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# Potential Use of Biochar from Various Waste Biomass as Biosorbent in Co(II) Removal Processes

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**Abstract:** The removal of Co(II) ions from aqueous media was done using three types of biochars obtained from algae waste biomass, mustard waste biomass, and soy waste biomass. The biochar samples were obtained by pyrolysis of waste biomass resulted from biofuels production, at relative low temperature (600–650 °C), and this procedure can be considered a suitable alternative to reduce the volume of such waste. FTIR spectra recorded for each type of biochar reveal the presence of several functional groups that can be used as binding sites for Co(II) retention. The batch biosorption experiments were performed as a function of initial Co(II) ions concentration and contact time, at constant solution pH (5.0), sorbent dose (8.0 g/L), and room temperature (25 ± 1 °C). The sorption experiments showed that the Co(II) ions retention reaches the equilibrium in maximum 60 min, and the maximum sorption capacity follows the order: Mustard biochar (MBC—24.21 mg/g) < soy biochar (SBC—19.61 mg/g) < algae biochar (ABC—11.90 mg/g). The modeling of experimental data proves that the retention of Co(II) ions from aqueous solution occurs through electrostatic interactions, and that the sorption process takes place until a monolayer coverage is formed on the outer surface of the biochar. This information is very useful in the design of a suitable desorption system. The desorption results showed that by treating the biochar samples loaded with Co(II) ions with 0.1 mol/L HNO<sub>3</sub> solution, over 92% of Co(II) ions are desorbed and can be recovered, and the biochar samples can be used in at least three sorption/desorption cycles. All the experimental observations sustain the potential use of biochar obtained from different types of waste biomass as a promising alternative sorbent for the removal of Co(II) ions from aqueous media.

**Keywords:** biochar; sorption; Co(II) ions; waste biomass; aqueous media

## 1. Introduction

All over the world, environmental pollution with heavy metals is a serious and real issue of major importance in everyday life. This is because increased quantities of heavy metals are discharged into the environment, and due to their toxicity, persistency and accumulation tendency have become

an important factor in the degradation of ecosystem quality [1]. The main source of environmental pollution with heavy metal ions is industrial activity. The development of industrial activities has led to increased emissions of heavy metals into the environment, with negative consequences for soils, plants, rivers, and underground waters [2–4]. One such example is cobalt, which is known as an element of great importance in many industrial sectors, such as, petrochemistry, cobalt-bearing mineral mining, smelting industry, nuclear industry, etc. [5,6]. All these industrial activities generate large volumes of wastewater with high concentration of Co(II) ions, which must be properly treated before their discharge into the environment. Although it is not considered a toxic heavy metal, the presence of high concentrations of cobalt has particularly serious human health consequences [7], and this is why the maximum admissible concentration at industrial wastewater discharge in the environment should be less than 0.05 mg/L [8]. Therefore, most industrial wastewater should be treated appropriately to reduce the Co(II) concentration before it is discharge into the aquatic environment.

Several physical and chemical processes are currently available on the industrial scale to remove Co(II) ions from wastewater, such as, chemical or electrochemical precipitation, coagulation, flocculation, reverse osmosis, ion exchange or adsorption [9–11]. Unfortunately, these methods are characterized by high energy consumption, low selectivity, moderate efficiency, generation of large amounts of secondary sludge, which is also a source of environmental pollution, etc. [1]. All these disadvantages significantly increase the cost of wastewater treatment systems.

Sorption is considered a cheap and easy adaptable alternative that can be used to efficiently remove heavy metal ions from aqueous media, under different experimental conditions [11–13]. In general, sorption involves the retention of metal ions from aqueous media on the surface of a solid material through specific interactions [14]. Therefore, the potential use of the sorption processes in the treatment of industrial effluents containing heavy metal ions, is mainly determined by the cost and efficiency of solid material used as sorbent.

