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Heavy Metals Decontamination Using a Renewable Source: Biochar

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Abstract

This research paper aims to address the issue of heavy metal contamination, which poses a significant threat to the environment and human health. Heavy metals are toxic compounds that occur naturally in the Earth's crust, but they have become a major problem due to their discharge into soil and water streams by industrial and agricultural activities. This paper proposes the use of biochar as a potential solution for heavy metal removal. Biochar is a porous and carbonaceous material that can be obtained from biomass through pyrolysis. It can be used to reduce waste biomass, increase soil fertility, decrease nutrient leaching, and adsorb organic and inorganic contaminants, such as heavy metals. The aim of this project is to test the efficiency of different biochar samples obtained from various biomass in the adsorption of heavy metals.

The study will evaluate the performance of various ligneous essences in adsorbing the most common heavy metals, and the pH of the water will be adjusted to further test their capability. The release tests will be conducted to determine whether the metal can be released over time at different pH values. The results of this study will contribute to the development of effective and sustainable solutions for heavy metal removal.

Introduction

The term heavy metal refers to a metallic compound with a relatively high density, about $5g/cm^3$, which is toxic at low concentrations. The most dangerous heavy metals are Mercury, Cadmium, Arsenic, Chromium, Thallium and Lead. These metals are naturally present on the Earth's crust. At low concentration they don't represent a problem for the living beings, but due to the massive usage in the industry and agriculture a huge amount of these compounds have been discharged into the soil and water streams (1). From the soil they are directly soaked up by plants, and then ingested by us and the animals. When they end up into water streams, they rapidly contaminate spring waters and seas, essential for life. Mercury could cause deafness, dysarthria, ataxia, peripheral nerve alterations. Excessive cadmium can lead to diarrhoea, stomach pain, vomiting, bone fractures, immune damage and psychological disorders, while chromium can lead to kidney and liver damage, respiratory problems, lung cancer and death. Excessive lead causes brain damage, birth defects, kidney damage, learning difficulties, destruction of the nervous system, and mercury damage to brain and DNA (2-4).

Among the potential materials of recent interest in water treatment, one of the most interesting is biochar. Biochar is a carbonaceous and porous material, deriving from biomass treated under non-oxidizing conditions in a process called pyrolysis. Depending on the starting feedstock and the pyrolysis parameters (temperature, time, heating rate), biochar will be characterized by peculiar properties. Biochar is also a potential carbon negative product: if waste wood is converted into biochar, instead of being incinerated, the carbon is fixed in its structure and when used in agriculture this carbon is stored into the soil for millennia. Biochar could represent a game-changing solution in many fields:

- It can help to optimize the disposal of waste biomass. Reducing its volume, permits to save energy and emissions linked to its transportation (5).
- It can increase soil fertility by burying the biochar and thus reducing the use of synthetic fertilizers, with lower expenditure for farmers, lower impact on the environment, lower consumption of resources and energy (6).

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- It can decrease nutrient leaching, permitting to optimize plants' nutrients uptake and preserving aquifers. Transforming biomass residues into a stable biochar permits to avoid the GHG (greenhouse gasses) emissions deriving from their degradation (7).
- It can be used as an adsorbent of organic and inorganic contaminants, like pesticides, PAH (polycyclic aromatic hydrocarbons) and heavy metals (8-10).

The aim of the project is to test the efficiency of various biochar, obtained from different biomass, in the adsorption of heavy metals. In the first phase various ligneous essences will be tested to determine their performance in adsorbing the most common and problematic heavy metals, dissolved in water. Secondly the pH of the water will be adjusted to stress even more their capability of adsorbing these compounds.

Finally, release tests were conducted on the same biochar samples to ascertain whether a metal could actually be released over time at different pH. Initially, a washing at pH 6, simulating the natural conditions of water, was carried out to verify the release of all the adsorbed metals only on the surface of the biochar. Subsequently, the biochar was placed in contact with an acid solution in order to try to force the possible release from the material.

Materials and Methods

Biomass and biochar selection

Biomass: Some biochar deriving from residual woody biomass were tested, such as pruning waste and corn cobs, renewable raw materials abundant in Europe. The essences used to produce biochar are the following:

1. Spruce
2. Corn cob
3. Mixed sawdust of poplar (or mixed sawdust)
4. Cherry tree
5. Acacia
6. Elderberry
7. Walnut wood
8. Jube
9. Plum
10. Fig
11. Commercial biochar
12. Commercial activated carbon.

The raw materials have different characteristics in terms of lightness, porosity, and hardness; these characteristics can positively influence the adsorbent capacity of biochar. The results obtained in terms of heavy metals abatement depends on the biomass used, this find accordance with the article of (11) and (10). Prune, walnut, cherry and the jube wood are hardwoods, we therefore expect similar behaviours. Spruce is instead a Conifer; fig and elder wood are light woods, not very valuable because they have poor mechanical properties. Corn cobs are completely different matrices from those just listed.

Biochar production: Together with the laboratory produced biochar, a commercial biochar has been tested.

To make samples homogeneous and representative, raw materials have been grinded with a knife mill (KNIFE MILL SM 300, Verder Scientific). Samples were then sieved to obtain sawdust of the size of the millimetre. For pyrolysis, a quartz tubular furnace (Horizontal opening tube furnace Est 12-450, Carbolite) with a sample-carrying crucible of about 50 cm long was used. All along the process, the furnace was continuously flushed with nitrogen to obtain anaerobic conditions, until the biochar was completely cooled. 50 g of ground wood samples were processed in the pyrolysis. The heating cycles were carried out at three different temperatures: 550 °C, 800 °C and 1100 °C, in total 30 samples were obtained. The heating rate (HR) was 10°C per minute with a residence time (RT) at the highest heating temperature (HHT) of 3 h. Synthesis gas produced during pyrolysis was condensed through a cooling system and all the treatments took place in a laminar flow suction hood with maximum aspiration level. Before using biochar as adsorbent material, an acid treatment with a 0.1 M solution of HCl was applied (8.3 mL of HCl 37% to 1 L volume). 3 g of biochar inserted into a 200 mL flask together with 100 mL of HCl 0,1 M. The flasks were put in an ultrasonic bath overnight. After this, samples were washed several times with water, neutralized with a very dilute solution of ammonia, washed again several times with deionized water using a vacuum filter flask, until the washing water had neutral pH. Finally, the biochar has been oven dried at 80 °C and further heated at 550 °C for 1 hour in the tubular oven (in anaerobic conditions) to completely remove any traces of reagents used. As a result, there were no major increases in pH caused by the calcination of the biochar. To work at pH 6 (conditions used in this research work) it was often necessary to slightly dab the solution with 10% acetic acid and 5% or 10% sodium acetate to avoid any pH increases.

