu et al., 2011). Glyphosate is considered as an endocrine disruptor in human cell lines (Richard et al., 2005). Therefore, it is an urgent subject to treat glyphosate from water. Adsorption is a kind of potential and effective method for the remediation of such pollutants, in terms of low cost, flexibility and simplicity of design, and ease of operation (Salman and Abid, 2013). Glyphosate contains functional groups that are positively (secondary amino group) or negatively (phosphonic and carboxylic group) charged in aqueous phase (Cáceres-Jensen et al., 2009) and the adsorption mechanisms of glyphosate have been suggested to be as ligand exchange (Piccolo et al., 1992), surface complexation (Morillo et al., 1997), precipitation reactions (Cáceres-Jensen et al., 2009), and coordination bonding (Cáceres-Jensen et al., 2009). Compared to conventional wastewater treatment protocol adsorption is applicable for largescale biochemical and purification applications which benefit from unique properties such as simple design, using non toxic and low cost adsorbents and high efficiency (Ghaedi et al., 2014).

Several studies have reviewed on using different materials, such as activated carbon (Speth, 1993), water industrial residues (Hu et al., 2011), clay substances (Gimsing and Borggaard, 2007) for glyphosate adsorptive removal. Recently, biochar is being widely focused as a universal sorbent similar to activated carbon, nevertheless biochar has drawn more attention due to its low cost and high removal capacity. However, residue remains after removal again to be dispose safely. In this case, a sorbent with high capacity would be an added advantage to the process. It is a carbonaceous material produced by thermal conversion of biomass under partial exclusion of oxygen using pyrolysis or gasification systems. The highly aromatic and porous structure, high negative surface charge and charge density is suggested to contribute high adsorption capacities of biochar (Zhang et al., 2013). Moreover, though biochar has demonstrated outstanding capabilities for the removal of organic pollutants from water (Zheng et al., 2010; Sun et al., 2012), little attention has been given to the adsorption of glyphosate onto biochar (Hagner et al., 2013). Biochar can be produced from any type of organic residue such as agricultural byproducts (Rehrah et al., 2014), plant residues (Zheng et al., 2010), animal manure (Zhang et al., 2013) and even from municipal solid waste (Jin et al., 2014). Hence, biochar has a high versatility of feedstocks. Not only that, biochar can be obtained as a waste byproduct from bioenergy industry. Very few studies reported the use of byproduct biochar on water contaminant remediation (Mohan et al., 2007). In our earlier study (Herath et al., 2015), waste woody biochar (dendro biochar) from a bioenergy production plant has been characterized and successfully used for immobilization of heavy metals. Nevertheless dendro biochar has not been explored for organic pollutant removal. The potential to combine bioenergy production, environmental remediation and waste management into one approach, using biochar may offer sustainable outcomes for our economy and environment. Thus, our aim was to examine the adsorption of glyphosate onto dendro biochar. The adaptability of different adsorption isotherm and kinetic models to describe the experimental equilibrium data was also investigated.

2. Materials and methods

2.1. Biochar production and characterization

Biochar was obtained as a waste byproduct from a bioenergy industry (Dendro) at Thirappane, Anuradhapura District, Sri Lanka, where biomass of *Gliricidia sepium* was gasified at 700–1000 °C in order to generate electricity. The collected dendro biochar was air dried and ground to less than 1 mm prior to use. Physico–chemical characterization of biochar was done in our earlier study using standard procedures (Herath et al., 2015). Accordingly parameters as moisture, mobile matter, ash content, resident matter, pH, elemental composition and BET surface area were determined.

