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A novel treatment for Cd-contaminated solution through adsorption on beech charcoal: the effect of bioactivation

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ABSTRACT

In this paper, biochar produced by pyrolysis of beech has been investigated as a potential adsorbent for remediation of cadmium-contaminated groundwater. The experimental activity included determination of the main physical–chemical characteristics of charcoal and the study of the adsorption kinetics and isotherms through batch tests. Adsorption column tests were also carried out and breakthrough curves determined. The same tests were repeated using the beech charcoal after the addition of specific bacterial strains able to produce a reactive monolayer biofilm. The results showed that both charcoal and bioactivated charcoal (biocharcoal) are effective adsorbents for Cd at initial concentration of 25 mg/L, with the latter providing slightly better performance. The pseudo-second-order model provided the best fitting of the kinetic data of both media, with the following values of the constants: q_e = 0.600 mg/g and k_s = 0.395 g/mg min for charcoal, and q_e = 1.409 mg/g and k_s = 0.061 g/mg min for biocharcoal, where q_e and k_s stand for the equilibrium adsorption capacity and the constant rate, respectively. Among the isotherm models, the Langmuir equation provided the best fitting of the experimental data for both charcoal and biocharcoal. The maximum adsorption capacity of biocharcoal was found to be about four times higher than that of charcoal (3.2 and 0.8 mg/g, respectively).

Keywords: Adsorption; Biocharcoal; Cadmium; Charcoal; Groundwater

1. Introduction

Cadmium (Cd) is introduced to the environment primarily as a residue of the activities of metal factories. Like all heavy metals, it is nondegradable and persistent; therefore, it can accumulate in the environment giving rise to high concentrations. The main exposure pathway to human beings is through the food chain and contact with contaminated waters [1]. Cadmium, like other heavy metals, has harmful effects on human health and is particularly dangerous when it is present at high concentrations in soil and water [2–4]. Due to the associated risks, Cd concentrations in water must be reduced below hazard thresholds (5 µg/L in groundwater according to Italian legislative decree no. 152/06).

Looking at the specialized literature, the adsorption process appears to be the most widely applied to this purpose. Only few references can be found reporting the application of a different technology. For instance, microbial electrolysis cells were able to accomplish a rapid removal (50%–67% in 24 h), regardless of the electric condition; however, cadmium concentration in solution increased after the electric current dropped with depleted organic substrate under applied voltage conditions [5]. Polyelectrolyte enhanced ultrafiltration process for the removal of cadmium ions from aqueous solution using poly(ammonium acrylate) provided a retention of Cd^{2+} of about 0.99 in the range of 10^{-2} to 10^{-1} mol/L polyelectrolyte monomer concentration [6].

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These methods require more complex operating conditions that make them less economically feasible, especially in the developing countries. By contrast, adsorption has demonstrated to be highly efficient, easy to implement at full-scale and to require lower costs [7,8].

So far, activated carbons have been among the more widely used adsorbent media [9]; however, their cost of production is relatively high and some contaminants cannot be efficiently removed. Therefore, there is the need to find out new adsorbent media offering high efficiency at a lower cost [10]. Biosorbents have emerged among the most suitable adsorbents for the removal of Cd from aqueous solution [11]. Charcoal can be conveniently produced from selected forestry residues otherwise destined to disposal. Therefore, it offers both economic and environmental values and its use in place of industrial adsorbents contributes to the virtuous closure of the green waste cycle. So far, charcoal has been mainly used as a 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 [12,13]. Therefore, with the aim of improving physical and chemical conditions of soil in the production of charcoal, vegetable substances with a high lignin content are favored, which regulates the amount of carbon contained in the final product [14]. As far as the temperature is concerned, a slow pyrolysis at moderate temperatures (≤700°C) favors the production of biochar at the expense of other heat treatment products such as bio-oil or syngas [15]. Indeed, after pyrolysis, the original structure of the raw material, as its carbon skeleton, porosity, and minerals, is maintained in the biochar [16]. Many researchers also underline the strong influence that the process temperature has on the physical structure of the biochar, as the total surface and the distribution of the pore size [17,18]. The process temperature influences also the amount of volatile organic compounds released from the raw material [19] with consequent development of porosity and specific surface area [20]. Biochar is a carbon-rich material with oxygen functional groups and aromatic surfaces [21]. Owing to its high surface-to-volume ratio and strong affinity for nonpolar substances, it can be a potential sorbent for various environmental contaminants, among which heavy metals, thus reducing their mobility and bioavailability in the environment [11]. Indeed, charcoal has demonstrated to be able to retain contaminants, particularly metal ions, through different mechanisms such as precipitation, adsorption, and electrostatic interaction [22]. It also exhibits adsorbance activities on multi-elements contaminated soils [23]. Adsorption is strongly bound to porosity and is also strictly dependent on the pH value particularly in the case of heavy metals [2,24].

