Biochars in treatment of spent solution after humic substances-based soil washing

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Introduction

Soil washing is one of the most used and studied off-site technique for remediation of metal-contaminated soils. Development of soil washing is based on searching for novel washing agents (WAs) enabling simultaneous metal removal and improvement the properties of remediated soil. Soluble humic substances (SHS) recovered from waste belong to new-generation WA for soil remediation.

The problem of soil washing is generation of liquid wastes in form of spent washing solution (SWS) that should be treated before their final disposal or be regenerated and reused for further washing. The SWS treatment is an integral part of a complete remediation process, but researches in this area are rare. The complex composition of SWS (various concentrations of soluble heavy metals and other co-existing contaminants, competitive cations and residual WA) makes its treatment challenging. Potentially, the same methods can be used for SWS treatment as for wastewater treatment, including adsorption, precipitation, advanced oxidation or membrane technologies. Adsorption seems to be more available with the possibility of using different adsorbents. Biochar is well-known adsorbent for the removal of complex inorganic and organic contaminants from different types of wastewater. Until now, pristine and modified biochars have been only used for treatment of waste SWS after washing of metal (Cd, Cu, Pb, Zn)-contaminated soil with $FeCl_3$ solution.

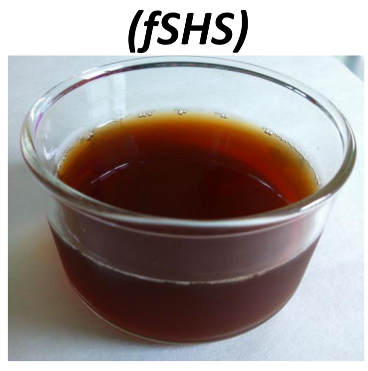
OBJECTIVE: to compare the efficiency of biochars produced from different feedstocks with commercial activated carbon in treatment of SWS after soil remediation with SHS recovered from municipal sewage sludge.

Materials and methods

① Extraction of soluble humic substances (SHS) from waste

Municipal sewage sludge (MSS)

fresh SHS solution (fSHS)



- 3 g MSS + 40 mL 0.1 M NaOH
- 150 rpm, 24h
- vacuum filtration (0.45 µm)

② Soil remediation with SHS

Metal-contaminated soil
47 mg Cd/kg, 1020 mg Cu/kg, 498 mg Ni/kg, 4094 mg Pb/kg, 2110 mg Zn/kg

fresh SHS solution (**fSHS**)
pH 4, conc. 2 g C/L

BATCH SOIL WASHING
1 g:40 mL ratio, 150 rpm, 24h

Centrifugation/filtration/ metal analysis

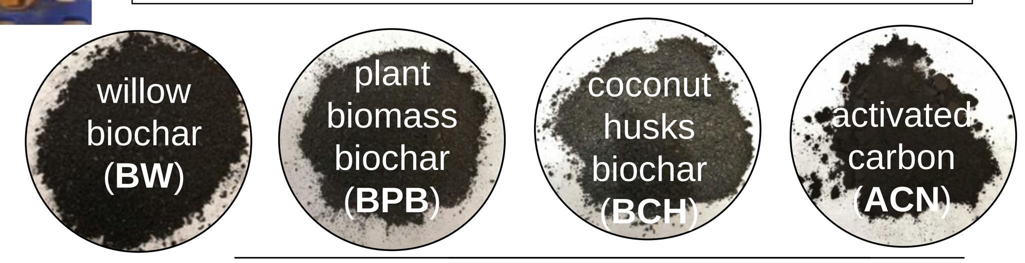
Remediated soil

spent SHS solution (**sSHS**)

③ Treatment of sSHS with biochars

spent SHS solution (**sSHS**)

BATCH ADSORPTION
adsorbent dosage (12.5-100 g/L), pH (4.8 and 7.0), adsorption time (30-180 min)