2.2. Sorption experiments

Glyphosate (98% purity) was purchased from Sigma Aldrich, USA. The working solution concentration was selected based on glyphosate concentrations reported in environmental water samples and especially in the wastewater produced in glyphosate manufacturing. The pH of the mixtures was adjusted using 0.1 M HNO₃ and 0.1 M NaOH. Distilled deionized water (resistivity: 18.2 $M\Omega cm^{-1}$) was used to prepare all the solutions throughout the experiment. A 1 g L^{-1} dose of biochar was added followed by shaking at 100 rpm for an equilibrium period of 4 h selected based on preliminary experiments. Solutions were then filtered and aqueous glyphosate concentrations were determined using the procedure given in elsewhere (Bhaskara and Nagaraja, 2006) with a few modifications. Briefly, 0.5 mL each of 1% ninhydrin and 1% sodium molybdate was added to 0.2 mL of filtered sample and kept in a water bath at 85-95 °C for 12 min. Then the samples were cooled to room temperature, quantitatively transferred to 5 mL volumetric flasks and the volume was made up with distilled deionized water. The absorbance of the resulted purple color complex was measured at 530 nm using UV-Vis spectrophotometer (model UV-160 A, Shimadzu, Japan) and the remaining glyphosate concentrations were obtained from the calibration curve plotted by using 4 appropriate standards 4, 6, 10, 15 mg L^{-1} .

Adsorption edge experiments were conducted at 20 mg L⁻¹ glyphosate at different pHs from 3 to 8 using different acetate and phosphate buffers for a biochar dosage of 1 g L⁻¹. Batch isotherm studies were carried out in the glyphosate concentration range of 5-100 mg L⁻¹. Both isotherm and kinetic experiments were conducted at pH 5 with a biochar dosage of 1 g L⁻¹, buffered to pH 5 using 0.1 M acetic acid and 0.1 M sodium acetate (tri-hydrate) and shaken at 100 rpm (Hinotek THZ-100). A 20 mg L⁻¹ glyphosate was used for kinetics experiments. Samples were taken at predetermined time intervals, filtered and analyzed for remaining glyphosate amount following the procedure mentioned above. The amount of glyphosate retained in the adsorbent phase was calculated using following equation (Mohan et al., 2011):

$$q_e = [C_0 - C_e]VM^{-1}$$

where q_e is the glyphosate amount adsorbed on biochar (mg g⁻¹); C_0 and C_e are the initial and equilibrium glyphosate aqueous phase concentrations (mg L⁻¹); *V* is the solution volume (L) and *M* is the biochar mass (g). In both isotherm and kinetic modeling, the non-linear regression analysis was conducted using Microcal Origin (Version 6).

2.3. FTIR investigations

Biochar sample pellets were prepared with fused-KBr. Infrared spectra of both the bare and the glyphosate adsorbed biochar samples were obtained using a Fourier Transform Infrared Spectrometer (FTIR Nicolet, model 6700, USA) in the range of $400-4000 \text{ cm}^{-1}$ with 128 scans and 1 cm⁻¹ resolution.

3. Results and discussion

3.1. Biochar characterization

Characteristics of the dendro biochar are listed in Table 1. The ultimate analysis indicates the carbon, hydrogen, oxygen as well as sulfur and nitrogen % in weight whereas proximate analysis gives the moisture, fixed carbon, volatile and ash contents of the biochar (Mohan et al., 2011). The oxygen content is relatively higher than that of other woody biochars reported (Mohan et al., 2011), may be due to the gasification process (Oian et al., 2013). Also the carbon content is similar to reported gasification based char (34%–50%). and lower than reported pyrolysis based char (typically > 60%) (Qian et al., 2013). Atomic H/C and O/C ratios are indices of aromaticity and polarity of biochars. The aromatic H/C ratio of 0.24 reflects high contents of aromatic compounds. The BET surface area of the biochar was an extremely higher value of 714 m² g⁻¹ than that of other biochars obtained from invasive plants (Rajapaksha et al., 2015) and green waste (Zheng et al., 2010). Similar observations have reported by Duman et al. and Qian et al. for woody biochars carbonized at high temperatures (Qian et al., 2013; Duman et al., 2014).