Many types of natural materials or agricultural and (or) organic industrial waste [14–16] have been used for the removal of Co(II) ions from aqueous solution, but unfortunately none of these have been applied so far to industrial wastewater treatment. One possible explanation might be that most of these materials have moderate sorption capacities, which makes the treatment of industrial effluents requiring a large amount of such sorbent materials [17]. This is why many studies in the literature have tested the functionalization of low-cost materials in order to improve their performance in removing heavy metal ions from aqueous media [18,19]. However, such functionalization procedures can significantly increase the preparation cost of adsorbent materials, which is not desirable for economic reasons.

More attractive seems to be the transformation of such organic waste in biochar, by pyrolytic conversion under oxygen-limited conditions at a specific temperature [20–22]. Pyrolytic conversion is a simple process that is very useful in environmental protection because it allows significant reduction in the amount of industrial or domestic waste that otherwise should be stored. Moreover, once the capture methods of the combustion gases have become more efficient, the pyrolytic conversion processes have become more environmentally friendly [22].

Besides the use to improve soil quality, in the last few years, numerous studies have been focused on the potential applications of biochar in retention of various inorganic or organic contaminants from aqueous media [22,23]. Thus, a wide variety of biomass wastes (ranging from different types of agricultural waste or wood processing to those from the food industry) [20,23,24] were used as feedstocks for biochars preparation, and the obtained biochars were tested as adsorbents for the removal of different pollutants, including heavy metal ions [25].

The encouraging results obtained in the adsorption processes of heavy metal ions from aqueous media using biochars as adsorbents is mainly related to the presence of some carboxyl, hydroxyl, and amine groups on biochars surface and their high specific surface area [26]. These characteristics make the biochars have good efficiency to remove heavy metal ions from aqueous media, sometimes superior to activated carbon [27].

In this study, three types of biochars, obtained from algae waste biomass (ABC), mustard waste biomass (MBC), and soy waste biomass (SBC), were used as sorbents for the removal of Co(II) ions from aqueous media. The biochar samples were obtained by pyrolysis of waste biomass resulted from biofuels production, in specific experimental conditions, and their sorption performances were evaluated as the function of initial Co(II) ions concentration and contact time. The isotherm and kinetics modeling of experimental results have allowed a quantitative description of the adsorption process, while desorption studies have highlighted the potential applicability of these adsorbents in the wastewater treatment processes. Transforming such waste biomass in biochar, which is then used as a sorbent to remove metal ions from aqueous media, could be a viable alternative for their valorization in agreement with the principles of circular economy.

## 2. Materials and Methods

### 2.1. Preparation of Biochar Samples

The raw materials used to obtain the biochar samples were waste biomass resulted after oil extraction, by solvent extraction technique (Soxhlet extractor, n-hexane, 30 h). At the end of the extraction step, algae waste biomass, mustard waste biomass, and soy waste biomass were dried in air (to remove the traces of organic solvent) and pyrolyzed at 600 °C or 650 °C, for 6 h, under oxygen-limited conditions. After cooling, the biochar samples obtained from algae waste biomass (ABC), mustard waste biomass (MBC), and soy waste biomass (SBC) were mortared for uniformity and were kept in desiccators for later use.

### 2.2. Characterization Methods

A Mettler 851 Derivatograph, (Mettler Toledo AG, Greifensee, Switzerland) was used to examine the thermal characteristics of biomass waste used to obtain biochar samples for this study. The biomass waste was heated to 900 °C at a rate of 10 °C/min in air, and the obtained derivatograms were then used to select the most appropriate temperature for the pyrolysis of each type of waste biomass. (Figure S1-Supplementary Materials).

The porosity parameters (pores volume, specific surface area) of the biochar samples were calculated from Brunauer–Emmett–Teller BET adsorption/desorption curves, recorded in nitrogen atmosphere. The superficial morphology and functional groups of each biochar sample were analyzed by scanning electron microscopy (SEM-Hitach S 3000N, Hitach, Germany) and FTIR spectrometry (Bio-Rad Spectrometers (Perkin Elmer, Waltham, MA, USA), spectral domain = 400–4000  $\text{cm}^{-1}$ , resolution = 4  $\text{cm}^{-1}$ , KBr pellet technique).