The commercial biochar derives from a mixture of chestnut, elm, ash, and pine wood equally proportioned.

Standard solution preparation: To assess the adsorbent capacity of biochar, a metal mix solution was prepared. For this purpose, metal salts were weighted (Sodium acetate, Sigma-Aldrich; Cadmium nitrate, Carlo Erba; Nickel nitrate, Merck; Lead nitrate, Merck; Copper nitrate, Carlo Erba; Aluminium nitrate, Merck; Chromium nitrate, Carlo Erba; Zinc acetate, Carlo Erba; Manganese acetate, Merck Vanadium pentoxide, Merck); all the elements were in the form of nitrates or acetates to avoid precipitation or complexation phenomena. The final concentration was 1 g/L for each cation. The solution was prepared using the previously dried salts in the oven. Salts were placed in a 1000 mL flask and made up to the volume with deionized water. The pH of the metal mix solution was 3.7. This solution was used to prepare more dilute solutions used to evaluate the removal potential of biochar.

Biochar post pyrolysis acid treatment: One of the problems initially met during the abatement tests is the pH increase due to the contact of the solution containing metals with the biochar. This phenomenon is caused by the biochar basicity, due to carbonates, oxides of alkaline and alkaline earth metals. The solution reached a pH of about 10-12. In this condition of alkaline pH, most metal cations precipitate and this can distort the abatement values. Following several buffered tests, it was preferred not to introduce large amounts of buffered salts, but to perform an acid treatment on all biochar samples by washing with 0.1 M hydrochloric acid. A 0.1 M solution of HCl was used (8.3 mL of HCl 37% to 1 L volume) and approximately 3 g of each biochar sample was inserted into 200 mL flasks together with 100 mL of HCl 0.1M. The flasks were introduced for a few minutes in an ultrasonic bath and rested overnight. Afterwards it was washed several times with water, neutralized with a very dilute solution of ammonia and washed again with deionized water using a vacuum filter flask, until the washing water had neutral pH. Finally, it has been oven dried at 80 °C and further heated to 550 °C for 1 hour (in anaerobic conditions) in the tubular oven to completely remove any traces of reagents. As a result, there were no major increases in pH caused by the calcination of the biochar. To work at pH 6 (conditions used in this research work) it was often necessary to dab the solution slightly with 10% acetic acid and 5% or 10% sodium acetate to compensate for any pH increases.

Abatement tests: Biochar abatement tests were performed: the tests measured the corresponding metal amount each type of biochar can absorb. These tests were carried out initially by putting in contact 0,5 g of biochar (which had previously undergone acid treatment), with 25 mL of solution containing cadmium, lead, aluminium, nickel, chromium, manganese, zinc and copper. 30 samples have been tested to perform abatement tests on the solution at pH= 6, with 2 mg/L for

Biomass	Wet weight [g]	Dry weight [g]	Moisture content [g]	Moisture content [%]
Spruce	1,7524	1,624	0,1284	7,3
Corn cob	1,7348	1,5548	0,1800	10,4
Sawdust	1,4704	1,4439	0,0265	1,8
Cherry	1,7206	1,5585	0,1621	9,4
Acacia	1,5341	1,3506	0,1835	12,0
Elder	1,7556	1,5537	0,2019	11,5
Walnut	1,8364	1,6930	0,1434	7,8
Jube	1,5526	1,4595	0,0931	6,0
Plum	1,6897	1,5896	0,1001	5,9
Fig	1,5255	1,3462	0,1793	11,8

Table 1: Determination of moisture content % (m/m) of woody biomass.

Biomass	Sawdust weight [g]	Ash weight [g]	Ash [%]
Spruce	1,6472	0,0110	0,67
Corn cob	1,5708	0,0344	2,19
Sawdust	1,3962	0,0169	1,21
Cherry	1,5704	0,0143	0,91
Acacia	1,3667	0,0143	1,05
Elder	1,5755	0,0308	1,95
Jube	1,4779	0,0299	2,02
Plum	1,5946	0,0227	1,42
Fig	1,3652	0,0513	3,76
Walnut	1,6310	0,0792	4,86

Table 2: Ash content % determination.

Biomass	Yield [%] 550 °C	Yield [%] 800 °C	Yield [%] 1100 °C
Spruce	27,80	24,02	23,11
Corn cob	25,03	24,50	24,07
Sawdust	27,11	26,62	25,16
Cherry	26,46	25,23	23,37
Acacia	26,51	23,75	21,67
Elder	29,43	24,88	23,65
Walnut	28,85	25,14	23,58
Jube	30,73	26,92	24,57
Plum	28,62	24,31	23,65
Fig	29,24	28,85	26,71

Table 3: Comparison of yield % in biochar at 550°C, 800°C and 1100°C.

each metal. 25 mL of 2 mg/L solution were introduced into Falcon-type plastic tubes containing 0,5 g of biochar, weighed on an analytical balance, sonicate for 5 minutes, and finally shake on the orbital stirrer for 24, 48 and 72 hours. After that, samples were centrifuged for 5 minutes, pH checked, filtered and on the filtrate, acidified with a few drops of nitric acid; the analysis was performed using ICP-OES (ICP-OES OPTIMA 7000 DV Perkin Elmer equipped with cyclonic nebulization chamber in Argon flow). Afterwards, abatement tests were carried out using the same procedure with solution of 1 and 0.1 mg/L at pH=6.

Results and Discussion

Biochar: biomass characterization

Moisture content: The determination of the moisture content of each wood was measured by weighing about 1-2 g of sawdust, placed on aluminium paper on an analytical balance. The samples were dried in the oven at 120 °C for 24 hours, and then weighed again to determine the dry weight [g] and consequently the moisture content [g]. In the following *table 1* the moisture content results.