3.2. Glyphosate sorption

Adsorption capacities were evaluated at different pHs as the pH is crucial for changes in the surface charge of adsorbents, the degree of ionization of the adsorbate as well as the speciation of the adsorbent (Mamindy-Pajany et al., 2014). Adsorption increases with the increase in pH from 11.03 mg/g to 21.6 mg/g and the maximum sorption was reached at the pH range of 5–6 and then the removal was dramatically decreased (Fig. 1a). Similar observations were reported with high glyphosate removal capacities, 85 and 114 mg/g, with water treatment residuals such as alum sludge, however, their adsorbent dosage is higher (3 and 5 g L^{-1})

 Table 1

 Proximate and ultimate analyses of dendro biochar²

Parameters	Value
рН	10.10
Proximate analysis	
Moisture (%)	6.5
Mobile matter (%)	9.9
Resident matter (%)	63.8
Ash (%)	19.7
Ultimate analysis	
C (%)	50
H (%)	1
O (%)	44
N (%)	0.5
S (%)	0.1
Molar H/C	0.24
Molar O/C	0.66
Molar $(O + N)/C$	0.89
BET Surface area $(m^2 g^{-1})$	714
Pore volume ($cm^3 g^{-1}$)	0.89
Pore diameter (nm)	4.08

^a (Herath et al., 2015).

compared to this study (Hu et al., 2011). The amino moiety of the glyphosate molecule becomes protonated at this pH range (Mohsen Nourouzi et al., 2010) and may interact with π electron rich biochar surface via $\pi - \pi$ electron donor-acceptor (EDA) interactions. Similarly, at pH 5, the BC surface is protonated as the zero point charge exceeds pH 5. Hence, acidic glyphosate ionizes in water and forms negative glyphosate ions which can easily react with positive charged BC surface and complex (Jin et al., 2014).

Sorption equilibrium data was tested on the Langmuir, Freundlich, Temkin and Dubinin Radushkevish isotherm models, respectively in order to understand the glyphosate removal mechanism. The data was best fitted with Freundlich model with $R^2 = 0.96$ (Table 2). Freundlich isotherm model describes adsorption occurring on heterogeneous and amorphous surfaces which have different adsorption energies not restricted to monolayer adsorption or finite sorbent uptake capacity (Mohan et al., 2011). The Freundlich exponent, n indicates favorability of the adsorption. Since n < 1 (0.406), the glyphosate adsorption can be suggested as a favorable process to heterogeneous biochar surface (Table 2). The experimental sorption isotherm was also well fitted ($R^2 = 0.92$) to Temkin equilibrium model indicating that glyphosate adsorption onto biochar could be a chemisorption process. The Langmuir model provides information on uptake capabilities. In this study, Langmuir model simulated a maximum adsorption capacity of 44 mg/g for dendro biochar, which is comparable (48 mg/g) to that reported for activated carbon (Mohsen Nourouzi et al., 2010). With a high initial concentration (500 mg L^{-1}) and high sorbent dosage (3 g/L) a study has observed higher sorption capacity of 117 mg/g (Hu et al., 2011). In comparison, the resin D301 have shown extremely high Langmuir maximum adsorption capacity of 400 mg/g at the room temperature and the capacity increased with increasing temperature (Chen et al., in press). In one other study, the Langmuir maximum adsorption capacity for glyphosate removal was found to be 98.5 mg/g for nano granular polianiline (Milojević-Rakić et al., 2013) (Table 3).

The Langmuir separation factor, R_L is used to predict whether a sorption system is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear $(R_L = 1)$ or unfavorable $(R_L > 1)$ in adsorption process. In our study, obtained R_L values lay between 0.15 and 0.88 confirming the favorable sorption in agreement with Freundlich model assumptions. The Dubinin Raduskevich (DR) model is applied to isotherm data in order to deduce the heterogeneity of the surface energies of adsorption and the characteristic porosity of the adsorbent. The constant B_D is related to the mean free energy of adsorption (E) per molecule of the adsorbate when transferred to the surface of the solid from infinity in solution. Values of $E < 8 \text{ kJ} \text{ mol}^{-1}$ indicate a physical adsorption process (Yu et al., 2012). The calculated E value for biochar was found to be 577 kJ mol⁻¹ (>8) indicating that the adsorption mechanism is not physisorption. Hence it can be proposed that glyphosate adsorption by dendro biochar may involve chemical adsorption between herbicide molecules and the heterogeneous nature of the biochar surface.