### 2.3. Chemical Reagents

Co(II) stock solution (600 mg/L) was prepared by dissolving 1.84 g of  $\text{Co}(\text{NO}_3)_2$  (purchased from Chemical Company, Iași, Romania) in 1 L of distilled water. The working solutions for each experiment were obtained from stock solution, by dilution with distilled water. A solution of 0.1 M  $\text{HNO}_3$  was used for the correction of the initial solution pH, and as a desorption agent. All the chemical reagents were analytical grade and were used as received.

### 2.4. Sorption/Desorption Experiments

The sorption performances of the studied biochars in the removal of Co(II) ions from aqueous media were examined as a function of initial Co(II) ions concentration and contact time, in batch experiments. In all experiments, 0.2 g of each biochar (ABC, MCB, and SBC) was mixed with 25 mL of Co(II) ions solution (12–240 mg/L), at pH 5.0 and room temperature ( $25 \pm 1$  °C). These experimental conditions have previously been established as being optimal [28]. To ensure the sorption process reaches equilibrium, all samples were intermittent stirred for 24 h. Then the two phases were separated through 0.45 mm filter paper, and the Co(II) ions concentration was determined with Digital

Spectrophotometer S 104D (JKI, Shanghai, China) (rubeanic acid,  $\lambda = 450$  nm, 1 cm glass cell, against distilled water). Kinetics experiments were performed in the same optimal conditions, using 25 mL of Co(II) ion solution with initial concentration of 48 mg/L and 0.2 g of from each biochar (ABC, MBC, and SBC), but the mixing interval was varied between 5 and 180 min. After filtration, Co(II) ions concentration in solution was analyzed using the spectrophotometric method described above.

The sorption capacity,  $q$  (mg/g) and the sorption percentage were calculated using the relations:

$$q = \frac{(c_0 - c) \cdot V}{m} \quad (1)$$

$$\% \text{Sorption} = \frac{c_0 - c}{c_0} \cdot 100 \quad (2)$$

where  $c_0$  and  $c$  are the initial and equilibrium Co(II) ions concentration in solution (mg/g);  $V$  is volume of solution (L); and  $m$  is the mass of biochar samples used in experiments (g).

In desorption studies, 0.2 g of each biochar sample loaded with a Co(II) ions was treated with 5 mL of 0.1 M  $\text{HNO}_3$  solution, mixed for 3 h and filtered. The obtained solution was used for Co(II) ions analysis. The efficiency of Co(II) ions desorption (%Desorption) from biochar samples was evaluated on the basis of following equation:

$$\% \text{Desorption} = \frac{c_d}{q \cdot m} \cdot 100 \quad (3)$$

where  $c_d$  is the concentration of Co(II) ions desorbed from biochar samples (mg/L);  $q$  is the sorption capacity (mg/g); and  $m$  is the amount of biochar used in desorption experiments.

All the experiments were performed in triplicate and the standard deviation calculated in each case from ANOVA statistical analysis, was lower than 3%.

## 2.5. Isotherm and Kinetics Models

The mathematical description of the sorption process of Co(II) ions on each type of biochar (ABC, MBC, and SBC) was done using different isotherm and kinetics models. Two isotherm models (Langmuir and Freundlich models) and three kinetics models (pseudo-first order, pseudo-second order, and intra-particle diffusion models) were used for the modeling of the experimental data.

If the Langmuir isotherm model (Equation (4)) assumes that metal ions retention occurs according to a standardized monolayer process, the Freundlich isotherm model (Equation (5)) considers that the sorption process takes place in multiple layers, until the sorbent saturation is reached [29,30].

$$\text{Langmuir model : } \frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} \cdot K_L} \cdot \frac{1}{c} \quad (4)$$

$$\text{Freundlich model : } \lg q = \lg K_F + \frac{1}{n} \cdot \lg c \quad (5)$$

where  $q$  is sorption capacity, (mg/g);  $q_{\max}$  is maximum sorption capacity required for the formation of monolayer, (mg/g);  $K_L$  is Langmuir constant, (g/L);  $K_F$  and  $n$  are Freundlich model parameters;  $c$  is the metal ions concentration at equilibrium, (mg/L).