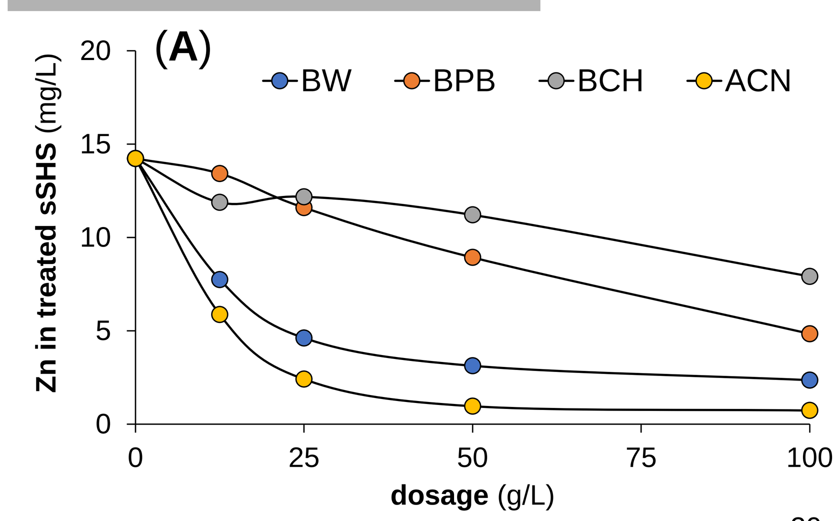


Pyrolysis at 650°C (Fluid S.A. Poland)

Adsorbent	pH	SA	PV	PS
	-	m^2/g	cm^3/g	nm
BW	10.3	243.2	0.11	1.8
BPB	7.9	0.53	0.00008	5.9
BCH	7.6	0.29	0.0011	15.9
ACN	9.6	653.1	0.61	3.7

SA is surface area
PV is pore volume
PS is pore size
ACN is Norit SX2

Results



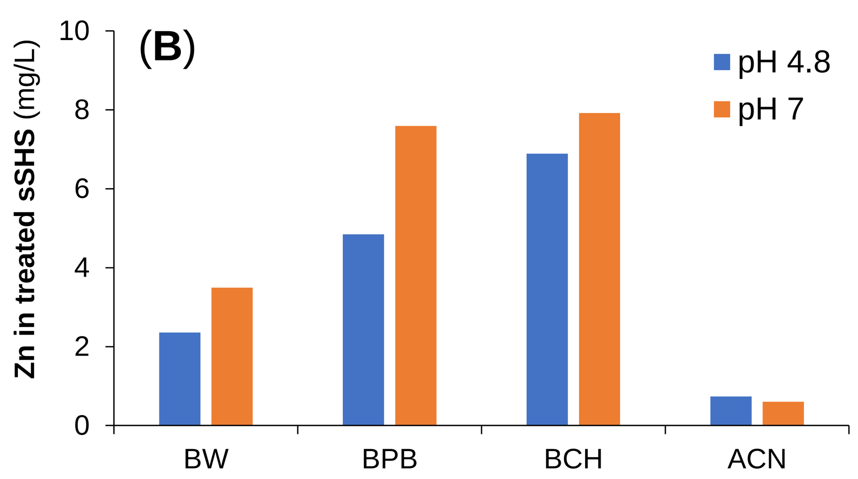
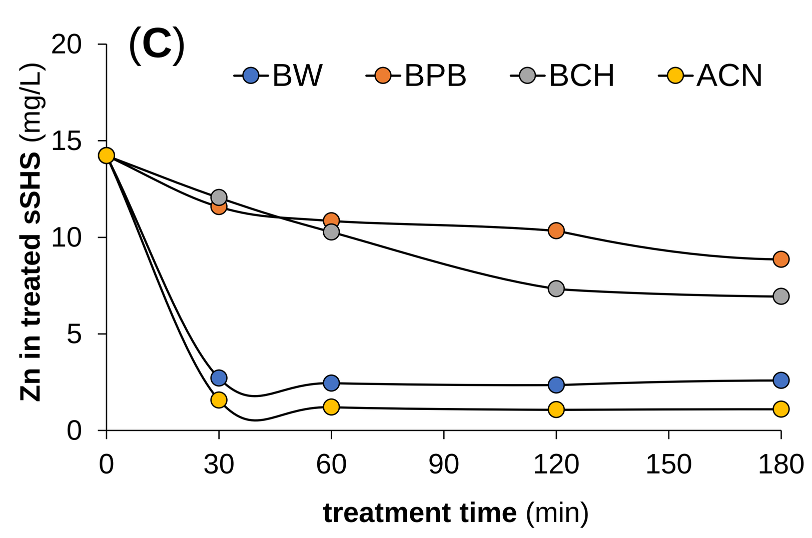