Sample	pH (average)
Spruce 550 °C	8,705
Spruce 800 °C	10,136
Spruce 1100 °C	10,423
Cherry tree 550 °C	8,974
Cherry tree 800 °C	10,472
Cherry tree 1100 °C	11,013
Fig 550 °C	8,620
Fig 800 °C	10,131
Fig 1100 °C	10,489
Acacia 550 °C	8,581
Acacia 800 °C	10,007
Acacia 1100 °C	10,331
Jube 550° C	8,691
Jube 800 °C	10,52
Jube 1100 °C	10,974
Walnut 550 °C	9,561
Walnut 800 °C	10,13
Walnut 1100 °C	10,573
Plum 550 °C	9,036
Plum 800 °C	10,426
Plum 1100 °C	10,975
Elderberry 550 °C	10,10
Elder 800 °C	10,485
Elder 1100 °C	10,621
Poplar Sawdust 550 °C	9,03
Poplar Sawdust 800 °C	11,808
Poplar Sawdust 1100 °C	11,696
Corn cob 550 °C	9,537
Corn cob 800 °C	11,76
Corn cob 1100 °C	11,003
Commercial biochar	9,794
Commercial activated carbon	8,723

Table 4: pH measured on aqueous solutions after 72 hours of contact with different biochar samples.

Ash content: Woody biomass consists essentially of carbon, oxygen, and hydrogen. The nitrogen content is less than 0.1%, while the ash content does not exceed 0.2-0.3 %. The determination of ash content was carried out by incineration at 550 °C for 12 hours in porcelain crucibles of 1-2 g of the dry samples, in the following *table 2* the results.

Biochar yields: Biochar corresponds to the solid carbon residue of the wood that has been heated in an oxygen-free environment (pyrolysis). This treatment removes moisture and volatile substances from the wood. *Table 3* shows the biochar production yield at three temperatures.

How it can be notice from *table 3*, biochar yield gradually decreases with the increase of the pyrolysis temperature.

pH determination: The effect of the biochar on the pH of the solution was evaluated. 0.5 g of each sample was inserted in 25 mL of water, placed inside Falcon-type tubes. The pH was measured after 72 hours of contact. The results show how the pH of the solution becomes alkaline because of the contact with biochar *(Table 4)*. This

Sample	Al		
Metal amount retained	*%*	*%*	*%*
Time	*24 h*	*48 h*	*72 h*
Spruce 550 °C	40,11	54,12	98,50
Spruce 800 °C	23,77	29,19	99,51
Spruce 1100 °C	67,48	99,76	99,97
Cherry tree 550 °C	82,21	92,15	99,70
Cherry tree 800 °C	64,88	70,87	99,82
Cherry tree 1100 °C	96,70	99,00	99,77
Fig 550 °C	93,54	100,0	99,20
Fig 800 °C	93,54	100,0	100,0
Fig 1100 °C	88,57	95,00	99,16
Acacia 550 °C	71,15	84,41	92,04
Acacia 800 °C	39,28	43,99	76,55
Acacia 1100 °C	76,17	88,96	94,04
Jube 550 °C	75,26	99,33	100,0
Jube 800 °C	49,35	61,03	81,64
Jube 1100 °C	93,54	99,76	100,0
Walnut 550 °C	46,07	61,91	94,40
Walnut 800 °C	90,74	99,00	99,89
Walnut 1100 °C	72,63	94,55	99,04
Plum 550 °C	59,07	87,87	93,21
Plum 800 °C	34,75	47,42	87,55
Plum 1100 °C	92,63	100,0	100,0
Elder 550 °C	79,00	80,00	88,90
Elder 800 °C	90,00	90,00	94,64
Elder 1100 °C	99,00	99,00	100,0
Poplar sawdust 550 °C	36,76	44,29	99,53
Poplar sawdust 800 °C	37,08	46,34	99,13
Poplar sawdust 1100 °C	92,47	97,20	99,54
Corn cob 550 °C	49,96	66,57	99,60
Corn cob 800 °C	83,33	97,73	100,0
Corn cob 1100 °C	79,37	70,60	99,68
Commercial biochar	82,06	94,08	100,0
Active carbon	-	-	100,0

Table 5: Abatement % of aluminum in solution (2 mg/L pH 6.)

Sample	Cr		
Metal amount retained	*%*	*%*	*%*
Time	*24 h*	*48 h*	*72 h*
Spruce 550 °C	30,62	33,50	33,18
Spruce 800 °C	25,20	34,02	38,90
Spruce 1100 °C	51,39	71,75	76,86
Cherry tree 550 °C	20,59	23,04	23,49
Cherry tree 800 °C	28,69	30,04	30,05
Cherry tree 1100 °C	58,29	60,57	65,09
Fig 550 °C	55,65	60,80	60,31
Fig 800 °C	73,23	80,12	81,64
Fig 1100 °C	99,66	99,00	99,48
Acacia 550 °C	54,32	54,76	53,23
Acacia 800 °C	39,84	40,95	37,88
Acacia 1100 °C	70,76	69,13	69,77
Jube 550 °C	62,21	63,14	63,67
Jube 800 °C	37,10	37,34	42,34
Jube 1100 °C	84,45	80,58	80,42
Walnut 550 °C	45,32	52,79	55,79
Walnut 800 °C	61,07	64,79	66,72
Walnut 1100 °C	61,54	62,64	69,83
Plum 550 °C	44,58	45,96	42,86
Plum 800 °C	40,39	41,11	42,55
Plum 1100 °C	75,05	79,05	75,70
Elder 550 °C	65,31	68,79	63,32
Elder 800 °C	66,81	69,59	69,42
Elder 1100 °C	99,12	99,50	99,87
Poplar sawdust 550 °C	27,22	30,09	30,23
Poplar sawdust 800 °C	29,01	37,24	39,40
Poplar sawdust 1100 °C	71,10	80,04	85,39
Corn cob 550 °C	41,19	47,64	47,44
Corn cob 800 °C	55,62	60,99	60,55
Corn cob 1100 °C	79,74	80,57	86,88
Commercial biochar	93,51	95,37	99,56
Active carbon	-	-	99,96

Table 6: % abatement of chromium in solution (2 mg/L at pH 6).

phenomenon is caused by carbonates and oxides of alkali and alkaline earth metals in biochar. The samples that give the most alkalinization phenomena are those produced at 1100 °C: generally the pH of biochar increases with the HHT rise

Abatement tests

The data and information collected during the various abatement tests are reported in following paragraphs. The results are expressed as percentage of metal retained; this value was obtained by analysing the solution before and after the contact with the biochar.

Abatement tests: 2 mg/L at pH 6: pH of water has been adjusted to 6, to make it representative with a common value for natural water. All the analyses were conducted after 24, 48 and 72 hours of biochar-solution contact.