The isotherm model that best describes the experimental data was selected based on the regression coefficients ( $R^2$ ), calculated from the statistical analysis.

Kinetics models are generally used to examine the mechanism of the sorption process [27]. Thus, pseudo-first order kinetic model (Equation (6)), pseudo-second order kinetic model (Equation (7)) and intra-particle diffusion model (Equation (8)) were used in this study to calculate the kinetics parameters of Co(II) ions sorption on each type of biochar [31,32].

$$\text{Pseudo - first order kinetic model : } \lg(q_e - q_t) = \lg q_e - \frac{k_1 \cdot t}{2.303} \quad (6)$$

$$\text{Pseudo – second kinetic model : } \frac{1}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (7)$$

$$\text{Intra – particle diffusion model : } q_t = k_{diff} \cdot t^{1/2} + c \quad (8)$$

where  $q_e$  and  $q_t$  are the sorption capacity at equilibrium and at time  $t$ , (mg/g);  $k_1$  is the rate constant of pseudo-first order kinetic model, (1/min);  $k_2$  is the rate constant of pseudo-second order kinetic model, (g/mg min);  $k_{diff}$  is the rate constant of intra-particle diffusion model, (mg/g min<sup>1/2</sup>); and  $c$  is concentration of Co(II) ions in aqueous solution at equilibrium, (mg/L).

And in the case of kinetics modeling, the best model that fits the experimental data was selected taking into account the values of correlation coefficients ( $R^2$ ), obtained from statistical analysis.

### 3. Results and Discussion

#### 3.1. Characterization of the Biochar Samples

One of the major advantages of transforming the waste biomass in biochar is the significant reduction of waste quantities, and the use of obtained biochar as adsorbent material. If this transformation is accompanied by an efficient capture of the combustion gases, then this process can be considered a clean one, and could be a solution for waste management [23,33].

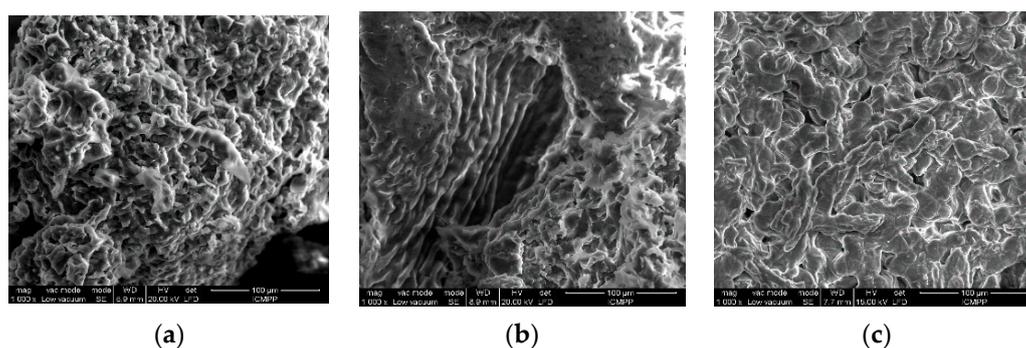
In this study, three types of biomass waste (algae biomass waste (ABC), mustard biomass waste (MBC), and soy biomass waste (SBC)) resulted after oil extraction, were pyrolyzed under oxygen-limited conditions at specific temperature, and some characteristics of the pyrolysis process together with the porosity parameters of the obtained biochars are summarized in Table 1.