Figure 1. The effect of adsorption conditions on Zn removal from sSHS:
(A) adsorbent dosage
(B) pH
(C) time



After treatment

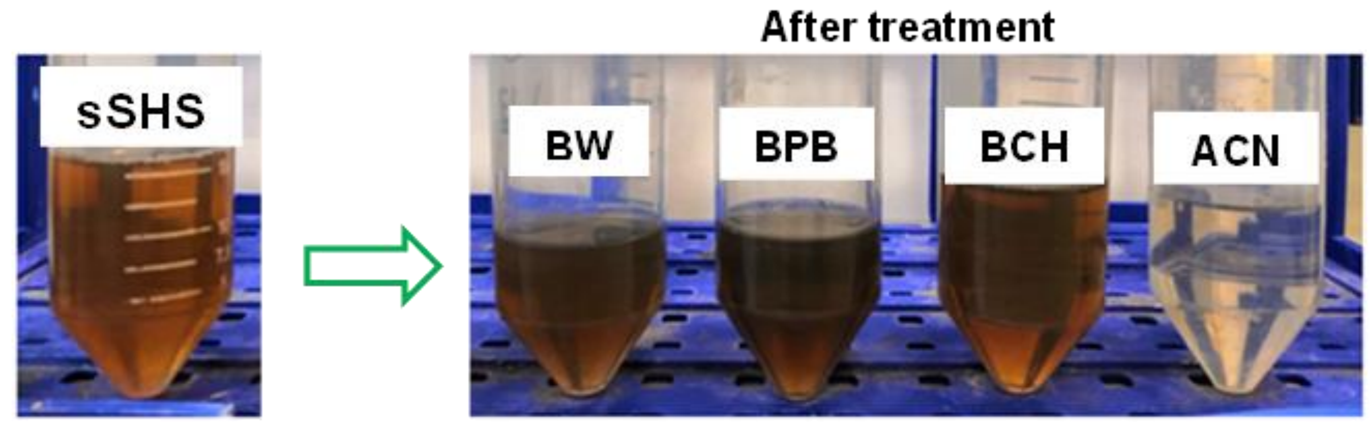


Figure 2. Characterization of sSHS before and after treatment with biochars (pH 4.8, dosage 100 g/L).

Solution	pH	EC	TOC	Cd	Cu	Ni	Pb	Zn	Na	Ca	Mg
	-	mS/cm	g/L					mg/L			
sSHS	4.9	64.9	1.9	0.52	10.3	3.1	7.8	14.2	1023	127.6	29.9
sSHS-**BW**	8.3	11.7	0.99	0.48	6.5	1.8	1.3	2.3	977	87.9	53.5
sSHS-**BPB**	7.4	20.7	1.7	0.18	6.1	2.3	1.9	4.8	496	158.1	42.7
sSHS-**BCH**	6.2	21.6	2.33	0.23	7.0	2.6	2.3	7.9	484	146.5	74.9
sSHS-**ACN**	7.9	18.8	0.12	0.05	0.99	0.31	0.40	0.73	488	46.8	21.4

EC is electrical conductivity, TOC is total organic carbon

Conclusions

sSHS treatment with BPB and BCH required higher adsorbent dosage (≥ 100 g/L) than with BW and ACN (50 g/L). The treatment was more effective at acidic than at neutral pH, and the treatment time of 60-120 min can be adopted as optimum. Among tested pristine biochars, the best effect of sSHS treatment for removal of soluble organics and heavy metals (especially Zn, Pb and Ni) was obtained for biochar made from willow, while the lowest effect was obtained for biochar made from coconut husks. Physical properties of biochars, such as their high surface area and pore volume are important for simultaneous removal of heavy metals and high molecular weight organic compounds like humic substances from the sSHS. Biochar from willow, after modification of its properties, has potential to be as effective in sSHS treatment as activated carbon.

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