Aluminium: According to the results from *Table 5*, aluminium is retained between 80 and 100% from all biochar for all three temperatures after 72 hours. Some samples such as fig, cherry, and elderberry biochar after only 24 hours achieve excellent results. Other features that improve abatement efficiency are the pyrolysis temperature: most of the best results have been found on biochar produced at 1100 °C. Aluminium abatement increases a lot with time (the best results are after 72 hours) and to a lesser extent with the pyrolysis temperature. Some biochar at 800 °C are less efficient than those produced at 550 °C and 1100 °C, probably because they lack the functional groups typical of biochar produced at 550 °C, at the same time they lack the peculiar graphitic structure resulting at 1100 °C. Fig and elderberry tree biochar show high abatement % no matter pyrolysis temperature.

Chromium: The resultsshow high chromium abatement already after 24 hours and stays constant during time. The best results are achieved in biochar produced at 1100 °C: abatement percentages are all between 70 and 100%. Chrome abatement increases with the pyrolysis temperature increment. Fig and Elderberry biochar at 1100 °C have the highest abatement rate between the laboratory produced biochar (*Table 6*).

Copper: Best results are found on biochar 1100 °C after 72 hours (*Table 7*).

Copper abatement % increases with both pyrolysis temperature and contact time increment. If it is considered only samples produced at 1100 °C, abatement percentage varies between 80% and 99% depending on the wood essence. Fig and elder biochar continue to be the most performant samples between the laboratory produced biochar.

Sample	Cu		
Metal amount retained	%	%	%
Time	*24 h*	*48 h*	*72 h*
Spruce 550 °C	21,17	27,39	43,35
Spruce 800 °C	20,83	30,41	47,57
Spruce 1100 °C	25,70	40,89	88,10
Cherry tree 550 °C	57,38	63,54	68,36
Cherry tree 800 °C	73,94	77,09	79,78
Cherry tree 1100 °C	91,73	93,19	93,45
Fig 550 °C	57,76	65,11	79,47
Fig 800 °C	90,90	94,26	94,96
Fig 1100 °C	97,46	98,26	98,80
Acacia 550 °C	47,00	58,45	67,81
Acacia 800 °C	38,54	38,96	63,31
Acacia 1100 °C	78,97	79,77	87,16
Jube 550 °C	56,75	77,21	80,14
Jube 800 °C	46,45	60,34	62,77
Jube 1100 °C	90,14	91,99	91,63
Walnut 550 °C	17,25	26,46	47,04
Walnut 800 °C	65,16	78,34	80,89
Walnut 1100 °C	84,01	91,19	93,29
Plum 550 °C	31,48	46,20	71,29
Plum 800 °C	64,82	77,17	77,03
Plum 1100 °C	84,68	90,24	91,16
Elder 550 °C	58,10	56,44	77,11
Elder 800 °C	95,63	97,26	99,69
Elder 1100 °C	98,86	99,11	98,88
Poplar sawdust 550 °C	13,47	15,83	32,69
Poplar sawdust 800 °C	32,21	38,69	53,47
Poplar sawdust 1100 °C	57,89	59,78	91,26
Corn cob 550 °C	26,65	37,48	51,90
Corn cob 800 °C	48,50	51,29	56,44
Corn cob 1100 °C	62,91	64,86	66,16
Commercial biochar	93,01	95,96	98,80
Active carbon	-	-	99,27

Table 7: Abatement of copper in solution (2 mg/L at pH 6).

Lead: Lead is retained in high percentages, very close to 100%, by all the samples pyrolyzed both at low and high temperatures and after 72 hours of contact. According to the analysis, the phenomenon depends mainly on the time and to a lesser extent on the temperature *(Table 8)*.

Zinc: Zinc abatement increases considerably with contact time and to a lesser extent with the pyrolysis temperature. Elder at 1100°C, cherry at 1100 °C and fig samples are the best performing biochar. Zinc abatement % is on average lower than those of previous metals and varies between 50 and 90% *(Table 9)*.

Cadmium: Cadmium retain percentages are lower than other metals and vary, on average, between 30 and 70% after 72 hours of contact. The abatement increases with contact time increment. The greatest abatement occurs with the samples produced at 1100 °C. Elder biochar at 1100 °C is the most performant among the laboratory produced biochar *(Table 10)*.

Manganese: Acceptable manganese removal results are achieved only after 72 h. Biochar produced at 1100°C are generally more performant. Fig and elder biochar continue to be the most effective sample, reaching more than 70% abatement at 1100 °C *(Table 11)*.

Sample	Pb		
Metal amount retained	%	%	%
Time	*24 h*	*48 h*	*72 h*
Spruce 550 °C	35,49	40,69	69,82
Spruce 800 °C	27,82	30,76	68,96
Spruce 1100 °C	20,68	38,15	85,84
Cherry tree 550 °C	40,05	59,46	69,04
Cherry tree 800 °C	43,61	64,14	75,34
Cherry tree 1100 °C	70,79	85,17	95,54
Fig 550 °C	90,45	97,00	97,70
Fig 800 °C	94,02	96,00	96,16
Fig 1100 °C	99,09	99,30	99,82
Acacia 550 °C	33,17	54,65	85,21
Acacia 800 °C	29,26	50,29	84,97
Acacia 1100 °C	49,49	67,75	93,90
Jube 550 °C	76,51	83,64	95,46
Jube 800 °C	50,92	54,75	85,16
Jube 1100 °C	99,01	99,10	99,47
Walnut 550 °C	73,83	75,51	87,78
Walnut 800 °C	88,86	89,00	95,73
Walnut 1100 °C	88,82	90,33	96,74
Plum 550 °C	49,62	54,35	82,36
Plum 800 °C	43,84	45,30	76,65
Plum 1100 °C	91,18	92,21	94,33
Elder 550 °C	48,17	75,47	94,07
Elder 800 °C	71,63	90,09	96,47
Elder 1100 °C	82,95	95,09	99,75
Poplar sawdust 550 °C	30,81	32,59	83,27
Poplar sawdust 800 °C	36,78	41,61	86,15
Poplar sawdust 1100 °C	54,67	54,80	96,15
Corn cob 550 °C	37,26	45,05	95,30
Corn cob 800 °C	65,70	78,99	96,99
Corn cob 1100 °C	65,16	68,70	97,55
Commercial biochar	98,59	99,00	99,73
Active carbon	-	-	99,97

Table 8: Abatement of lead in solution (2 mg/L pH 6).

Nickel: Nickel behaves in a similar way to manganese and cadmium: the percentages of abatement are generally medium-low (they vary between 30 and 60%) and increase with time. Samples at 1100 °C are usually more performant, especially fig and elder tree biochar *(Table 12)*.