Spruce and beech are the most widespread wood types in Europe, and they are also very popular in the woodworking industry, leading to a large amount of waste sawdust [25]. The aim of this work was to verify the ability of beech charcoal and of beech charcoal inoculated with bacterial strain 15A, to remove cadmium from contaminated waters. It has been recently observed that some bacterial strains can react with metal ions and form functional groups, to protect the cytoplasm. Thus, bacteria generate a biofilm which is able to immobilize the metals [3]. Some works have examined the ability of biochar to mitigate pollution also synergistically with the bacteria, particularly in the removal of organic pollutants [26,27]. The novelty of this work is to use a beech charcoal for the treatment of cadmium contaminated solution and to compare its adsorption capacity after it has been "engineered" with the bacterial strains inoculated directly on the media. The beech charcoal used in the present study has a further added value, having obtained the PEFC (Programme for the Endorsement of Forest Certification schemes) certification as a vegetal coal.

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.

It is noteworthy that, as far as it is in the knowledge of the authors, this is the first application of beech charcoal as adsorbent media in column plant for cadmium removal from water.

2. Materials and methods

2.1. Charcoal and biocharcoal

Charcoal used in this was produced from beech woody biomass collected in Monte Amiata (Italy). Beech charcoal derived from mobile plant carbonization furnace (a prototype) able to provide PEFC-certified vegetal coal with high quality standard for food and environmental application (EN 1860-1/2/3). The average pyrolysis temperature is in the range 400°C–800°C. Since it is an in situ-treatment plant, the operating parameters can be adapted as a function of the characteristics of the input feed. The output is considered an eco-sustainable product because the pyrolysis process can be controlled with the aim to have a product low in pyrolignic acid content; furthermore, the low temperature reduces harmful emissions.

Before the experiments, charcoal was ground to obtain a 2 mm particle size. A fraction of charcoal (hereinafter referred to as biocharcoal) was subjected to a sessile colonization by cell population of *Pseudomonas fluorescens*, specifically the strain 15A, belonging to the bacterial collection of Soil Laboratory (DAFNE, University of Tuscia, Italy). The strain was isolated and characterized as model PGPR (Plant Growth Promoting Rhizobacteria) in previous experiments which documented its cadmium tolerance [28].

Biofilm formation was obtained with the growth control of the 15A strain on beech charcoal. The biofilm growth was induced through a batch incubation (96 h) using a rotary drum bioreactor system. Therefore, biocharcoal was produced by a sessile colonization of coal miming a natural process where microbial cells attach to the solid support.

The following physical–chemical characteristics were determined on charcoal and biocharcoal: bulk density, porosity, field capacity and moisture content, ash content, pH, and pH 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. Representative samples of charcoal and biocharcoal were used for the characterization.

2.2. Batch experiments

Batch experiments were carried out using the jar-tester apparatus to determine the kinetic characteristics of the adsorption process of cadmium onto charcoal and biocharcoal. The contaminated solution used was obtained by adding a known amount of a concentrated solution of cadmium chloride in ultrapure water, so as to obtain a final solution of 25 mg/L of cadmium. This value was selected, being very high and far above the limits imposed by the Italian legislation (5 μg/L for groundwater), in order to test the adsorption capacity of the media under severe conditions.

