**Supplementary information**

**An application of waste algae biochar in aquaculture water to remove co-existed Cadmium and PAHs and the corresponding mechanism**

Qian Wang 1, \*, Li Zhang 1, Yiqin Chen 1, Jie Yin 1, Juan-ying Li 1

*1* *College of Marine Ecology and Environment, Shanghai Ocean University, Pudong, Shanghai,*

**\***Address correspondence to Dr. Qian Wang; Email: q\_wang@shou.edu.cn;

Tel: + 86 021 61908338; Fax: + 86 021 61900431

**Note: The values retain two significant digits in the supplementary material.**

**Table S1 Water quality of the sampling ponds.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Ponds number | Locations | pH | Dissolved oxygen (mg·L-1) | Temperature(°C) | DOC (mg·L-1) |
| 1 | Shanghai | 9.5 | 9.8 | 36 | 0.67 |
| 2 | Luan, Anhui | 7.5 | 8.1 | 36 | 0.69 |
| 3 | Chuzhou, Anhui | 7.6 | 5.8 | 31 | 0.91 |
| 4 | Huzhou, Zhejiang | 7.9 | 6.2 | 31 | 0.78 |
| 5 | Huzhou, Zhejiang | 8.0 | 5.4 | 31 | 0.93 |
| 6 | Yancheng, Jiangsu | 8.5 | 9.6 | 28 | 1.2 |
| 7 | Wuxi, Jiangsu | 7.5 | 2.2 | 29 | 0.88 |
| 8 | Taizhou, Zhejiang | 7.2 | 3.0 | 19 | 0.93 |
| 9 | Ningde, Fujian | 8.3 | 11 | 20 | 0.98 |

**Table S2 Specific parameters for each batch experimental system (pH=7.0).**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Types | System | Pollutants | Concentration | Volume (mL) | Dosage (g) |
| Sorption kinetic  | Single chemical system | Cd2+ | 50 mg·L-1 | 20 | 0.050 |
| FLU | 1000 μg·L-1 | 100 | 0.0050 |
| PHE | 1000 μg·L-1 |
| FLT | 200 μg·L-1 |
| PYR | 100 μg·L-1 |
| BaP | 100 μg·L-1 |
| Cd2+-PAHs co-existingsystem | Cd2+ | 50 mg·L-1 | 100 | 0.070 |
| PAHs | Same as those in the single chemical systems |
| Sorption isotherm  | Single chemical system | Cd2+ | 5.0, 10, 15, 25, 50, 80, 100 and150 mg·L-1 | 20 | 0.050 |
| FLU | 100-2000 μg·L-1 | 100 | 0.0050 |
| PHE | 100-1000 μg·L-1 |
| FLT | 20-250 μg·L-1 |
| PYR | 10-150 μg·L-1 |
| BaP | 20-200 μg·L-1 |
| Cd2+-PAHs co-existingsystem | Cd2+ | 1.0, 2.0, 3.0, 5.0, 8.0, 10 and 15 mg·L-1 | 200 | 0.090 |
| PAHs | Same as those in the single chemical systems |

**Table S3 Models of sorption kinetic, isotherm and calculations of the corresponding parameters.**

|  |  |  |
| --- | --- | --- |
| Types | Names | Equations |
|  | Sorption capacity (qt) |  |
|  | Equilibrium sorption capacity (qe) |  |
| Kinetic model | Pseudo-second-order | t/qt=1/(K2·qe2)+t/qe |
| Isotherm models | Langmuir | =  |
| Freundlich | = |

Note: Ct: sorption concentration (mg·L-1) at time t (h), V: volume of the solution (L), m: amount of biochar (g). qt: sorption capacity (mg·g-1) at time t (h), t: sorption time (h), qe: equilibrium sorption capacity (mg·g-1), K2: rate constant of Pseudo-second-order (g·mg-1·min-1), KL: Langmuir constant (L·mg-1), qm: maximum sorption capacity (mg·g-1), KF: Freundlich constant (mg·g-1·(L·mg-1)1/n), n: constant indicative of the intensity of the sorption or surface heterogeneity.

**Table S4 Detection limits and recoveries of Cd2+ and PAHs.**

|  |  |  |
| --- | --- | --- |
| Analytes | MDL | Recovery (%) |
| Cd | 1.0 μg·L-1 | 100 |
| FLU | 0.71 ng∙L-1 | 71 |
| PHE | 0.20 ng∙L-1 | 87 |
| FLT | 0.18 ng∙L-1 | 84 |
| PYR | 0.23 ng∙L-1 | 85 |
| BaP | 0.44 ng∙L-1 | 96 |