Abatement tests trends: According to the analysis, most effective biochar samples are the one produced at 1100°C with a contact time of 72h. These biochar almost totally retain metals such as aluminium, copper and lead while zinc and chromium are broken down in lower percentages but still greater than 50%. For commercial activated carbon only a 72 hours abatement test has been done, being the results of the laboratory biochar abatement significant in that time range *(Figure 1)*.

Cadmium, manganese, and nickel show a different pattern: they are cut down in lower percentages, on average between 30 and 80%, the abatement increases mainly with time and to a lesser extent with the pyrolysis temperature, although biochar 1100 °C are the best performing *(Figure 2)*.

Sample	Zn		
Metal amount retained	%	%	%
Time	*24 h*	*48 h*	*72 h*
Spruce 550 °C	10,85	40,98	48,22
Spruce 800 °C	11,96	41,72	45,29
Spruce 1100 °C	17,48	53,04	59,71
Cherry tree 550 °C	19,66	26,85	76,22
Cherry tree 800 °C	20,13	23,78	76,55
Cherry tree 1100 °C	22,89	33,19	94,99
Fig 550 °C	22,69	28,89	91,19
Fig 800 °C	25,68	32,62	95,78
Fig 1100 °C	79,84	86,84	96,50
Acacia 550 °C	27,88	28,40	50,61
Acacia 800 °C	21,94	27,73	49,22
Acacia 1100 °C	23,55	29,37	51,64
Jube 550 °C	19,46	26,36	46,76
Jube 800 °C	18,83	28,64	47,13
Jube 1100 °C	20,98	28,98	51,93
Walnut 550 °C	22,96	48,97	75,36
Walnut 800 °C	25,02	46,80	75,25
Walnut 1100 °C	27,29	45,28	76,77
Plum 550 °C	11,42	15,44	52,11
Plum 800 °C	9,64	14,47	52,85
Plum 1100 °C	10,89	17,69	53,76
Elder 550 °C	18,50	21,72	61,44
Elder 800 °C	31,54	32,39	76,02
Elder 1100 °C	72,75	80,69	93,45
Poplar sawdust 550 °C	9,74	11,82	64,67
Poplar sawdust 800 °C	9,60	45,07	64,83
Poplar sawdust 1100 °C	10,91	12,84	66,68
Corn cob 550 °C	10,50	34,29	68,02
Corn cob 800 °C	12,13	51,13	67,00
Corn cob 1100 °C	15,27	71,57	66,26
Commercial biochar	84,95	92,34	93,85
Active carbon	-	-	93,28

Table 9: Reduction of zinc in solution (2 mg/L pH 6).

Sample	Cd		
Metal amount retained	%	%	%
Time	*24 h*	*48 h*	*72 h*
Spruce 550 °C	5,13	6,56	46,65
Spruce 800 °C	5,64	6,88	45,98
Spruce 1100 °C	1,06	1,64	50,38
Cherry tree 550 °C	28,12	39,95	37,34
Cherry tree 800 °C	26,72	38,57	44,74
Cherry tree 1100 °C	28,00	35,29	63,84
Fig 550 °C	25,78	34,39	56,56
Fig 800 °C	20,18	24,95	63,52
Fig 1100 °C	61,68	76,66	77,21
Acacia 550 °C	27,93	37,60	51,32
Acacia 800 °C	25,43	30,32	45,32
Acacia 1100 °C	26,80	42,67	61,60
Jube 550 °C	19,91	26,65	60,01
Jube 800 °C	8,87	13,61	46,13
Jube 1100 °C	19,88	25,20	71,10
Walnut 550 °C	12,95	18,81	36,44
Walnut 800 °C	20,61	30,18	32,89
Walnut 1100 °C	9,73	15,40	37,70
Plum 550 °C	8,84	13,88	49,60
Plum 800 °C	7,79	10,99	49,25
Plum 1100 °C	9,95	14,17	57,25
Elder 550 °C	28,53	39,46	69,61
Elder 800 °C	27,79	42,86	62,49
Elder 1100 °C	47,62	53,82	89,34
Poplar sawdust 550 °C	5,73	35,25	39,80
Poplar sawdust 800 °C	5,60	36,79	36,70
Poplar sawdust 1100 °C	4,58	37,33	41,52
Corn cob 550 °C	3,95	6,18	47,37
Corn cob 800 °C	5,59	8,33	45,21
Corn cob 1100 °C	3,02	25,02	56,45
Commercial biochar	56,84	65,63	97,85
Active carbon	-	-	95,64

Table 10: Reduction of cadmium in solution (2 mg/L pH 6).

