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

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Soil washing is one of the most used and studied off-site technique applied to the remediation of metal contaminated soil (Andreozzi *et al* 2020). Beside treated soil, soil washing generates some waste in form of spent solution that should be treated before its final disposal or can be regenerated and reused for next soil treatment. Although proper management of spent washing solution is an integral part of a complete remediation process, researches in this area are rare. So far, the attempt of treatment of spent washing solutions were performed mainly for conventional chelating washing agents, such as EDTA, EDDS or plant biosurfactants, e.g. saponin to recover these agents and make soil remediation process more cost-effective (Fabbricino *et al* 2018; Gusiatin *et al* 2020). Although soil washing is effective for metal removal from soil, the treatments of spent washing solution after soil washing is a significant social problem. Real spent soil washing solutions are complex in their composition. They contain soluble metals at different concentrations, residual spent washing solution, competitive cations washed from soil, and other co-existing soil contaminants. Thus, they need selection of suitable treatment method. So far, adsorption, precipitation, advanced oxidation processes or membrane technology have been applied (Gusiatin *et al* 2020). Among these methods, adsorption is more available in treating waste soil washing solutions.

Biochar is well-known adsorbent for the removal of complex inorganic contaminants and organic contaminants. Current researches are directed toward replacement activated carbon through biochar to diminish the treatment process cost and avail the specific characteristic properties of biochar. Biochar properties are related to the type of feedstock, feedstock pre-treatment technology, thermal process, and post-treatment of biochars. Due to porous characteristics, well developed surface area and the presence of functional groups including phenolic, hydroxyl and carboxyl, biochars show strong adsorption capabilities (Li *et al* 2019). The source of biomass for biochar production is from a wide range of diverse organic materials such as plant residue, sewage solids, manures, agro-industrial biomass etc. Thus, it enables improvements in waste management and sustainable resource use. Biochars have become increasingly important as a solution to remediate pollutants in the industrial and agricultural sectors for improving environmental quality. They have a great potential to be used for treatment different types of wastewaters such as industrial, municipal, agricultural and stormwater (Xiang *et al* 2020). The ability of biochar to simultaneous removal of inorganic and organic pollutants, makes biochar potentially proper type of adsorbent to be used for treatment of wastewater generated after washing of soil contaminated with heavy metals. Based on literature review, there is only one paper on application of pristine and modified biochar to treat waste $FeCl_3$ washing effluent after treatment of soil contaminated with Cd, Cu, Pb and Zn (Zhan and Chen, 2020).

In this paper, spent washing solution after batch soil washing with soluble humic substances (SHS) was treated with biochars. The SHS was recovered from municipal sewage sludge. The SHS is a new type of washing agent for remediation of metal contaminated soil, which generation is a results of development soil washing technology and using waste as resources according to strategy of circular economy. New washing agents show a great potential to replace conventional washing agents due to their high efficiency in metal removal, low cost and positive impact on soil quality.

The spiked loamy soil contained high levels of heavy metals: 47 mg/kg (Cd), 1020 mg/kg (Cu), 498 mg/kg (Ni), 4094 mg/kg (Pb) and 2110 mg/kg (Zn). The SHS was extracted from dried and milled municipal sewage sludge with the 0.1M NaOH. Before SHS extraction, non-humic substances (e.g., sugars and proteins) and fats, waxes and bitumens were removed from sewage sludge by sludge washing with distilled water and defatted with a mixture of chloroform:methanol (Gusiatin *et al* 2020). The batch soil washing was performed at mass to SHS volume of 1:40 (w/v) for 24 h. The spent washing solution was separated from soil by centrifuging and filtration through 0.45 μm filters. The fresh SHS solution (fSHS) and spent washing solution (sSHS) were characterized for pH with Hanna HI221pH meter, electrical conductivity (EC) with Hanna HI 8733 conductometer, total organic carbon (TOC) with Shimadzu Liquid TOC-VCSN analyzer, heavy metals and selected macroelements, i.e. Na, Ca, Mg with flame atomic absorption spectrometer (AA280FS, Varian) (Table 1).

Table 1. The main characteristics of fSHS and sSHS.

