**Supplementary Information**

**A review of biochar-based sorbents for separation of heavy metals from water**

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**Table S1**. Important heavy metals in water and their permissible limit set by EPA.

|  |  |  |
| --- | --- | --- |
| Rank (CERCLA)\* | Heavy metals | Permissible limit (mg L-1) |
| 2 | Pb | 0.015 |
| 3 | Hg | 0.002 |
| 7 | Cd | 0.005 |
| 17 | Cr | 0.1 |
| 52 | Co | - |
| 57 | Ni | - |
| 75 | Zn | 5.0 |
| 97 | U | - |
| 125 | Cu | 1.3 |
| 140 | Mn | 0.05 |

\*Permissible limit according to Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), 2011 and Environment Protection Agency (EPA).

**Table S2.** The common types and operating conditions of pyrolysis for the production of biochar and other products.

|  |  |  |  |
| --- | --- | --- | --- |
| Process | Residence time | Temperature (oC) | Yields % |
|  | **Bio-oil** | **Syngas** | **Biochar** |
| Torrefacation | ~ 10-60 min | ~290 | 0 | 20 | 80 |
| Hydrothermal carbonization (HTC) | 1-16 h | 180-300 | 5-20 | 2-5 | 50-80 |
| Gasification | 10-20 s | ~750-900 | 5 | 85 | 10 |
| Fast pyrolysis | <2 s | 500-1000 | 75 | 13 | 12 |
| Intermediate pyrolysis | 10-20 s | ~500 | 50 | 30 | 20 |
| Slow pyrolysis | Hour-days | 300-700 | 30 | 35 | 35 |

**3. Feedstock for biochar preparation**

*3.1 Agriculture-based materials*

High sorption potential of biochar generated for agricultural-based wastes/residues could be due to the surface properties of the feed-stock biocmass as illustrated in Figure 2. Tran et al. ([2017](#_ENREF_14)) determined that the presence of oxygen-rich functional groups such as hydroxyl (–OH), carboxyl (–COOH) and carbonate (CO32−) group on orange peel biochar provided the anionic surface structure for attachment of Cd from aqueous solution. In another study, [Lu *et al.* (2012)](#_ENREF_13) investigated that Pb sorption onto biochar produced from biosolid was majorly attributed to complexation of Pb with –OH and –COOH groups. [Xu *et al.* (2016)](#_ENREF_16) examined the Hg sorption capacity of biochar produced bagasse and confirmed that Hg sorption was due to the appearance of (–O)2Hg and (–COO)2Hg complexes. Moreover, thiol (–SH) groups were also responsible for Hg sorption on the surface of biochars produced from various feedstocks as indicated by extended X-ray absorption ﬁne structure analyses. [Dong *et al.* (2011)](#_ENREF_2) illustrated that oxygen containing surface functional groups can facilitate the Cr(VI) sorption onto biochar from aqueous phase by its reduction to Cr(III).

[Xu *et al.* (2013)](#_ENREF_17) conducted an experiment and proved that biochar from dairy manure was more successful for removal of Cu, Zn Pb and Cd from contaminated water with the sorption capacity of > 486 mmol kg-1 for all metals. [Han *et al.* (2017)](#_ENREF_3) analyzed that Cd sorption was linked with the sorption onto C–O and C=O groups present on the surface of biochar produced from animal manure.

**5. Mechanisms of heavy metals removal by biochar from aqueous media**

Biochars have been reported to have great potential to be used as sorbent for the separation of heavy metals from aqueous media owing to its high surface are, porosity and heterogeneous structure ([Kasozi *et al.* 2010](#_ENREF_10)). High surface area and porous structures of biochars have great attraction for heavy metals in aqueous solutions because these could be physically sorbed on the surface of biochars and remained in the cavities ([Kumar *et al.* 2011](#_ENREF_11)). Previous research has shown that the surface of biochars was negatively charged and could bind/sorb cationic metals via electrostatic interactions. Speciﬁc surface functional groups or ligands such as hydroxyl (–OH), carboxyl (–COOH), alkyl, amino (–NH2) and carbonate (CO32−) groups on biochars can also react with different metal ions to form complexes ([Liu and Zhang 2009](#_ENREF_12); [Dong *et al.* 2011](#_ENREF_2); [Wang *et al.* 2015](#_ENREF_15)) or precipitates at the solid-mineral phases ([Cao *et al.* 2009](#_ENREF_1); [Inyang *et al.* 2011](#_ENREF_5); [Inyang *et al.* 2012](#_ENREF_7)).

**6. Modification of biochar for enhance heavy metal sorption**

*6.1.1 Physical activation*

For instance, previous research has revealed that bagasse biochar produced at pH 10.93 successfully precipitated Pb ions by making hydrocerrusite [(Pb3(CO3)2(OH)2] on biochar surface ([Inyang *et al.* 2010](#_ENREF_6)). [Cao *et al.* (2009)](#_ENREF_1) demonstrated that for biochar produced at 200, 250 and 350 ºC temperatures, precipitation was the main mechanism for sorption (84-87%) of Pb from aqueous solution by making Pb phosphate and Pb carbonate minerals. This was also conﬁrmed by FTIR spectroscopy, X-ray diffraction and chemical speciation data.