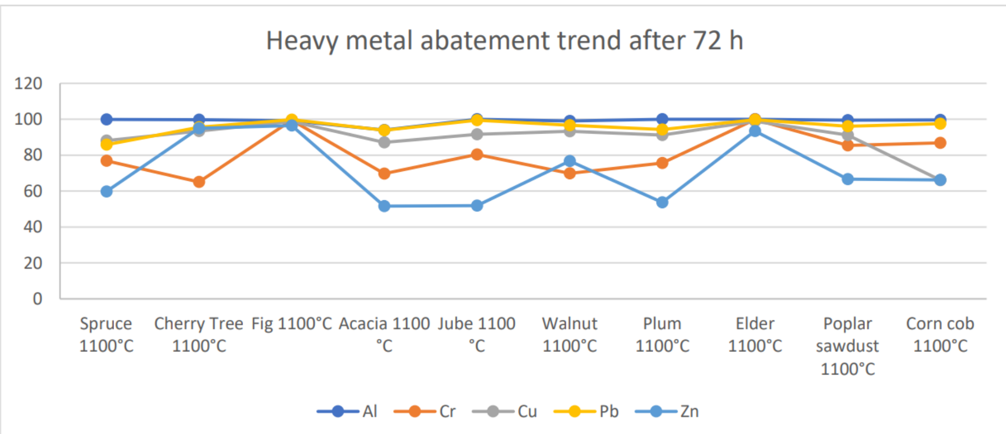

Figure 1: Heavy metal abatement after 72h

Sample	Mn		
Metal amount retained	%	%	%
Time	*24 h*	*48 h*	*72 h*
Spruce 550 °C	6,61	6,93	32,91
Spruce 800 °C	7,36	8,06	36,17
Spruce 1100 °C	2,79	4,20	45,87
Cherry tree 550 °C	7,51	10,63	32,44
Cherry tree 800 °C	8,14	17,61	36,39
Cherry tree 1100 °C	9,35	20,24	45,66
Fig 550 °C	13,92	17,85	53,23
Fig 800 °C	12,23	15,40	52,96
Fig 1100 °C	33,92	36,09	73,30
Acacia 550 °C	26,43	29,40	35,25
Acacia 800 °C	24,77	31,22	38,51
Acacia 1100 °C	25,20	29,89	47,31
Jube 550 °C	12,14	14,66	30,80
Jube 800 °C	11,42	15,16	33,71
Jube 1100 °C	13,00	17,66	52,23
Walnut 550 °C	8,91	14,17	31,62
Walnut 800 °C	6,16	11,16	31,45
Walnut 1100 °C	8,52	12,32	35,24
Plum 550 °C	10,95	15,09	36,79
Plum 800 °C	10,78	12,51	35,76
Plum 1100 °C	10,48	14,19	44,94
Elder 550 °C	26,18	27,79	55,68
Elder 800 °C	24,20	28,04	47,38
Elder 1100 °C	28,89	43,96	72,74
Poplar sawdust 550 °C	6,93	6,98	27,82
Poplar sawdust 800 °C	6,96	8,36	25,54
Poplar sawdust 1100 °C	6,60	8,41	31,96
Corn cob 550 °C	5,61	7,73	28,90
Corn cob 800 °C	7,26	9,32	32,39
Corn cob 1100 °C	5,81	5,79	35,12
Commercial biochar	56,53	69,98	86,15
Active carbon	-	-	81,49

Table 11: Abatement % of manganese in solution (2 mg/L pH 6).

Sample	Ni		
Metal amount retained	%	%	%
Time	*24 h*	*48 h*	*72 h*
Spruce 550 °C	4,02	6,00	39,25
Spruce 800 °C	5,40	5,41	42,21
Spruce 1100 °C	8,66	10,28	46,65
Cherry tree 550 °C	26,82	27,46	41,60
Cherry tree 800 °C	25,04	26,49	44,84
Cherry tree 1100 °C	26,80	27,46	54,48
Fig 550 °C	13,08	18,07	43,65
Fig 800 °C	21,70	27,03	56,99
Fig 1100 °C	51,83	58,59	73,66
Acacia 550 °C	26,43	36,33	43,48
Acacia 800 °C	24,54	26,06	45,31
Acacia 1100 °C	24,43	29,37	56,12
Jube 550 °C	11,28	13,97	48,16
Jube 800 °C	7,97	12,34	43,74
Jube 1100 °C	14,33	19,75	60,65
Walnut 550 °C	7,59	11,64	33,13
Walnut 800 °C	20,58	30,57	38,65
Walnut 1100 °C	7,31	13,83	42,25
Plum 550 °C	7,32	12,22	45,41
Plum 800 °C	7,48	10,98	45,06
Plum 1100 °C	9,04	13,34	48,66
Elder 550 °C	27,44	32,31	62,28
Elder 800 °C	25,82	39,71	68,81
Elder 1100 °C	47,66	60,33	89,06
Poplar sawdust 550 °C	5,65	5,80	36,45
Poplar sawdust 800 °C	5,36	7,47	33,92
Poplar sawdust 1100 °C	2,84	6,25	39,44
Corn cob 550 °C	3,83	5,41	42,16
Corn cob 800 °C	5,31	8,87	44,38
Corn cob 1100 °C	1,51	3,01	43,40
Commercial biochar	24,36	52,57	96,40
Active carbon	-	-	95,97

Table 12: Reduction of nickel in solution (2 mg/L pH 6).