3.3. Kinetics of glyphosate adsorption

Adsorption of glyphosate occurred very rapidly in dendro biochar with an apparent equilibrium reached around 50 min–1 h (Fig. 1c). The equilibration time is considerably less than the reported data (Jin et al., 2014; Carneiro et al., 2015). Kinetic data was fitted to pseudo-first order, pseudo-second order, Elovich, parabolic diffusion and power function models. In pseudo-first order model, adsorption phenomenon is assumed to be a non-dissociating molecular adsorption on to the adsorbent. The pseudo-second order model is based on the assumption of chemical sorption involving valence forces through sharing or exchange of electrons between

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Fig. 1. (a) Effect of solution pH on glyphosate adsorption onto dendro biochar (b) Freundlich and Temkin adsorption isotherms of glyphosate by dendro biochar (c) Pseudo-second order, pseudo-first order and Elovich models on kinetic data.

the adsorbent and the adsorbate. The Elovich equation describes the kinetics of heterogeneous chemisorption whereas the parabolic model indicates that diffusion control phenomena are rate limiting. Power function model is commonly used to describe homogenous chemisorption kinetics. Calculated R² values from non-linear regression (Table 2) indicate that the best fit is obtained with pseudo second order model which suggests a chemisorption mechanism in agreement with best fitting to Freundlich and Temkin isotherm models. An adsorption capacity (q_e) of 22.78 mg g⁻¹ was predicted by pseudo-second order model for glyphosate sorption onto biochar. The best

Table 2

Langmuir, Freundlich, Temkin and Dubinin-Radushkevish isotherm parameters for glyphosate adsorption onto dendro biochar at pH ~5. All parameters were calculated by non-linear regression.

Model	Non linear equation	Description	Isotherm parameters	Value	R ²
Langmuir	$q_{ads} = \frac{q_{max}K_LC_e}{1+K_LC_e}$	$q_{ads} (mg g^{-1})$ is the amount of adsorbate adsorbed per unit weight of adsorbent $q_{max} (mg g^{-1})$ is the maximum adsorption capacity K_L (L mg ⁻¹) is the Langmuir affinity parameter $C_e (mg L^{-1})$ is the equilibrium adsorbate aqueous phase concentration	$q_{max}(mg g^{-1})$ $K_L (L g^{-1})$	44.01 0.088	0.91
Freundlich	$q_{ads} = K_F C_e^n$	K_F is the $((\text{mg g}^{-1})/(\text{mg L}^{-1})^n)$ is the Freundlich affinity—capacity parameter <i>n</i> is the Freundlich exponent	$K_F(\text{mg g}^{-1})/(\text{mg L}^{-1})^n)$ n	7.272 0.406	0.96
Temkin	$q_{ads} = \frac{RT}{b} \ln(AC_e)$	R is the universal gas constant (8.314 JK ⁻¹ mol ⁻¹) T is the absolute temperature (K) b is the heat of adsorption (J) A is the binding constant (L mg ⁻¹)	A(L mg ⁻¹) b	1.788 321.0	0.92
Dubinin— Radushkevish	$q_{ads} = q_D \exp(-B_D [RT \ln(1+1/C_e)]^2$	q_D is the monolayer adsorption capacity (mg g ⁻¹) B_D is the mean free energy of sorption (mol ² KJ ⁻¹)	$q_D(\text{mg g}^{-1})$ $(\text{mol}^2 \text{Kj}^{-1})$ B_D $E (\text{KJ mol}^{-1})$	30.313 1.5 × 10 ⁻⁶ 577.0	0.64

Table 3Kinetic parameters of glyphosate adsorption on dendro biochar.

