Cd-contaminated solution treatment by activated and non-activated beech charcoal

Bonı M.R.[1], Chiavola A.[1*], Antonucci A.[1], Dı Mattıa E.[2] And Marzeddu S.[1]

[1]Sapienza University of Rome, Faculty of Civil and Industrial Engineering, Department of Civil, Building and Environmental Engineering (DICEA), Via Eudossiana 18, Zip code 00184, Rome, Italy

[2]University of Tuscia, Department of Agricultural and Forestry Sciences (DAFNE), Via San Camillo de Lellis snc, Zip code 01100, Viterbo, Italy

*corresponding author: agostina.chiavola@uniroma1.it

Abstract Biochar obtained from pyrolysis of vegetable waste has been recognized to possess adsorbent capacity. Furthermore, it represents an economic and environmentally sustainable alternative to commercial adsorbents because, being a waste product, its use allows to avoid industrial activities for adsorbent production as well as to reduce the amount of waste to be disposed of.

In this paper, the biochar produced by pyrolysis of beech has been investigated as a potential adsorbent for remediation of cadmium-contaminated groundwater.

So far, beech charcoal has been mainly used as a soil amendment and only few experiences have been reported about its use as an adsorbent medium. The present experimental activity started with a series of analyses to obtain the main physical-chemical characteristics of charcoal. Adsorption kinetics and isotherms through batch experiments were then determined. Furthermore, breakthrough curves were obtained through column experiments. The same tests were repeated using the beech charcoal after modification through the addition of specific bacterial strains able to produce a reactive monolayer biofilm. The results showed that bio-activated charcoal has enhanced adsorption capacity for cadmium-contaminated solution.

Therefore, charcoal and bio-activated charcoal may be considered valid options as adsorbents for the remediation of solution contaminated by cadmium.

Keywords: Beech charcoal, Biochar, Cadmium, Groundwater, Remediation.

1. Introduction

Cadmium (Cd) is introduced to the environment primarily as a residue of the activities of metalliferous industry. Like all heavy metals, it is non-degradable and persistent: therefore, it accumulates in the environment up to high concentrations. The main exposure pathway to human beings is through the food chain, following contact with contaminated waters.

It is mandatory to reduce Cd concentrations in water below hazard thresholds. Several technologies have been applied to this purpose. Adsorption has demonstrated to be highly efficient and easy to implement at full-scale. So far, activated carbons have represented the main adsorbent media; however, their cost of production is relatively high. So, there is the need to find out new adsorbent media offering high efficiency at a lower cost. Waste products from incineration or pyrolysis have proved to be potentially a valid alternative. Charcoal is obtained from pyrolysis of vegetable wastes. It is currently used as fertilizer, since it is able to improve agronomic characteristics of soil; it has been also demonstrated its ability of CO_2 sequestration in soil, thus contributing to the control of climate change (Novak *et al* 2010, He *et al*, 2017). Charcoal also possesses a high specific surface area which can be favorably exploited for the adsorption of high amounts of metals, thus reducing their mobility and bioavailability.

It has been recently observed that some bacterial strains can react with the metal ions and form functional groups, to protect the cytoplasm. Thus, bacteria generate a biofilm able to immobilize the metals (Harrison *et al*, 2005).

The aim of this work was to verify the ability of charcoal beech and of charcoal beech inoculated with bacterial strain 15A, to remove cadmium from contaminated waters. Experimental activities through batch and column tests were conducted with the purpose of characterizing the two types of vegetable charcoal and determining their adsorption kinetics and uptake capacity.

2. Materials and Methods

Charcoal used in the present study was produced from beech woody biomass collected in Monte Amiata (Italy). Prior to the experiments, it has been grounded to a 2 mm grain size. A fraction of charcoal (hereinafter referred to as biocharcoal) has been subjected to a sessile colonization by bacteria belonging to the 15A strain (*Pseudomonas fluorescens*) in the Laboratory of Microbiology of the Soil of the University of Tuscia (DAFNE, Italy). The strain was isolated and characterized as model PGPR (Plant Growth promoting Rhizobacteria) in previous experiments which documented its cadmium tolerance (Di Mattia & Paladini, 2015).