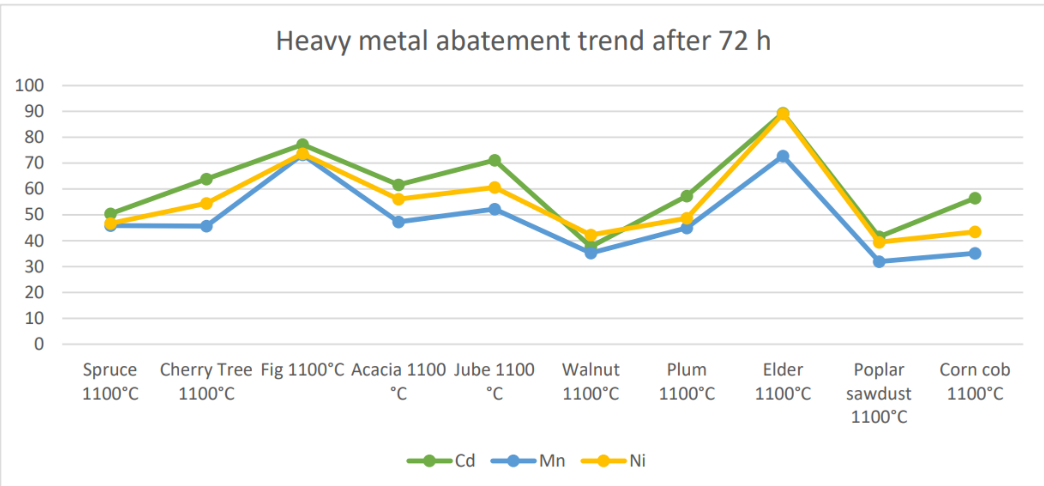

Figure 2: Heavy metal abatement after 72h

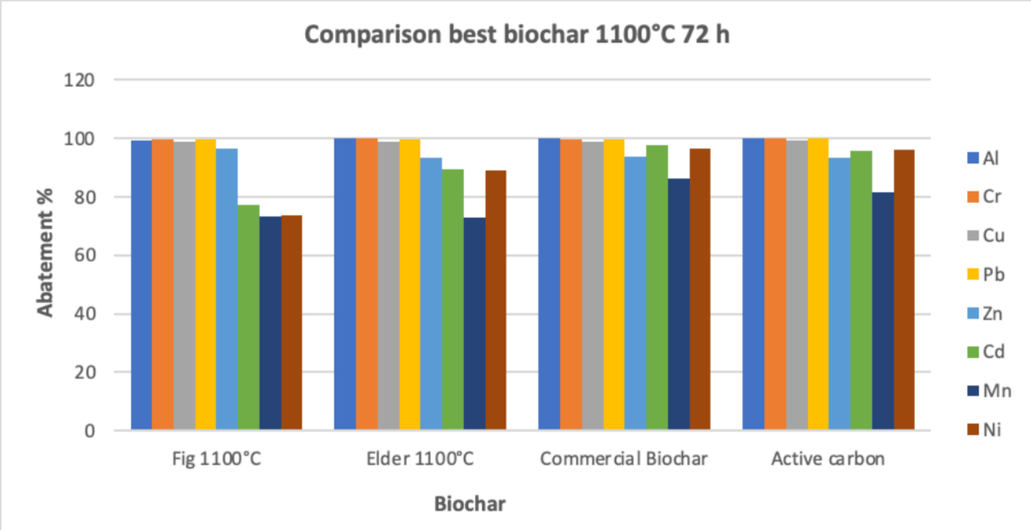

Figure 3: Biochar comparison HHT: 1100°C RT: 72h

Abatement % 1 mg/L	Al average	Cd average	Cr average	Cu average	Mn average	Ni average	Pb average	Zn average
72 h, pH= 6	%	%	%	%	%	%	%	%
Commercial biochar	99,5	93,3	99,9	98,9	53,1	94,9	95,3	73,7
Cherry tree 1100 °C	100	76,7	86,2	93,6	65,7	70,1	96,1	37,9
Fig 1100 °C	97,5	88,8	99,9	99	78,8	93,6	95,5	89,6
Walnut 1100 °C	99,5	73,2	99,3	91,9	67,1	72,8	97,1	39,2
Elder 1100 °C	99,9	79,5	99	94,7	61,2	66,5	97,2	40

Table 13: % of metal reduction with a metals concentration of 1 mg/L and pH 6 on best performing samples.

Abatement [%] 0,1 mg/L	Al	Cd	Cr	Cu	Mn	Ni	Pb	Zn
72 h, pH= 6	%	%	%	%	%	%	%	%
Commercial biochar	44,2	40,8	56,6	74,5	0,0	45,8	67,2	0,0
Cherry tree 1100 °C	100,0	7,6	80,6	69,0	5,4	7,1	68,0	2,8
Fig 1100 °C	86,9	21,3	91,7	87,1	11,0	21,5	83,5	3,2
Walnut 1100 °C	56,9	51,1	96,3	89,8	17,0	17,1	0,0	0,0
Elder 1100 °C	100,0	8,4	93,7	72,0	6,8	8,8	69,1	1,4

Table 14: % of metal reduction with a metals concentration of 0.1 mg/L and pH 6 on best performing samples.

% Retained after 30 min in water (pH 6)	Al	Cd	Cr	Cu	Mn	Ni	Pb	Zn
Commercial biochar	99,9	98,5	100,0	100,0	90,4	97,6	100,0	97,6
Fig 1100 °C	100,0	77,9	100,0	99,8	79,5	91,8	100,0	89,8
Elder 1100 °C	100,0	65,7	99,9	99,3	79,4	82,4	99,2	81,9
Cherry tree 1100 °C	99,9	68,5	99,3	94,3	87,4	81,4	89,2	75,4
Walnut 1100 °C	100,0	70,8	99,8	94,5	87,6	89,0	84,1	71,1

Table 15: % of metal retained after 30 minutes.

Type of sample	Al media	Cd media	Cr media	Cu media	Mn media	Ni media	Pb media	Zn media
Commercial biochar	99	95	100	100	74	95	100	97
Fig 1100 °C	100	52	100	99	71	73	98	68
Elder 1100 °C	92	58	91	96	79	61	63	55
Cherry tree 1100 °C	84	66	87	87	85	81	72	75
Walnut 1100 °C	74	65	73	55	84	77	39	71

Table 16: % metal retained after 5 days of permanence of the biochar in a buffer solution of pH 4.

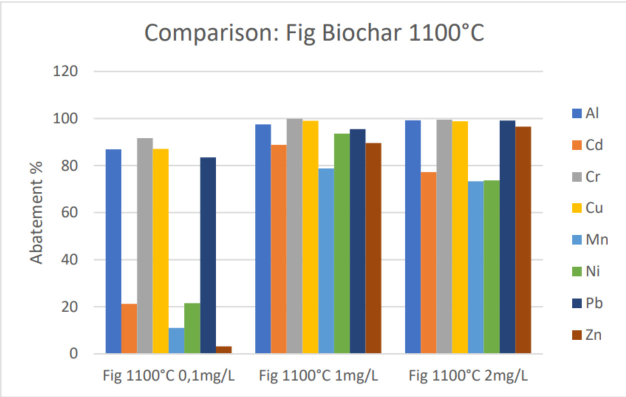

Figure 4: Fig Biochar abatement % at different concentrations

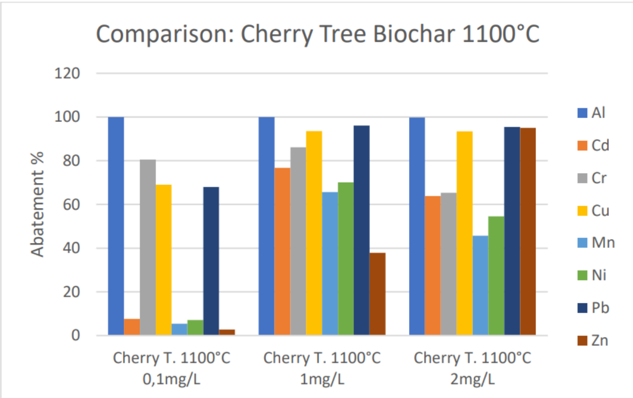

Figure 5: Cherry tree Biochar abatement % at different concentrations

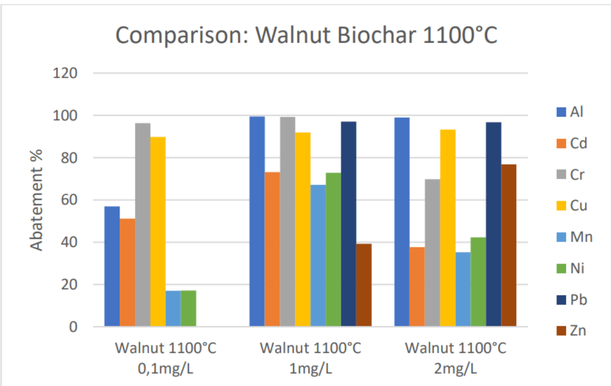

Figure 6: Walnut Biochar abatement % at different concentrations

Commercial biochar vs active carbon: a comparison: Commercial biochar and activated carbon reduced at least 95% all metals tested (except for manganese which is cut down by around 80%). A comparison on most efficacious samples is shown in the following graph *(Figure 3)*.