**Table S5 Levels of the contaminants in the leaching experiment of the biochar and the corresponding environmental impacts.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Leaching levels (ng·g-1) | Sediment quality guidelines (ng·g-1 ) | Probable effect levels (ng·g-1) | PEL-Q (Probable effect levels quotient) |
| Cd2+ | 270±40 | 600 | 3500 | 0.076±0.011 |
| FLU | 6.0±8.5 | 21.2 | 144 | 0.042±0.059 |
| PHE | 2.6±0.52 | 41.9 | 515 | 0.0050±0.0010 |
| FLT | 0.78±0.19 | 111 | 2355 | 0.00033±0.000082 |
| Mean PEL-Q |  |  |  | 0.031±0.018 |

**Note:** PEL-Q= Leaching levels / Probable effect levels;

The biochar would not trigger any adverse impact on the aquatic species, if meanPEL-Q was lower than 0.5 ([MacDonald et al., 2000](#_ENREF_6)).

**Table S6 Concentrations of the contaminants in the aquaculture water before and after sorption. Note: BaP was non-detectable in the collected samples.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Samples | Cd2+ (µg·L-1) | FLU (ng·L-1) | PHE (ng·L-1) | FLT (ng·L-1) | PYR (ng·L-1) |
| Before  | After  | Before  | After  | Before  | After  | Before  | After  | Before  | After  |
| S1 | 3.7±0.16 | 2.0±0.17 | 530±46 | 79±40 | 210±31 | 14±0.070 | 71±4.4 | 4.8±0.77 | 54±8.5 | 2.9±0.040 |
| S2 | 6.5±0.24 | 3.3±0.77 | 900±59 | 99±9.4 | 460±37 | 52±4.2 | 120±4.4 | 19±0.78 | 77±2.1 | 15±1.7 |
| S3 | 1.1±0.040 | 0.84±0.020 | 540±60 | 34±2.7 | 270±35 | 13±0.050 | 61±9.4 | 4.6±0.54 | 50±5.1 | 2.7±0.070 |
| S4 | 5.9±0.34 | 2.3±0.24 | 2000±45 | 230±80 | 850±10 | 190±0.080 | 200±9.2 | 7.2±0.11 | 210±60 | 2.7±0.060 |
| S5 | 2.1±1.1 | 0.63±0.15 | 610±48 | 58±0.10 | 210±19 | 7.8±0.040 | 56±11 | 3.0±0.080 | 48±2.7 | 1.7±0.020 |
| S6 | 11±0.20 | 4.8±0.59 | 1900±91 | 180±3.4 | 810±37 | 42±1.9 | 200±13 | 3.1±0.15 | 180±23 | 1.7±0.13 |
| S7 | 2.9±0.41 | 1.8±0.13 | 1000±60 | 150±12 | 420±16 | 65±0.12 | 100±7.8 | 16±2.4 | 91±1.9 | 22±5.2 |
| S8 | 3.3±0.73 | 2.3±0.21 | 1000±17 | 120±9.0 | 500±11 | 58.±4.6 | 150±1.8 | - | 120±1.1 | - |
| S9 | 8.4±0.43 | 2.6±0.23 | 1900±32 | 260±9.5 | 810±19 | 59±4.1 | 210±6.1 | 47±5.1 | 170±2.7 | 78±18 |
| Mean concentration | 5.0±3.2 | 2.3±1.3 | 1100±600 | 140±78 | 500±260 | 56±55 | 130±63 | 13±15 | 110±62 | 16±26 |
| Mean removal rate (%) |  | 49±16 |  | 88±3.0 |  | 90±6.1 |  | 91±7.6 |  | 88±15 |

**Table S7 Toxicity data of the studied chemicals.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Chemicals | Type of organisms | NOECs or EC50 (ng·L-1) | PNEC (ng·L-1) | AF |
| Cd | Algae, crustaceans, fish, invertebrates, mollusks, worms | - | 7300 a | 2 a |
| FLU | Fish | 1100000 b | 11000 c | 100 c |
| PHE | Fish | 3000000 b | 30000 c | 100 c |
| FLT | Fish | 616000 b | 6160 c | 100 c |
| PYR | Fish | 700000 b | 7000 c | 100 c |
| BaP | Fish | 1400 b | 14 c | 100 c |

Note：NA, not available; NOEC is the no observed effect concentration (ng·L-1); EC50 is the half effective concentration (ng·L-1); PNEC is the predicted no effect concentration of a compound (ng·L-1); AF is the assessment factor.

a Data obtained from the study of [Park et al. (2019)](#_ENREF_7).

b Data obtained from the study of [Liang et al. (2019)](#_ENREF_5).

c Data obtained from the investigation of [Cui et al. (2016)](#_ENREF_1).