**Table 1.** Characteristics of pyrolysis process and porosity parameters of the obtained biochars.

Biomass Waste	Algae Waste Biomass	Mustard Waste Biomass	Soy Waste Biomass
Pyrolysis temperature, °C	600	650	650
Mass decrease, %	40.08	53.17	49.82
Pores volume, m <sup>2</sup> /g	0.31	0.40	0.37
BET surface area, m <sup>2</sup> /g	289.70	354.07	329.93

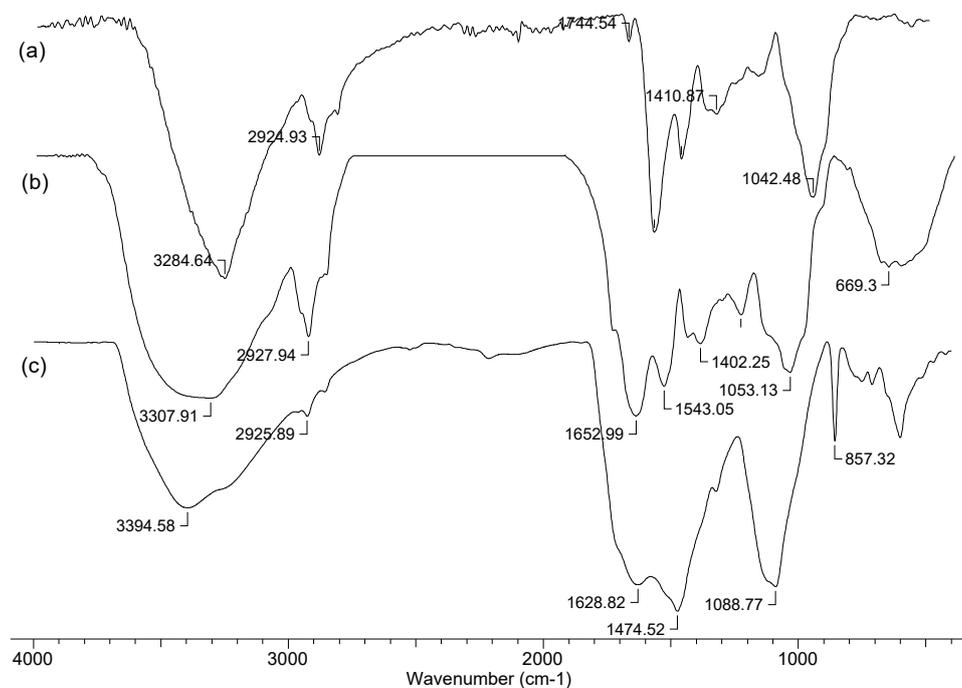
The pyrolysis temperature was selected for each type of waste biomass from derivatograms (Figure S1—Supplementary Materials), to allow burning of biomass waste without being completely transformed to ash. Thus, it can be observed that mustard waste biomass and soy waste biomass required a high pyrolysis temperature (650 °C) compared with algae waste biomass (600 °C). This can be explained if the biomass of algae waste is considered to have a low content of cellulose and hemicellulose [34], and therefore the temperature required to carbonize the protein molecules in its structure is lower. However, it should be noted that in the mentioned pyrolysis conditions, the mass decrease is higher than 40% and the order is: Mustard waste biomass > soy waste biomass > algae waste biomass.

Besides high surface area (see Table 1), SEM images (Figure 1) demonstrate that all types of biochar have porous and permeable structure, different sizes, and opening shapes, and these characteristics are very important in the removal processes of metal ions from aqueous media.



**Figure 1.** SEM images of mustard biochar (MBC) (a), soy biochar (SBC) (b), and algae biochar (ABC) (c).

However, the biosorptive performances of the biochars are not only dependent on their surface area and porosity, but also on the number and nature of superficial functional groups. From this point of view, FTIR spectra are the most useful tools that can be used to characterize the nature of functional groups from the surface of the biochars [35,36]. In Figure 2, FTIR spectra for the three types of biochars used in this study are shown.