The following physical-chemical characteristics were determined on charcoal and biocharcoal: bulk density, porosity, field capacity and moisture content, ash content, pH and point of zero charge. Scanning Electron Microscope (SEM) was used to investigate the microscopic structure and for elemental analysis of charcoal before and after inoculation.

Batch experiments were carried out to determine the kinetic characteristics of the adsorption process of cadmium from the contaminated solution to charcoal and biocharcoal. Specifically, 20 g of charcoal were added to 250 ml of Cd-contaminated solution at 25 mg/l, and maintained in contact up to 96 h. Once the equilibrium time was determined, then the isotherms were calculated through batch tests by using different adsorbents dosages of charcoal and biocharcoal for the same Cd concentration (25 mg/l).

Batch tests were carried out at a constant temperature of 20 ± 0.1 ° C, using a jar-tester with a mixing speed fixed at 120 rpm. Cadmium concentration was measured by atomic absorption spectrophotometry (Perkin-Elmer model 3030B).

Cadmium removal percentage (R%), cadmium adsorbed per unit weight of adsorbent (mg/g) at time t (q_t) and at the equilibrium time (q_e), were calculated through the following equations (1, 2 and 3, respectively):

$$R\% = \frac{(C_0 - C_t)}{C_0} 100\% \qquad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (2)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (3)$$

where V is the volume of the aqueous solution (l), m is the mass of charcoal (g), C_0 is the initial concentration of cadmium in the aqueous phase (mg/l), C_t is cadmium concentration in the liquid phase at time t (mg/l), C_e is the equilibrium concentration of cadmium in the liquid phase (mg/l).

The following kinetic models were investigated and the best fitting one determined based on the value of R^2: zero, first, second, saturation, pseudo-first and pseudo-second.

Column tests were carried out by using two columns having the same geometrical dimensions, and filled with different media composition. The diameter and the length of the columns were 1.0 cm and 18.0 cm, respectively; columns were filled with an upper and bottom layer of sand and a 0.6 cm central layer of charcoal-sand and biocharcoal-sand mixed layers, respectively. The mass of charcoal and biocharcoal in the columns were 0.1 g. The influent solution (at 25 mg/l Cd), was applied to the top of the columns at 23 ml/h flow rate. By sampling the eluate from each column at hourly intervals, it was possible to determine the breakthrough curves of the charcoal - cadmium filled system.

3. Results and Discussion

3.1 Adsorbent characterization

Charcoal and biocharcoal differed only by microbiological characteristics, while had common physical and chemical properties. The values determined of these properties are shown in Table 1.

Table 1. Physical and chemical properties of charcoal and biocharcoal

Physical and chemical properties	**Unit**	**Values**
Bulk density, γ_s	g/cm^3	1.64
Specific weight, γ_d	g/cm^3	0.440
Field capacity, ω_c	g in 100 g	164.21
Porosity, n	%	73.13
Effective porosity, n_e	%	164.21
Carbon, (C)	%	94.14
Oxygen, (O)	%	4.65
Nitrogen, (N)	%	0.79
Potassium, (K)	%	0.42
Moisture content, ω	%	3.35
Ash content, cc	%	20.09
pH	-	9.8
pH_{PZC}	-	9.5