In the batch tests, 20 g of charcoal were added to 250 mL of Cd-contaminated solution at 25 mg/L, and maintained under mixing conditions for 96 h, taking samples at different times: particularly, at 5, 15, 30, 45, and 60 min in the first hour, and then at 2 h interval time until the end of the tests. Through the above batch tests it was possible to determine the equilibrium time of the adsorption process. The kinetics data were analyzed using the following models: zero, first, second, saturation, pseudo-first, and pseudo-second order. The best fitting model between the experimental and the modeled data was determined based on the value of R^2.

Further batch tests were conducted with the aim to obtain the isotherms, which present the amount of solute adsorbed per unit mass of adsorbent as a function of equilibrium concentration in the bulk solution. To this purpose, different adsorbents dosages of charcoal and biocharcoal were added to 250 mL solution at 25 mg/L Cd concentration and maintained under mixing conditions for a duration equal to the equilibrium time previously determined. At the end of the tests, liquid samples were collected and analyzed for the residual Cd concentration in the liquid solution. The equilibrium data obtained from these tests were fitted to the Freundlich and Langmuir isotherms. The best fitting model was determined based on the value of R^2.

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

Cadmium percentage removal ($R\%$), 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 Eqs. (1), (2), and (3), respectively, obtained through the mass balance of cadmium between the liquid and the solid phases [29]:

$$R\% = \frac{\left(C_0 - C_t\right)}{C_0} \times 100\% \tag{1}$$

$$q_t = \frac{\left(C_0 - C_t\right)V}{m} \tag{2}$$

$$q_e = \frac{\left(C_0 - C_e\right)V}{m} \tag{3}$$

where V is the volume of the aqueous solution (L), m is the mass of charcoal (g), C_0 (equal to 25 mg/L), C_t, and C_e indicate cadmium concentration in the liquid phase at time t = 0, t, and equilibrium, respectively (mg/L).

Batch experiments were conducted in duplicate and the results obtained averaged.

2.3. Column tests

Column tests were carried out on two clean glass columns having the same geometrical dimensions (1.0 cm diameter and 18.0 cm length), and containing charcoal and biocharcoal, respectively. Particularly, the columns were packed with an upper and bottom layers of sand (3 and 6.4 cm, respectively), a 6 cm central layer of mixed charcoal-sand or biocharcoal-sand, a 1 cm sand layer below, followed by a 0.6 cm layer of soil. Masses of charcoal and biocharcoal in the columns were both 0.1 g.

The columns were continuously fed in a down-flow mode using a peristaltic pump. The influent solution, at C_0 = 25 mg/L Cd, was applied to the top of the columns at a constant flow rate of 23 mL/h (corresponding to a surface loading rate, C_{is}, of 0.48 cm/min).

Effluent concentration, C, from each column was measured at hourly intervals. By plotting C/C_0 versus the feeding volume, V, it was possible to draw the breakthrough curves. The breakthrough and exhaustion conditions were considered to be achieved for $C/C_0 = 5\%$ and $C/C_0 = 95\%$, respectively.

3. Results and discussion

3.1. Adsorbent characterization

Characterization provided the main physical and chemical properties of charcoal and biocharcoal. The results obtained are listed in Table 1; since both media showed only differences in the microbiological content while the other parameters were very similar, table reports only one column of values.