Name	Equation	Parameter	Value	R ²
Pseudo first order	$q_t = q_e(1 - e^{-k_2 t})$	k ₁	0.038	0.940
		q_e	19.812	
Pseudo second order	$q_t = \frac{qe^2k_1t}{1+k_1taa}$	k_1	0.002	0.983
	- I TKIIde	q_e	22.774	
Elovich	$q_t = \frac{1}{h} \ln(ab) + \frac{1}{h} \ln(t)$	a	2.170	0.873
		b	0.215	
Parabolic	$q_t = a + kp\sqrt{t}$	а	5.729	0.702
		k_P	1.078	
Power function	$q_t = b(t^{kf})$	b	4.588	0.776
		k_f	0.285	

fitting order of kinetic model is determined to be pseudo second order > pseudo first order > Elovich > power function > parabolic diffusion.

3.4. FTIR analysis

The FTIR spectra of glyphosate adsorbed and bare biochar are depicted in Fig. 2. The peak found at 3437 cm⁻¹ in dendro biochar before adsorption was ascribed to phenolic -OH stretching (Xu et al., 2011). This peak have shifted to 3422 cm⁻¹ after adsorption suggesting that chemical interactions occurred between glyphosate molecule and phenolic groups in dendro biochar. The peaks at 1799 and 1089 cm⁻¹ in bare biochar were assigned to C–O–C stretching vibrations (Gu et al., 2012). Amides (-NH₂) in biochar surface can be distinguished by the peak present at 1429 cm⁻¹ (Devi and Saroha, 2013). Splitting of this peak in glyphosate adsorbed biochar may indicate the involvement of -NH2 in glyphosate adsorption. Aromatic CH out-of-plane deformation condensing smaller aromatic units into larger sheets is indicated by the peak at 875 $\rm cm^{-1}$ in dendro biochar. In glyphosate adsorbed biochar, appearance of a new band at 2926 $\rm cm^{-1}$ showed an increase in $-\rm H$ bonding after glyphosate sorption (Vithanage et al., 2015). The peak at 1618 cm^{-1} indicated the presence of –COOH and peaks at 1315, 1109 cm^{-1} were recognized to be P=O groups due to the attachment of glyphosate molecule on biochar surface after adsorption. Small peak at 669 cm^{-1} can be attributed to liberation of –OH. Thus the FTIR results clearly delineate the involvement of functional groups like phenolic, amine, carboxylic and phosphate in glyphosate adsorption process.



Fig. 2. FTIR spectra of bare and glyphosate adsorbed biochars.

4. Conclusions

Adsorption of glyphosate on dendro biochar varied significantly with solution pH achieving the maximum at pH range 5–6 due $\pi-\pi$ electron donor–acceptor interactions. Results of the sorption experiments showed that adsorption isotherm favored Freundlich and Temkin models and the adsorption process could be explained by the pseudo second order kinetics. Hence the adsorption mechanism is assumed to be a heterogenous chemisorption process with electrostatic attractions between glyphosate molecules and biochar surface, which was further confirmed from variations in functional groups. The maximum adsorption capacity simulated by the Langmuir equation is 44 mg g⁻¹. The FTIR spectral analysis of dendro biochar before and after glyphosate adsorption elucidated that the characteristic functional groups such as phenolic, amine, carboxylic and phosphate play an important role in the adsorption process.