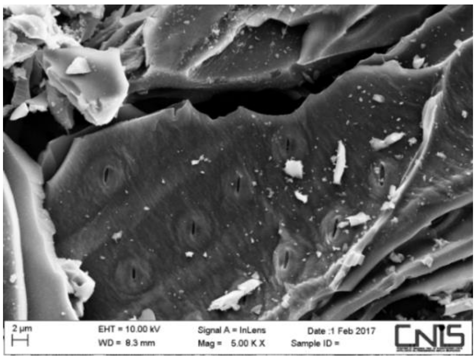

Fig. 1 Porous structure of charcoal

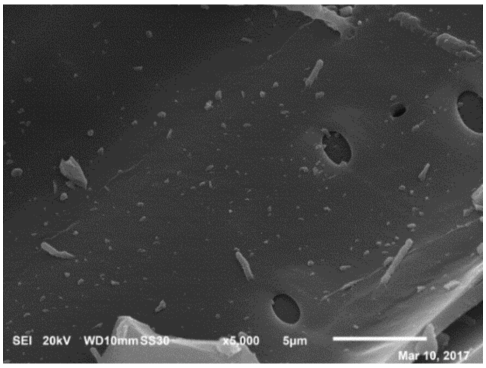

Fig. 2 Porous structures and bacteria of biocharcoal

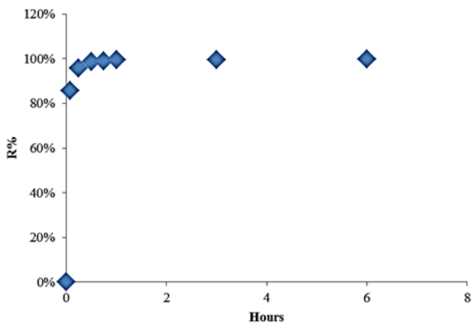

Fig. 3 Percentage of cadmium removal versus contact time with charcoal

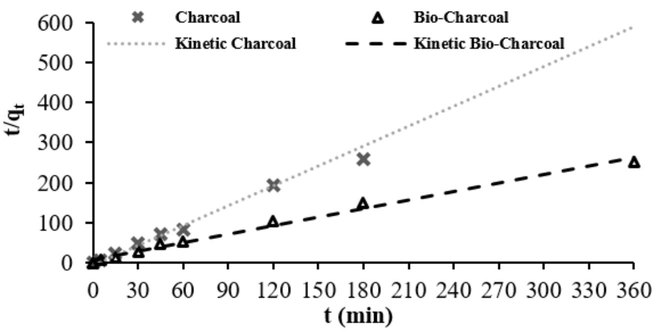

Fig. 4 Fitting of experimental points with the pseudo second order kinetic model

Charcoal characteristics were shown to be comparable to those of an activated coal. Porosity of the media and the presence of bacteria on biocharcoal are highlighted by SEM images reported in Figures 1 and 2. In the case of biocharcoal SEM images show that the surface is uniformly colonized by the bacterial strain without substantial modifications in the porous structure with respect to charcoal.

3.2 Batch tests

The equilibrium time of the adsorption process of cadmium on charcoal was found to be about t_e=6 h (Figure 3). The linearized form of different kinetic models was

used to find out the best fitting model. The pseudo second order proved to be the most suitable to describe the kinetic behavior of the two adsorbents, as shown in Figure 4The following equation was used to the purpose (Ho & McKay, 1999):
second order model. Values of the kinetic parameters of Equation (4) are presented in Table 2

$$\frac{t}{q_t} = \frac{1}{k_s\, q_e^2} + \frac{1}{q_e}\, t \qquad (4)$$

where k_s (g/mg min) is the constant rate of pseudo

Regarding adsorption process characteristics, the experimental data could be sufficiently well described by a Langmuir isotherm for both charcoal and bio charcoal, as shown in Figure 5. The isotherm parameters are listed in Table 3

Tab. 2 Pseudo-second-order kinetic parameters

Sample	**$q_{e,calc}$** (mg/g)	**k_s** (g/mg min)	**R^2**
Charcoal	0.6002	(-) 0.3954	0.9949
Biocharcoal	1.4092	0.0613	0.9883

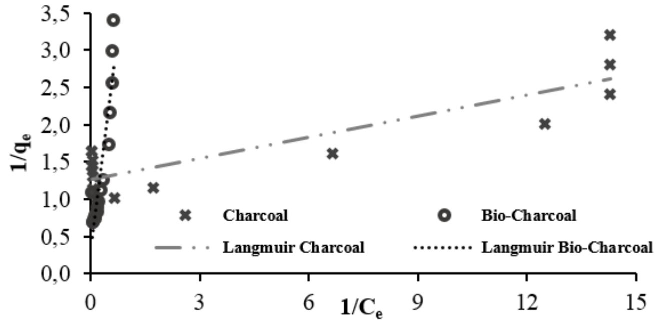

Fig. 5 Experimental isotherms points fitting by the Langmuir linearized model

Table 3. Langmuir isotherm constants

Sample	**q_{max} (mg/g)**	**b (l/mg)**	**R^2**
Charcoal	0.79	13.30	0.78
Biocharcoal	3.19	0.08	0.87