Elemental analysis was obtained by the technical sheet of charcoal, while the other parameters were determined experimentally. Carbon and oxygen contents were similar to those reported in Ref. [20] for pyrolysis of beech at 700°C. With respect to the biochar used in Ref. [11], which was produced from *Ipomoea fistulosa*, charcoal and biocharcoal presented

Table 1
Physical and chemical properties of charcoal and biocharcoal (% on dry weight)

Physical and chemical properties	Values	Methods and instruments
Bulk density γ_s (g/cm^3)	1.64	[30,31]
Specific weight γ_d (g/cm^3)	0.440	[30,31]
Field capacity ω_c (g in 100 g)	164.21	[30,31]
Porosity n (%)	73.13	[30,31]
Effective porosity n_e (%)	164.21	[30,31]
Carbon C (%)	94.14	Zeiss Auriga
Oxygen O (%)	4.65	Zeiss Auriga
Nitrogen N (%)	0.79	Zeiss Auriga
Potassium K (%)	0.42	Zeiss Auriga
Moisture content ω (%)	3.35	[30,31]
Ash content cc (%)	20.09	[30,31]
pH	9.8	[30,31]
Point of zero charge pH_{PZC}	9.5	[32]

similar pH and moisture content, while differed for carbon and oxygen; in this study charcoal showed a higher value of carbon and a much lower content of oxygen.

Porosity of the media and the presence of bacteria on biocharcoal are highlighted by SEM images reported in Figs. 1 and 2, respectively. In the case of biocharcoal, SEM images show anchored cell in active growth; it can be also seen 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

Fig. 3 shows cadmium percentage removal versus time in the batch tests conducted with charcoal. This test was used to determine the minimum time for the adsorption process to reach equilibrium. The time-removal profile shows two phases: a rapid removal in the first hour, followed by a slower phase that reached equilibria in about 2 h. Negligible variations are observed afterwards. This result is consistent with the scientific literature; in Ref. [11] it is reported a similar profile of adsorption of Cd onto biochar from *I. fistulosa* pyrolyzed at 350°C and 400°C, although at a slower rate since equilibria was reached after 5 h.

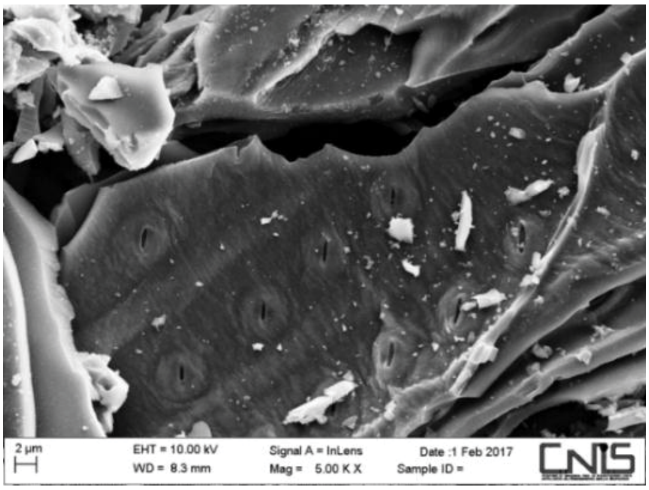

Fig. 1. Porous structure of charcoal.

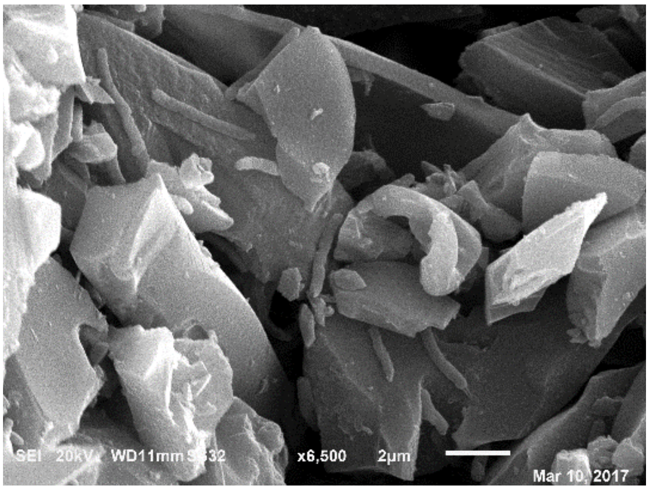

Fig. 2. Porous structure and bacteria of biocharcoal.