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References

- Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J.-C., García-Río, L., 2008. The mobility and degradation of pesticides in soils and the pollution of groundwater resources. Agric. Ecosyst. Environ. 123, 247–260.
- Battaglin, W., Meyer, M., Kuivila, K., Dietze, J., 2014. Glyphosate and its degradation product AMPA occur frequently and widely in US soils, surface water, groundwater, and precipitation. JAWRA J. Am. Water Resour. Assoc. 50, 275–290.
- Bhaskara, B.L., Nagaraja, P., 2006. Direct sensitive spectrophotometric determination of glyphosate by using ninhydrin as a chromogenic reagent in formulations and environmental water samples. Helv. Chim. Acta 89, 2686–2693.
- Borggaard, O.K., Gimsing, A.L., 2008. Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: a review. Pest Manag. Sci. 64, 441–456.
- Cáceres-Jensen, L., Gan, J., Baez, M., Fuentes, R., Escudey, M., 2009. Adsorption of glyphosate on variable-charge, volcanic ash—DERIVED soils. J. Environ. Qual. 38, 1449–1457.
- Carneiro, R.T.A., Taketa, T.B., Gomes Neto, R.J., Oliveira, J.L., Campos, E.V.R., de Moraes, M.A., da Silva, C.M.G., Beppu, M.M., Fraceto, L.F., 2015. Removal of glyphosate herbicide from water using biopolymer membranes. J. Environ. Manag, 151, 353–360.
- Chen, F.-x., Zhou, C.-r., Li, G.-p., Peng, F.-f., Thermodynamics and kinetics of glyphosate adsorption on resin D301. Arab. J. Chem., (in press).
- Devi, P., Saroha, A.K., 2013. Effect of temperature on biochar properties during paper mill sludge pyrolysis. Int. J. Chem. Tech. Res. 5, 682–687.
- Duman, G., Uddin, M.A., Yanik, J., 2014. The effect of char properties on gasification reactivity. Fuel Process. Technol. 118, 75–81.
- Ghaedi, M., Ánsari, A., Habibi, M.H., Asghari, A.R., 2014. Removal of malachite green from aqueous solution by zinc oxide nanoparticle loaded on activated carbon: kinetics and isotherm study. J. Ind. Eng. Chem. 20, 17–28.
- Gimsing, A.L., Borggaard, O.K., 2007. Phosphate and glyphosate adsorption by hematite and ferrihydrite and comparison with other variable-charge minerals. Clays Clay Miner. 55, 108–114.
- Gu, R., Konar, S., Sain, M., 2012. Preparation and characterization of sustainable polyurethane foams from soybean oils. J. Am. Oil Chem. Soc. 89, 2103–2111.
- Hagner, M., Penttinen, O.-P., Tiilikkala, K., Setälä, H., 2013. The effects of biochar, wood vinegar and plants on glyphosate leaching and degradation. Eur. J. Soil Biol. 58, 1–7.
- Herath, I., Kumarathilaka, P., Navaratne, A., Rajakaruna, N., Vithanage, M., 2015. Immobilization and phytotoxicity reduction of heavy metals in serpentine soil using biochar. J. Soils Sediments 15, 126–138.
- Hu, Y., Zhao, Y., Sorohan, B., 2011. Removal of glyphosate from aqueous environment by adsorption using water industrial residual. Desalination 271, 150–156.
- 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. Bioresour. Technol. 169, 622–629.
- Ke, S., 2013. Market and outlook of the top ten herbicides in the world. Agrochemicals 5, 004.

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- Mamindy-Pajany, Y., Sayen, S., Mosselmans, J.F.W., Guillon, E., 2014. Copper, nickel and zinc speciation in a biosolid-amended soil: pH adsorption edge, μ-XRF and μ-XANES investigations. Environ. Sci. Technol. 48, 7237–7244.
- Milojević-Rakić, M., Janošević, A., Krstić, J., Nedić Vasiljević, B., Dondur, V., Ćirić-Marjanović, G., 2013. Polyaniline and its composites with zeolite ZSM-5 for efficient removal of glyphosate from aqueous solution. Microporous Mesoporous Mater. 180, 141–155.
- Mohan, D., Pittman, C.U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P.H., Alexandre-Franco, M.F., Gomez-Serrano, V., Gong, H., 2007. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. J. Colloid Interface Sci. 310, 57–73.Mohan, D., Rajput, S., Singh, V.K., Steele, P.H., Pittman, C.U., 2011. Modeling and
- Mohan, D., Rajput, S., Singh, V.K., Steele, P.H., Pittman, C.U., 2011. Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent. J. Hazard. Mater. 188, 319–333.
- Mohsen Nourouzi, M., Chuah, T., Choong, T.S., 2010. Adsorption of glyphosate onto activated carbon derived from waste newspaper. Desalination Water Treat. 24, 321–326.
- Morillo, E., Undabeytia, T., Maqueda, C., 1997. Adsorption of glyphosate on the clay mineral montmorillonite: effect of Cu (II) in solution and adsorbed on the mineral. Environ. Sci. Technol. 31, 3588–3592.
- Piccolo, A., Celano, G., Pietramellara, G., 1992. Adsorption of the herbicide glyphosate on a metal-humic acid complex. Sci. Total Environ. 123, 77–82.
 Qian, K., Kumar, A., Patil, K., Bellmer, D., Wang, D., Yuan, W., Huhnke, R.L, 2013.
- Qian, K., Kumar, A., Patil, K., Bellmer, D., Wang, D., Yuan, W., Huhnke, R.L., 2013. Effects of biomass feedstocks and gasification conditions on the physiochemical properties of char. Energies 6, 3972–3986.
- Rajapaksha, A.U., Vithanage, M., Zhang, M., Ahmad, M., Mohan, D., Chang, S.X., Ok, Y.S., 2015. Pyrolysis condition affected sulfamethazine sorption by tea waste biochars. Bioresour. Technol. 166, 303–308.
- Rehrah, D., Reddy, M., Novak, J., Bansode, R., Schimmel, K., Yu, J., Watts, D., Ahmedna, M., 2014. Production and characterization of biochars from agricultural by-products for use in soil quality enhancement. J. Anal. Appl. Pyrolysis 108, 301–309.
- Richard, S., Moslemi, S., Sipahutar, H., Benachour, N., Seralini, G.-E., 2005. Differential effects of glyphosate and Roundup on human placental cells and aromatase. Environ. Health Perspect. 113, 716–720.