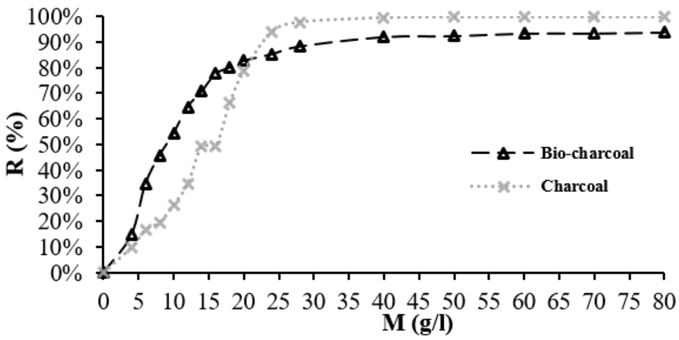

Fig. 6 Percentage of cadmium removal versus different charcoal and biocharcoal mass/volume

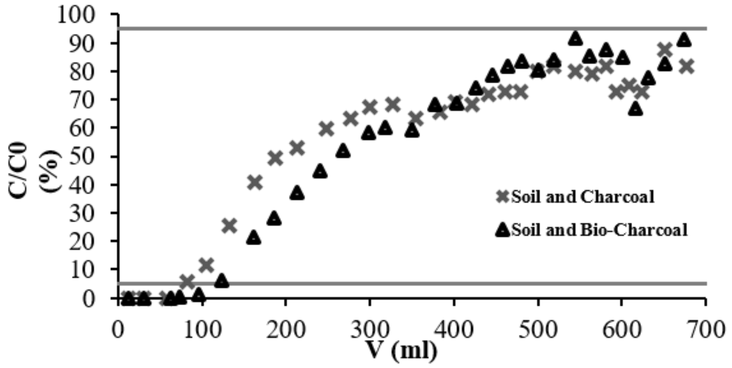

Fig. 7 Breakthrough curves

The ability of charcoal and biocharcoal to remove cadmium as a function of the adsorbent mass is shown in Figure 6. It can be noted that the maximum adsorption capacity is significantly enhanced by bio-activation of charcoal. It can be observed that biocharcoal, up to a dosage of 20 g/l, showed higher and more rapid removal; saturation was reached at about 15 and 25 g/l for biocharcoal and charcoal, respectively.

3.2 Column tests

Figure 7 shows breakthrough curves obtained by means of the column tests on charcoal and biocharcoal. It can be noted that biocharcoal reached the breakthrough conditions for treated volumes higher than soil and charcoal. None of the adsorbent media seems to have reached saturation at the end of the test, i.e. after about 700 volumes of contaminated solution fed to the columns. This highlights the high adsorption capacity of the media. Nonetheless, these experiments will be repeated for longer working times to assess the final efficiency and compare the adsorption capacity.

4 Conclusion

Charcoal and biocharcoal from pyrolysis of beech woody biomass showed to have high adsorption capacity of cadmium from liquid solution.

In the batch tests, removal rate of 25 mg/l Cd was very rapid, reaching equilibrium conditions in less than 6 h, for solid/liquid ratio of 80 g/l. The best kinetic model of the experimental data was found to be the pseudo-second order with the following values of the constants: $q_{e,calc}$=0.60 mg/g and k_s=0.395 g/mg min for charcoal, and $q_{e,calc}$= 1.40 mg/g and k_s=0.061 g/mg min for biocharcoal. Langmuir isotherm showed to best fitting the experimental data for both charcoal and biocharcoal. The maximum adsorption capacity of biocharcoal was found to be about 3 times higher than that of charcoal (0.8 and 3.2 mg/g, respectively). Biocharcoal showed higher adsorption capacity also in the column tests: the breakthrough conditions were reached later than in the case of charcoal.

Based on these first results it can be assessed that charcoal and biocharcoal can be used as effective adsorbents for Cd removal even at high metal concentration. Further experiments are required to better understand the behavior of both media.

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