Solution	pH	EC	TOC	Cd	Cu	Ni	Pb	Zn	Na	Ca	Mg
	-	mS/cm	g/L	mg/L							
fSHS	4.0	36.6	2.1	0.1	6.1	0.1	0.9	3.0	1025	15.6	15.1
sSHS	4.9	64.9	1.9	0.5	10.3	3.1	7.8	14.2	1023	127.6	29.9

Three types of biochars (sieved through 1mm sieve) were made from pyrolysis of willow (**BW**), plant biomass (**BPB**) and coconut husks (**BCH**) at 650 °C (Fluid S.A., Poland) were used to treat sSHS in batch adsorption. As reference adsorbent, activated carbon Norit SX2 (**ACN**) was used. All adsorbents differed in pH, BET surface area (SA), pore volume (PV) and pore size (PS) (Table 2). The effectiveness of sSHS treatment was determined depending on adsorbent dosage (12.5-100 g/L), pH (4.9 and 7.0) and adsorption time (30-180 min).

Table 2. The main characteristics of adsorbents used for sSHS treatment.

Adsorbent	pH -	SA m^2/g	PV cm^3/g	PS nm
ACN	9.58	653.1	0.61	3.7
BW	10.35	243.2	0.11	1.8
BPB	7.90	0.53	0.00008	5.9
BCH	7.65	0.29	0.0011	15.9

The treatment of sSHS strongly depended on adsorbent dosage. With the use of biochars, the process was more efficient at dosage of 100 g/L compared to ACN, which high efficiency was noticed at lower dosages. The treatment was more effective at acidic than neutral pH. Removal of SHS (as TOC) and heavy metals occurred most intensively during the first 30 min., and the time of 60 min. can be adopted as optimum. The removal efficiency of SHS with tested adsorbents decreased in the order: 93.8% (ACN) > 48.7% (BW) > 13.5% (BPB). SHS were not removed from sSHS with the use of BCH. Adsorbents differed in the efficiency of Cd, Cu, Ni, Pb and Zn removal: 90.1-94.8% (ACN), 37.0-84.6% (BW), 26.8-74.8% (BPB) and 17.5-69.7% (BCH). BPB and BCH showed comparable efficiency in Na removal as ACN (52.1% on average). All biochars enriched the treated sSHS solution in Mg, while BCH and BPB in Ca. Comparison of the sSHS solution after treatment with adsorbents with untreated sSHS is shown in Figure 1.

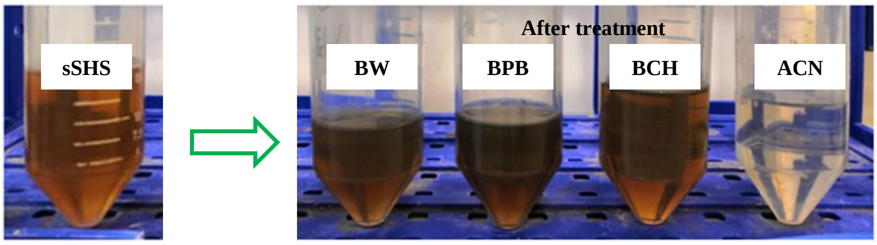

Figure 1. The sSHS before and after treatment with adsorbents (pH 4.8, 100 g/L).

Among tested pristine biochars, the best effect of sSHS treatment in terms of soluble organics and heavy metals removal was obtained for biochar made from willow, while the lowest effect was obtained for biochar made from coconut husks. The data indicate that physical properties of biochars, such as their high surface area are important for effective and simultaneous removal of humic substances and heavy metals from spent solution after soil washing. Biochar from willow, after modification of its properties, has potential to improve sSHS treatment and be as effective as activated carbon.

References

1. Andreozzi *et al* (2020). Simultaneous removal of Cr (III) from high contaminated soil and recovery of lactic acid from the spent solution. J. Environ. Manage. 268, 110584.
2. Fabbricino *et al* (2018). Soil washing optimization, recycling of the solution, and ecotoxicity assessment for the remediation of Pb-contaminated sites using EDDS. Sustainability, 10(3), 636.
3. Gusiatin *et al* (2020). New-generation washing agents in remediation of metal-polluted soils and methods for washing effluent treatment: a review. Int. J. Environ. Res. Public Health, 17(17), 6220.
4. Li *et al* (2019). Biochar as a sorbent for emerging contaminants enables improvements in waste management and sustainable resource use. J. Clean. Prod. 210, 1324-1342.
5. Xiang *et al* (2020). Biochar technology in wastewater treatment: A critical review. Chemosphere, 252, 126539.
6. Zhan and Chen (2020). The improvement effects of different treatment methods of soil wastewater washing on environmental pollution. Water, 12(9), 2329.

Acknowledgement: Participation in this conference was financially supported by Minister of Education and Science in the range of the program entitled “Regional Initiative of Excellence” for the years 2019–2022, project No. 010/RID/2018/19, amount funding 12,000,000 PLN.