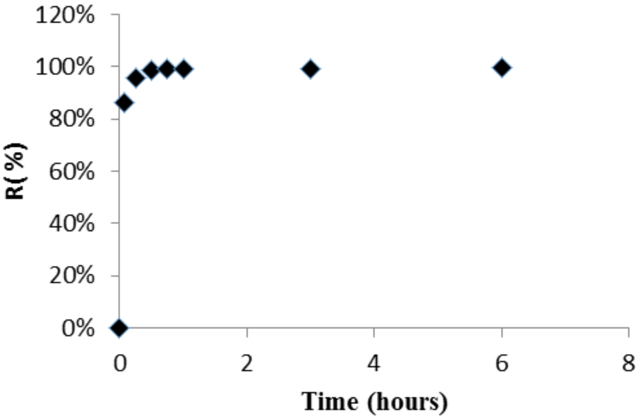

Fig. 3. Cadmium percentage removal versus contact time for charcoal.

The first phase could be attributed to rapid occupation of easily accessible external surface sorption sites while the slow phase could be related to the formation of inner layer complexes or to the saturation of sorption sites [11].

The linearized form of the equation of the different kinetic models was used to find out the best fitting between the experimental and the modeled data. The following equation [30] represents the linearized form of the pseudo-second-order model which provided the best agreement for both adsorbents (higher R^2 value):

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \tag{4}$$

In Eq. (4), q_e and q_t are the amounts of Cd adsorbed per unit of mass of biochar at equilibrium and at time t, respectively, and k_s is the rate constant of the pseudo-second-order adsorption. The plots of t/q_t versus t gave a straight line, as shown in Fig. 4; measurements of the slope and intercept of this line allowed to determine the value of the pseudo-second-order rate constants, which are shown in Table 2.

This table also indicates the value of $q_{e,\exp}$ which represents the amounts of Cd adsorbed per unit mass of adsorbents calculated experimentally at t = 120 min, assumed to be the

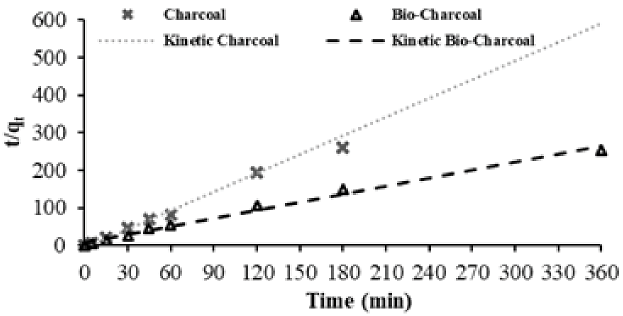

Fig. 4. Fitting of experimental data by the pseudo-second-order kinetic model.

Table 2
Pseudo-second-order kinetic parameters

	$q_{e,\exp}$ (mg/g)	q_e (mg/g)	k_s (g/mg min)	R^2
Charcoal	0.6000	0.6002	(–)0.3954	0.9949
Biocharcoal	1.2000	1.4092	0.0613	0.9883

equilibrium time. It can be noted that the values determined for charcoal and biocharcoal do not differ appreciably from the adsorption capacities predicted by the model (q_e).

Pseudo-second-order equation assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. The adsorption rate is related to the concentration of the activated sites on the surface of the adsorbent [30].

Comparison of the q_e values obtained for charcoal and biocharcoal highlights that bioactivation enhanced the adsorption capacity more than double times.

The adsorption isotherms were also studied. The linear form of the Freundlich and Langmuir equations was used to determine the model that best fitted the equilibrium data.

The Langmuir model [31], whose equation is shown as follows, provided a better agreement of the experimental data for both adsorbents (higher R^2):

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{b q_{\max} C_e} \tag{5}$$

In Eq. (5), $q_{\max}$ is the amount of solute adsorbed per unit mass of adsorbent required for monolayer coverage of the surface, also called monolayer capacity, and b is the Langmuir constant related to the affinity between the sorbent and sorbate, whereas q_e and C_e have the same meaning as previously reported. The plots of $1/q_e$ against $1/C_e$, as reported in Fig. 5, presented a straight line. Values of the maximum adsorption capacity, $q_{\max}$, and the constant b were obtained from the slope and intercept of the line and are shown in Table 3.