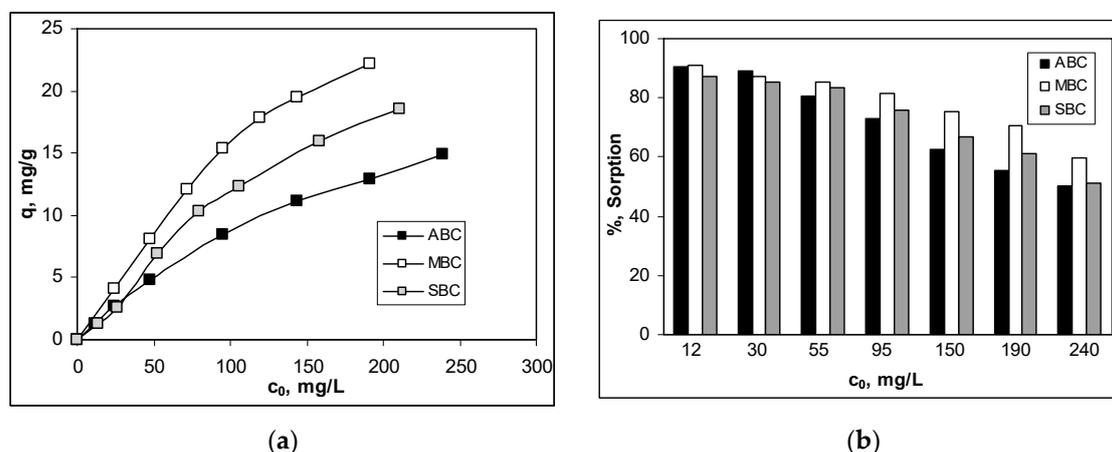
**Figure 2.** FTIR spectra of MBC (a), SBC (b), and ABC (c).

In all the biochars samples, the broad band at 3300–3400 cm<sup>-1</sup> indicates the presence of hydroxyl groups (from alcohols or phenols) and N–H bonds from aliphatic amines. The bands at 1600–1700 cm<sup>-1</sup> can be attributed to C=O bonds from aldehydes, ketones, or carboxylic acids, while the strong bands from 1000–1100 cm<sup>-1</sup> correspond to axial deformation of C–O bonds from oxygenated compounds (ethers, esthers, etc.). Also, the bands from 1930 cm<sup>-1</sup> denoted the presence of methylene groups from aliphatic radical. The low intensity of these bands indicates that most of the aliphatic chains from all types of waste biomass have been decomposed during of pyrolysis process.

All these observations suggest that all types of biochars have different kinds of functional groups on their surface, and these groups can represent the binding sites for Co(II) ions from aqueous media. The presence of functional groups on the biochars surface, together with their porous structure, are arguments which highlight the possible use of these materials as adsorbents in the removal processes of metal ions.

### 3.2. Effect of Initial Co(II) Concentration and Isotherms Modeling

Initial metal ions concentration is one the most important factors which influences the efficiency of the sorption process. The experimental results indicate that Co(II) ions sorption on the three types of biochars (Figure 3) increase with the increase of initial metal ions concentration, and the saturation is not obtained even at the highest initial Co(II) ions concentration (240 mg/L).



**Figure 3.** Effect of initial Co(II) ions concentration on sorption capacity (a) and sorption efficiency (b) on the three types of biochars (Experimental conditions: Initial pH = 5.0; biochar dose = 8 g/L; contact time = 24 h; temperature = 25 °C).