Precipitation was observed to be the dominant mechanism for Cd sorption on dairy manure biochar and the increase in temperature (200 to 350 ºC) caused an increase in Cd sorption from 31.9 to 51.4 mg g-1 largely because of the higher mineral contents particularly soluble carbonate in dairy manure biochar (Table 2) ([Xu *et al.* 2013](#_ENREF_17)). The FTIR spectra and Visual MINTEQ modeling showed that most of the Cd (88%) sorption was due to the precipitation of Cd with carbonate and phosphate contents of biochar obtained at 350 ºC whereas p-bonding mechanism resulted in only 12% Cd sorption ([Xu *et al.* 2013](#_ENREF_17)). Cadmium-carbonate precipitates accounted for 98% of Cd sorption, while only <3% of Cd-phosphate precipitation was observed during the overall precipitation (88%) process owing to low soluble P contents in dairy manure biochar pyrolyzed at 350 ºC. Furthermore, precipitation caused 100% Cd sorption onto biochar generated at 200 ºC, off which 78 and 22% Cd sorption were due to carbonate and phosphate precipitates, respectively ([Xu *et al.* 2013](#_ENREF_17)). Cadmium sorption by water hyacinth biochar was associated with phosphate and carbonate minerals confirmed by X-ray diffraction analyses ([Zhang *et al.* 2015a](#_ENREF_19)).

*6.1.2.2. Alkaline solutions*

Phosphoric acid treatment of pine tree saw dust biochar significantly enhanced porosity, surface area and total pore volume of the biochar ([Zhao *et al.* 2017](#_ENREF_21)). Activation by phosphoric acid and resulting P–O–P bonds into carbonaceous structure improved Pb removal by > 20%, than that of untreated biochar which could be owing to precipitation of phosphate with Pb and surface attachment ([Zhao *et al.* 2017](#_ENREF_21)). The activation of biochar by using strong acids could be costly and may cause environmental problems such as disposal of acidic solutions, thus research has been directed towards the use of H2O2 as an alternative activation agent which is more cost-effective and environmentally suitable. [Huff and Lee (2016)](#_ENREF_4) demonstrated that pine wood biochar treatment with 30% H2O2 caused a substantial increase in the abundance of oxygen-rich surface functional groups. Moreover, the increase in surface functional groups of H2O2 treated pinewood biochar offered more exchange sites for metal ions and thus the cation exchange capacity of treated biochar was found to be nearly two times more as compared to untreated pinewood biochar. [Xue *et al.* (2012)](#_ENREF_18) observed that hydrochar treatment with 10% H2O2 solution significantly improved Pb sorption than that of untreated hydrochar which was associated with higher contents of carboxyl functional groups making complexes with Pb.

Although, similar mineral composition of acid treated and untreated biohcrar was observed by [Xue *et al.* (2012)](#_ENREF_18) but treatment of acid dissolves and eliminates mineral contents of biochar matrix. The mineral contents such as Ca, K, Na, P and Mg are specifically vital for the precipitation of cationic metals from aqueous solutions by some biochars therefore in some cases acid activation may decrease sorption of metal ions by precipitation process ([Xu *et al.* 2013](#_ENREF_17)).

*6.2.2 Organic compounds*

Chitosan has also been employed to enhance the impregnation of biochars with the metal oxides which results in magnetic biochars production ([Zhang *et al.* 2015b](#_ENREF_20)). Mixing of chitosan biochars with ϒ-Fe2O3-biochar composites led to the abundance of functional groups, specially amino groups, which displayed increased sorption capacity of Cr(VI) from contaminated water ([Zhang *et al.* 2015b](#_ENREF_20)).

[Zhou *et al.* (2014)](#_ENREF_22) produced the biochar-based composites by mixing different quantities of bamboo biochar, zero valent iron (ZVI) and chitosan which demonstrated much greater sorption potential for Cr(VI) and Pb as compared to original bamboo biochar. Modification of biochar with chitosan only (no ZVI), significantly increased the removal capacity of Cr(VI) and Pb from aqueous solutions. Although, this increased sorption of metal ions was particular attributed to the strong interactions of amino groups with aqueous metal ions but the addition of ZVI to chitosan-modified biochar further enhanced the Pb and Cr(VI) removal from contaminated water.

*6.2.3 Coating with carbon-rich materials*

Biochar coated with carbon nanotubes (CNT) was prepared and analyzed for sorption of heavy metals from water ([Inyang *et al.* 2014](#_ENREF_8); [Inyang *et al.* 2015](#_ENREF_9)). The CNT were well coated on the biochar leading to higher pore volume, increased surface area and abundant negative surface charges ([Inyang *et al.* 2014](#_ENREF_8)). Lead sorption was increased significantly when hickory chips biochar was coated with CNT, while CNT incorporation had non-significant effect on sugarcane biochar for Pb sorption ([Inyang *et al.* 2015](#_ENREF_9)). CNT mixing with a surfactant (sodium dodecyl benzene sulfonate) before biomass coating increased the Pb sorption capacity of both types of biochar coated with CNT ([Inyang *et al.* 2015](#_ENREF_9)).