If we compare commercial samples with best performing biochar produced in the lab (fig and elderberry biochar 1100 °C), it can be noticed that activated carbon and commercial biochar perform a slightly higher abatement percentages than elderberry biochar for cadmium, manganese, and nickel. This difference is probably due to the industrial processes to produce activated carbon and commercial biochar. Commercial biochar and activated carbon performed similar heavy metals abatement.

Abatement tests: 1 mg/L at pH 6 on best performing samples: This abatement test was carried out only on the most effective biochar samples applying 0.5 g biochar with 50 mL of 1 mg/L solution of metals into Falcon type specimens. By decreasing the concentration but doubling the volume, the absolute metal amount stays constant. Analysis at the ICP-OES was performed on the solution taken after 72 hours of contact with biochar. The purpose of this test is to assess how the abatement varies as the metal concentration of the solution diminished. According to the results, the abatement rates are very high for all metals, even for those that were absorbed less (Cd, Mn and Ni) during the tests with 2 mg/L concentration. Only commercial biochar was used for this abatement test, being its abatement behaviour similar, and in most of the cases slightly higher, compared to active carbon *(Table 13)*.

Abatement tests: 0.1 mg/L at pH 6 on best performing samples: The abatement tests on the 0.1 mg/L metals solutions were carried out on the most efficacious biochar, applying 1g of biochar in 1L of solution. A contact time of 72 hours was used. The purpose of this test was to assess the trend of biochar abatement in a substantial diluted solution *(Table 14)*.

These results show a lower abatement performance, which leads to the conclusion that when biochar is too dispersed, its abatement efficiency is lowered.

Abatement tests at pH=6: a comparison: The following graphs show how abatement percentages vary according to the concentrations of both biochar and metals present in the solution. The comparison concerns three tests carried out at pH=6, with metal concentrations of 0,1 mg/L, 1 mg/L and 2 mg/L, using the best performing biochar samples *(Figure 4-8)*.

Lowest abatement percentages are found in all the samples during the test at 0.1 mg/L. The commercial biochar and elder biochar

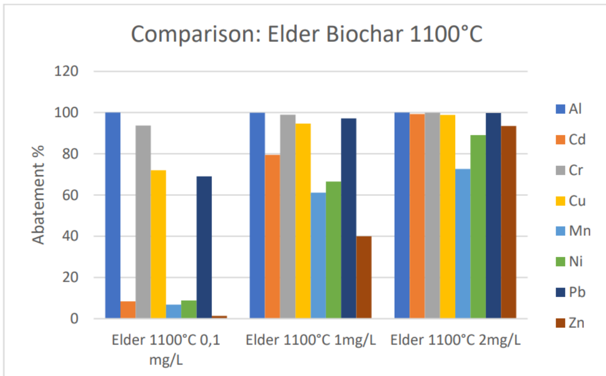

Figure 7: Elderberry Biochar abatement % at different concentrations

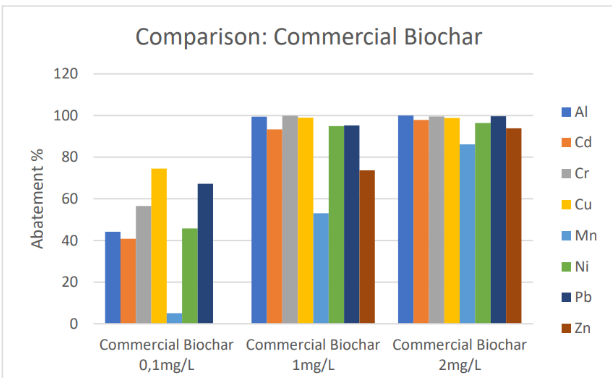

Figure 8: Commercial Biochar abatement % at different concentrations

produced at 1100 °C are more effective during the test conducted on 2 mg/L, vice versa, the other samples show on average higher abatement during the test carried out at 1 mg/L. Aluminium, chromium, copper and lead are cut down in high percentages at all three concentration conditions by all the biochar samples, excluding walnut and commercial biochar which show lower values. During the 2 mg/L test, zinc is retained in higher percentages by all samples; cadmium, manganese and nickel are better retained better during the 1 mg/L test, but this does not occur with commercial and elder tree biochar samples.

Release tests: Release trials were carried out after the abatement test at pH=6 with 2 mg/L of metal concentration. It was also intended to check whether any pH changes in aqueous matrix may cause metals release back to the solution. These measurements were performed on the samples which showed the best abatement feature. Biochar containing the adsorbed metals were placed in contact with 50 mL of ultrapure water buffered with acetate buffer to reach the desired pH. After 30 minutes the first withdrawal was made. If the release of metals was found at this stage, the abatement mechanism could be traced back to ionic exchange phenomena. Subsequently the pH was lowered from 6 to 4 and after 5 days the analysis was carried out again. The results obtained are shown in the tables and are expressed as a withheld percentage *(Table 15)*.

Observing the results, it emerges that the commercial biochar can retain almost all the metals, excluding manganese which is retained at 90%. The other biochar samples totally retain aluminium and chromium, while copper; manganese, nickel and lead are retained in percentages between 80-100%. Cadmium and zinc are released in higher amounts, but the retained percentages remain significant (65-90%). According to the data, it can be stated that the ionic exchange phenomena influence only a small part of the abatement process. In the following *table 16* the retained percentages are shown, measured after 5 days of permanence of the biochar with a buffer solution of pH 4.

Looking at the results in *table 16* we can adduce that the commercial biochar continues to retain more than 95% of all metals. How it can be discerned, aluminium and chromium are again the most retained metals, whereas cadmium is the least (65-50%); other metals are retained in high percentages, between 60 and 90%.

Conclusion

In this study the effectiveness of adsorption of different heavy metals using biochar has been investigated.

- The results show that different feedstock influence the physical and chemical properties of biochar and its heavy metal abatement power.
- The HHT at which the laboratory biochar has been produced highly influencesthe abatement performance; the best results have been obtained at 1100 °C.
- Most effective heavy metals reduction has been obtained after 72 h of contact time.
- According to the results biochar could be a very efficacious material to remove Al, CU and Pb, with an almost total adsorption of these metals in various conditions. Zinc and chromium are broken down in lower percentages but still greater than 50%.

In light of the results we can ascertain a great potential of this material in the heavy metals removal from water. Biochar, if produced from waste biomass, could be an excellent example of circular economy. It can replace some types of active carbon whoseproduction is highly energy-intensive and sometimes deriving from non-renewable materials (like coal). Besides, biochar could be a powerful, but low cost, material for the communities with a difficult access to potable water.

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