Langmuir model assumes a monolayer adsorption of solutes onto a surface comprised of a finite number of identical sites with homogeneous adsorption energy [31]. This means that once a molecule occupies a binding site, no further adsorption can happen at that site [31,32].

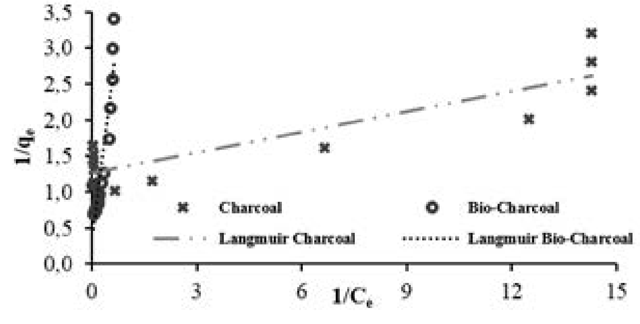

Fig. 5. Experimental isotherms points fitting by the Langmuir linearized equation.

Table 3
Langmuir isotherm constants

	$q_{\max}$ (mg/g)	b (L/mg)	R^2
Charcoal	0.79	13.30	0.78
Biocharcoal	3.19	0.08	0.87

Table 3 highlights that the agreement of the Langmuir equation with the experimental data in the case of charcoal was not as good as for biocharcoal; however, this model still provided a better fitting than Freundlich.

It can be noted in Fig. 5 that charcoal and biocharcoal showed a very different behavior; this was likely due to the presence of bacteria on the latter that modified its adsorption properties as highlighted by the wide difference in the values of the constants.

In terms of implementation, adsorbents with the highest possible $q_{\max}$ and a high value of b are the most desirable. Based on the data listed in Table 3, biocharcoal, having the highest value of $q_{\max}$, can be considered the preferable adsorbent in the present conditions.

The maximum adsorption capacity found for charcoal and biocharcoal are within the range of values reported by the literature [11] for different biochars for Cd removal from water. With respect to Ref. [20] where beech charcoal was also used, the initial Cd concentration in this study was higher (2.8 vs 0.1–1 mmol/L, respectively) as well as the maximal adsorbed amount from the Langmuir equation for biocharcoal (0.36 vs 0.06–0.10 mmol/g, respectively); charcoal provided a lower value of the adsorption capacity at equilibrium. The differences are likely due to the different operating conditions of the pyrolysis process which are known to affect the porosity and microstructure of the adsorbents [20].

The essential characteristic of the Langmuir isotherm can be evidenced by the dimensionless constant called equilibrium parameter, R_L, calculated according to the following Eq. (6):

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

where b is the Langmuir constant and C_0 is the initial Cd concentration.

R_L values indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$) [33,34]. In this study, R_L values were calculated to be above zero for both adsorbents (i.e., 0.00299 and 0.33 for charcoal and biocharcoal, respectively), although slightly, thus indicating that the adsorption process of Cd was always favorable, with biocharcoal being preferable.

The ability of charcoal and biocharcoal to remove cadmium as a function of the adsorbent mass is shown in Fig. 6. It can be noted that the rate of adsorption was significantly enhanced by bio-activation of charcoal. Saturation of the active sites on charcoal occurred more rapidly; however, the highest removal was slightly above that observed for biocharcoal.