**References**

Cao, X, Ma, L, Gao, B, Harris, W. 2009. Dairy-manure derived biochar effectively sorbs lead and atrazine. Environ. Sci. Technol. 43:3285-3291

Dong, X, Ma, LQ, Li, Y. 2011. Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. J. Hazard. Mater. 190:909-915

Han, L, Sun, H, Ro, KS, Sun, K, Libra, JA, Xing, B. 2017. Removal of antimony (III) and cadmium (II) from aqueous solution using animal manure-derived hydrochars and pyrochars. Bioresour. Technol. 234:77-85

Huff, MD, Lee, JW. 2016. Biochar-surface oxygenation with hydrogen peroxide. J. Environ. Manage. 165:17-21

Inyang, M, Gao, B, Ding, W, Pullammanappallil, P, Zimmerman, AR, Cao, X. 2011. Enhanced lead sorption by biochar derived from anaerobically digested sugarcane bagasse. Sep. Sci. Technol. 46:1950-1956

Inyang, M, Gao, B, Pullammanappallil, P, Ding, W, Zimmerman, AR. 2010. Biochar from anaerobically digested sugarcane bagasse. Bioresour. Technol. 101:8868-8872

Inyang, M, Gao, B, Yao, Y, Xue, Y, Zimmerman, AR, Pullammanappallil, P, Cao, X. 2012. Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass. Bioresour. Technol. 110:50-56

Inyang, M, Gao, B, Zimmerman, A, Zhang, M, Chen, H. 2014. Synthesis, characterization, and dye sorption ability of carbon nanotube–biochar nanocomposites. Chem. Eng. J. 236:39-46

Inyang, M, Gao, B, Zimmerman, A, Zhou, Y, Cao, X. 2015. Sorption and cosorption of lead and sulfapyridine on carbon nanotube-modified biochars. Environmental Science and Pollution Research. 22:1868-1876

Kasozi, GN, Zimmerman, AR, Nkedi-Kizza, P, Gao, B. 2010. Catechol and humic acid sorption onto a range of laboratory-produced black carbons (biochars). Environ. Sci. Technol. 44:6189-6195

Kumar, S, Loganathan, VA, Gupta, RB, Barnett, MO. 2011. An assessment of U (VI) removal from groundwater using biochar produced from hydrothermal carbonization. J. Environ. Manage. 92:2504-2512

Liu, Z, Zhang, F-S. 2009. Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. J. Hazard. Mater. 167:933-939

Lu, H, Zhang, W, Yang, Y, Huang, X, Wang, S, Qiu, R. 2012. Relative distribution of Pb2+ sorption mechanisms by sludge-derived biochar. Water Res. 46:854-862

Tran, HN, You, S-J, Hosseini-Bandegharaei, A, Chao, H-P. 2017. Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review. Water Res. 120:88-116

Wang, S, Gao, B, Zimmerman, AR, Li, Y, Ma, L, Harris, WG, Migliaccio, KW. 2015. Physicochemical and sorptive properties of biochars derived from woody and herbaceous biomass. Chemosphere. 134:257-262

Xu, M, Gao, Z, Wei, Q, Chen, G, Tang, D. 2016. Label-free hairpin DNA-scaffolded silver nanoclusters for fluorescent detection of Hg 2+ using exonuclease III-assisted target recycling amplification. Biosensors Bioelectron. 79:411-415

Xu, X, Cao, X, Zhao, L. 2013. Comparison of rice husk-and dairy manure-derived biochars for simultaneously removing heavy metals from aqueous solutions: role of mineral components in biochars. Chemosphere. 92:955-961

Xue, Y, Gao, B, Yao, Y, Inyang, M, Zhang, M, Zimmerman, AR, Ro, KS. 2012. Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: batch and column tests. Chem. Eng. J. 200:673-680

Zhang, F, Wang, X, Yin, D, Peng, B, Tan, C, Liu, Y, Tan, X, Wu, S. 2015a. Efficiency and mechanisms of Cd removal from aqueous solution by biochar derived from water hyacinth (Eichornia crassipes). J. Environ. Manage. 153:68-73

Zhang, M-m, Liu, Y-g, Li, T-t, Xu, W-h, Zheng, B-h, Tan, X-f, Wang, H, Guo, Y-m, Guo, F-y, Wang, S-f. 2015b. Chitosan modification of magnetic biochar produced from Eichhornia crassipes for enhanced sorption of Cr (vi) from aqueous solution. RSC Advances. 5:46955-46964

Zhao, L, Zheng, W, Mašek, O, Chen, X, Gu, B, Sharma, BK, Cao, X. 2017. Roles of phosphoric acid in biochar formation: synchronously improving carbon retention and sorption capacity. J Environ Qual. 46:393-401

Zhou, Y, Gao, B, Zimmerman, AR, Chen, H, Zhang, M, Cao, X. 2014. Biochar-supported zerovalent iron for removal of various contaminants from aqueous solutions. Bioresour. Technol. 152:538-542