**Table S8 Ecological risk quotients (RQs) of the target pollutants for the samples from different ponds.**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Samples | Cd2+ | FLU | PHE | FLT | PYR | ∑ Cd2+ + PAHs |
| Before  | After  | Before  | After  | Before  | After  | Before  | After  | Before  | After  | Before  | After  |
| S1 | 0.51 | 0.28 | 0.048 | 0.0072 | 0.0071 | 0.00050 | 0.012 | 0.00080 | 0.0078 | 0.00040 | 0.58 | 0.29 |
| S2 | 0.89 | 0.45 | 0.082 | 0.0090 | 0.016 | 0.0017 | 0.019 | 0.0031 | 0.011 | 0.0021 | 1.0 | 0.47 |
| S3 | 0.15 | 0.12 | 0.049 | 0.0031 | 0.0089 | 0.00040 | 0.0099 | 0.00070 | 0.0071 | 0.00040 | 0.22 | 0.12 |
| S4 | 0.80 | 0.31 | 0.18 | 0.021 | 0.028 | 0.0063 | 0.032 | 0.0012 | 0.030 | 0.00040 | 1.1 | 0.34 |
| S5 | 0.28 | 0.086 | 0.055 | 0.0053 | 0.0070 | 0.00030 | 0.0091 | 0.00050 | 0.0069 | 0.00020 | 0.36 | 0.093 |
| S6 | 1.5 | 0.66 | 0.17 | 0.016 | 0.027 | 0.0014 | 0.033 | 0.00050 | 0.026 | 0.00020 | 1.8 | 0.68 |
| S7 | 0.40 | 0.25 | 0.088 | 0.014 | 0.014 | 0.0022 | 0.017 | 0.0026 | 0.013 | 0.0031 | 0.53 | 0.27 |
| S8 | 0.46 | 0.31 | 0.094 | 0.011 | 0.017 | 0.0019 | 0.024 | - | 0.017 | - | 0.61 | 0.32 |
| S9 | 1.1 | 0.35 | 0.17 | 0.024 | 0.027 | 0.0020 | 0.034 | 0.0077 | 0.024 | 0.011 | 1.4 | 0.40 |
| Min | 0.15 | 0.086 | 0.048 | 0.0031 | 0.0070 | 0.00030 | 0.0091 | 0.00050 | 0.0069 | 0.00020 | 0.22 | 0.093 |
| Max | 1.5 | 0.66 | 0.18 | 0.024 | 0.028 | 0.0063 | 0.034 | 0.0077 | 0.030 | 0.011 | 1.8 | 0.68 |
| Mean RQ | 0.68±0.44 | 0.31±0.17 | 0.10±0.054 | 0.012±0.0071 | 0.017±0.0087 | 0.0019±0.0018 | 0.021±0.010 | 0.0019±0.0024 | 0.016±0.0088 | 0.0020±0.0036 | 0.84±0.51 | 0.33±0.18 |
| **Total reduction rate (%)** | 58±11 |



**Fig. S1 SEM for BE400 before (a) and after (b) sorption of Cd2+ and PAHs.**

**References**

[1]Cui, S., Fu, Q., and Li, T., *Sediment-Water Exchange, Spatial Variations, and Ecological Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in the Songhua River, China*. Water 8(2016), 334.

[2]Enders, A., Hanley, K., and Whitman, T., *Characterization of biochars to evaluate recalcitrance and agronomic performance*. Bioresour. Technol. 114(2012), pp. 644-653.

[3]Figueiredo, C.C.d., Pinheiro, T.D., and de Oliveira, L.E.Z., *Direct and residual effect of biochar derived from biosolids on soil phosphorus pools: A four-year field assessment*. Sci. Total Environ.739(2020), 140013.

[4]Hossain, M.Z., Bahar, M.M., and Sarkar, B., *Assessment of the fertilizer potential of biochars produced from slow pyrolysis of biosolid and animal manures*.J. Anal. Appl. Pyrolysis. 155(2021), 105043.

[5]Liang, X., Junaid, M., and Wang, Z., *Spatiotemporal distribution, source apportionment and ecological risk assessment of PBDEs and PAHs in the Guanlan River from rapidly urbanizing areas of Shenzhen, China*. Environ. Pollut. 250(2019), pp. 695-707.

[6]MacDonald, D.D., Ingersoll, C.G., and Berger, T.A., *Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems*. Arch. Environ. Contam. Toxicol. 39(2000), pp. 20-31.

[7]Park, J., Lee, S., and Lee, E., *Probabilistic ecological risk assessment of heavy metals using the sensitivity of resident organisms in four Korean rivers*. Ecotoxicol. Environ. Saf. 183(2019), 109483.

[8]Son, E.B., Poo, K.M., and Chang, J.S., *Heavy metal removal from aqueous solutions using engineered magnetic biochars derived from waste marine macro-algal biomass*. Sci. Total Environ. 615(2018), pp. 161-168.

[9]Wang, Y., Hu, Y., and Zhao, X., *Comparisons of Biochar Properties from Wood Material and Crop Residues at Different Temperatures and Residence Times*. Energ. Fuel. 27(2013), pp. 5890-5899.