- Salman, J., Abid, F., 2013. Preparation of mesoporous activated carbon from palmdate pits: optimization study on removal of bentazon, carbofuran, and 2, 4-D using response surface methodology. Water Sci. Technol. 68, 1503–1511.
- Speth, T.F., 1993. Glyphosate removal from drinking water. J. Environ. Eng. 119, 1139–1157.
- Sun, K., Gao, B., Ro, K.S., Novak, J.M., Wang, Z., Herbert, S., Xing, B., 2012. Assessment of herbicide sorption by biochars and organic matter associated with soil and sediment. Environ. Pollut. 163, 167–173.
- Tzaskos, D.F., Marcovicz, C., Dias, N.M.P., Rosso, N.D., 2012. Development of sampling for quantification of glyphosate in natural waters. Ciênc. Agrotecnol. 36, 399–405.
- Veiga, F., Zapata, J., Marcos, M.F., Alvarez, E., 2001. Dynamics of glyphosate and aminomethylphosphonic acid in a forest soil in Galicia, north-west Spain. Sci. Total Environ. 271, 135–144.
- Vithanage, M., Rajapaksha, A.U., Ahmad, M., Uchimiya, M., Dou, X., Alessi, D.S., Ok, Y.S., 2015. Mechanisms of antimony adsorption onto soybean stover-derived biochar in aqueous solutions. J. Environ. Manag. 151, 443–449.
- Waiman, C.V., Avena, M.J., Garrido, M., Fernández Band, B., Zanini, G.P., 2012. A simple and rapid spectrophotometric method to quantify the herbicide glyphosate in aqueous media. Application to adsorption isotherms on soils and goethite. Geoderma 170, 154–158.
- Xu, R.-k., Xiao, S.-c., Yuan, J.-h., Zhao, A.-z., 2011. Adsorption of methyl violet from aqueous solutions by the biochars derived from crop residues. Bioresour. Technol. 102, 10293–10298.
- Yu, F., Chen, J., Yang, M., Zhou, L., Jin, L., Su, C., Li, F., Chen, L., Yuan, Z., Yu, L., Ma, J., 2012. A facile one-pot method for synthesis of low-cost magnetic carbon nanotubes and their applications for dye removal. New J. Chem. 36, 1940–1943.
- Zhang, P., Sun, H., Yu, L., Sun, T., 2013. Adsorption and catalytic hydrolysis of carbaryl and atrazine on pig manure-derived biochars: impact of structural properties of biochars. J. Hazard. Mater. 244, 217–224.
- Zheng, W., Guo, M., Chow, T., Bennett, D.N., Rajagopalan, N., 2010. Sorption properties of greenwaste biochar for two triazine pesticides. J. Hazard. Mater. 181, 121–126.