Fig. 6 shows that by increasing adsorbent mass up to about 30 g/L, the removal percentage enhanced almost linearly;

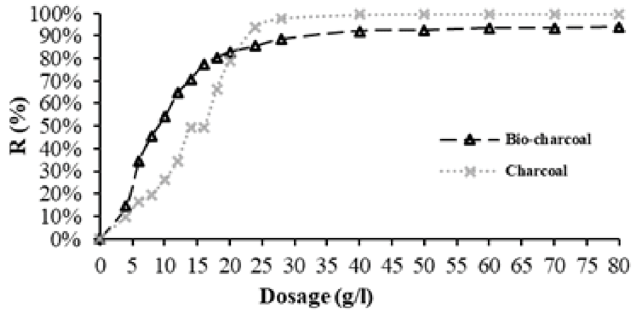

Fig. 6. Percentage of cadmium removal versus different charcoal and biocharcoal dosage.

above this dosage, further increases did not determine an appreciable improvement of R(%), which remained at approximately 90% and close to 100% for biocharcoal and charcoal, respectively.

With respect to the existing Italian legislation (which sets Cd limit in groundwater at 5 μg/L), these results indicate that using a dosage of 30 g/L of charcoal would be able to reduce contamination below the limits set for groundwater if the initial concentration of cadmium did not exceed 50 μg/L.

3.3. Column tests

Fig. 7 shows breakthrough curves obtained by means of the column tests conducted with charcoal and biocharcoal mixed with soil.

It can be noted that with respect to the column filled with charcoal, in the case of biocharcoal the breakthrough condition (i.e., $C/C_0 = 5\%$) was reached for higher values of the liquid volume, V (130 vs 80 mL, respectively); furthermore, after breakthrough, effluent concentration increased more slowly. After the volume, V, exceeded 400 mL, behavior of the media became approximately the same; it seems that at this point contribution of bioactivation had been used up. None of the adsorbent media reached the exhaustion condition (i.e., $C/C_0 = 95\%$) at the end of the test, that is, after about 700 mL volume of contaminated solution fed to the columns. This highlights the high adsorption capacity of both media. Nonetheless, these experiments will be repeated for longer working times to assess the final efficiency and compare their adsorption capacity.

None reference could be found in the specialized literature on the application of beech charcoal as adsorbent media in column plant for cadmium removal from water. Therefore, these data could not be evaluated in comparison with other experimental studies.

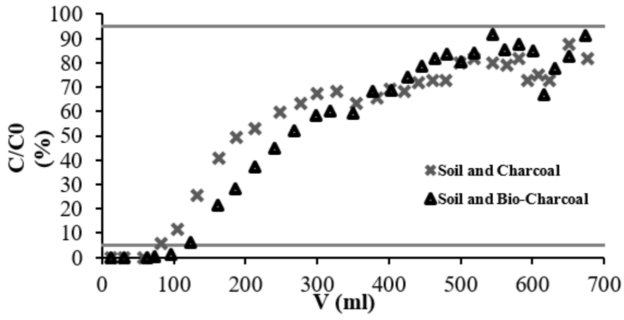

Fig. 7. Breakthrough curves.

4. Conclusions

This study shows the preliminary results of the application of charcoal and bio-activated charcoal from pyrolysis of beech woody biomass to the adsorption of cadmium from water.

Both media performed very satisfactorily, although biocharcoal showed a slightly higher adsorption capacity. In the batch tests, removal rate of 25 mg/L Cd was very rapid, reaching equilibrium conditions in about 2 h, for solid/liquid ratio of 80 g/L. The best fitting kinetic model of the experimental data was found to be the pseudo-second order with the following values of the constants: $q_e = 0.600$ mg/g and $k_s = -0.395$ g/mg min for charcoal, and $q_e = 1.409$ mg/g and $k_s = 0.061$ g/mg min for biocharcoal.

Langmuir isotherm provided the best fitting of the equilibrium data for both charcoal and biocharcoal. The maximum adsorption capacity of biocharcoal was found to be about four times higher than that of charcoal (3.2 and 0.8 mg/g, respectively).

Biocharcoal showed a higher adsorption capacity also when it was used as filling media of the column plant; the breakthrough condition was 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 from water even at high metal concentration. This would allow to reduce the environmental impact of the industrial production of commercial adsorbents; furthermore, residues from pyrolysis would find a new application in place of being disposed of, thus fulfilling the aims of the circular economy.

Further experiments are required to better understand the behavior of both media and to assess their final removal capability.

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