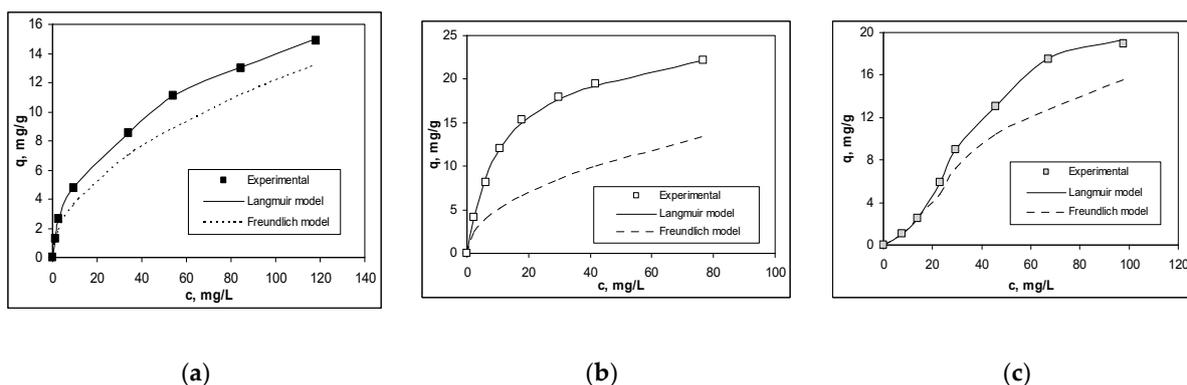
In the low initial concentration range (up to 55 mg Co(II)/L), the three biochars have a similar efficiency in the sorption process, and the values of the removal percentage are higher than 85%, in all the cases. When the initial Co(II) ions concentration increases, the differences between sorption capacities obtained for each type of biochar are more significant, and follow the order: ABC < SBC < MBC (Figure 3a). The better sorption performances of MBC for Co(II) ions from aqueous media can also be seen from the variation of the sorption percentages (Figure 3b), which decreases from 91% to 60%, compared with SBC (from 89% to 52%) and ABC (from 90% to 50%), respectively. Decreasing the sorption percentages by increasing the initial Co(II) ions concentration is a common variation, and indicates that the number of binding sites on the surface of the biochars, are limited [17,37]. However, the different behavior of the three types of biochars in Co(II) ions removal is probably determined by their different structural characteristics. Thus, as can be seen from FTIR spectra (Figure 2), MBC and SBC have more and diverse functional groups in their structure, compared with ABC. On the other hand, MBC has a higher specific surface area than SBC and ABC (Table 1). Consequently, the concerted action of these two characteristics (high surface area and numerous and diverse functional groups) makes MBC a more efficient sorbent for removal of Co(II) ions from aqueous media.

To quantify the sorption process of Co(II) ions on the three types of biochars (ABC, MBC, and SBC), the experimental sorption isotherms were analyzed using the Langmuir and Freundlich models. Figure 4 shows the experimental data and the fitted isotherms, and the calculated parameters for each isotherm model are given in Table 2.

As can be seen from Figure 4, the Langmuir isotherm model fits better with the experimental results obtained at Co(II) ions sorption on the biochars, than the Freundlich model. This observation is also supported by the  $R^2$  values presented in Table 2, which indicate the applicability of the Langmuir equation in describing the studied sorption processes.

**Table 2.** Isotherm models parameters for the sorption of Co(II) ions on the three types of biochars.

Biochar		ABC	MBC	SBC
Langmuir model	$R^2$	0.9924	0.9975	0.9983
	$q_{max}$ , mg/g	11.9047	24.2131	19.6078
	$K_L$ , g/L	0.1034	0.0921	0.0983
Freundlich model	$R^2$	0.9872	0.9465	0.9524
	$1/n$	0.5104	0.4766	0.5231
	$K_F$ , g/L	1.1559	1.6932	1.4132

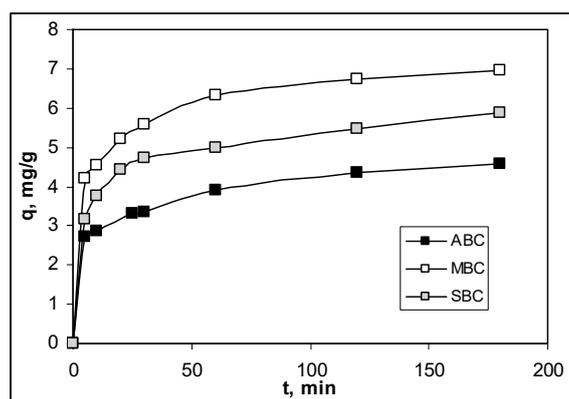
**Figure 4.** Isotherm modeling of Co(II) ions sorption on (a): ABC, (b): MBC, and (c) SBC (Experimental conditions: Initial pH = 5.0; 8.0 g biochar/L; contact time = 24 h; 25 °C).

Therefore, it can be said that the sorption of Co(II) ions from aqueous media takes place on the surface of the biochars until a monolayer coverage is formed, after which the driving force of the sorption process decreases drastically, and the equilibrium is reached. The amount of Co(II) ions required to obtain the monolayer coverage depends on the type of biochar, and the values of maximum sorption capacity ( $q_{max}$ , mg/g), calculated from the Langmuir model (see Table 2) follow the order: MBC > SBC > ABC.

The different values of maximum sorption capacity indicate that in the sorption process the structural characteristics of biochar play an important role. Thus, MBC, which has a high specific surface area (see Table 1, Figure 1) and high number of superficial functional groups (see Figure 2) can retain larger amounts of Co(II) ions from aqueous solution, and can be considered more effective (2.03 times) compared with SBC (1.64 times), or ABC. This comparison demonstrates that the biochars can be considered as potential sorbents for Co(II) ions, but their effectiveness depends on the structural particularities of the raw biomass and the preparation conditions.

### 3.3. Effect of Contact Time and Kinetics Modeling

The effect of contact time and sorption kinetics has been studied to highlight the dynamics of the Co(II) sorption process on the three types of biochars. Figure 5 shows the sorption of Co(II) ions by each type of biochar (ABC, MBC, and SBC), at different contact times (5–180 min).



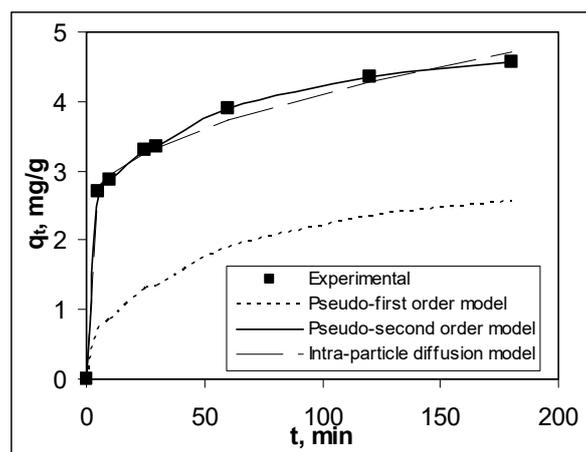
**Figure 5.** Effect of contact time on Co(II) sorption on the three types of biochars. (Experimental conditions: Initial pH = 5.0; biochar dose = 8 g/L;  $c_0 = 72$  mg Co(II)/L; temperature = 25 °C).

The sorption efficiency increases with contact time increase up to 60 min (Figure 5) for all three types of biochars, after that the amount of Co(II) ions retained on the biochars remains almost constant. The fast sorption of Co(II) ions at the initial contact time is determined by the abundance of functional groups on the biochars surface, which is the driving forces of the sorption process. When the superficial functional groups are occupied, the retention of Co(II) ions becomes more slower, because the Co(II) ions have to diffuse inside of the biochars pores to find free functional groups to bind [32,37]. However, it should be noted that the contact time required to achieve the equilibrium does not depend on the type of biochar, and the optimal value was selected as 60 min for all the sorbent materials.

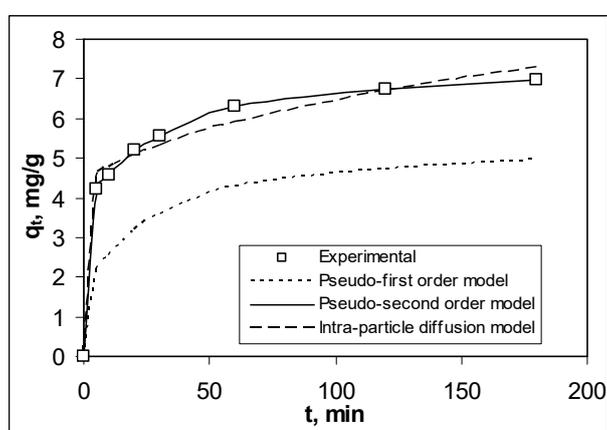
The kinetics modeling of experimental data has been done to better understand the dynamics of Co(II) sorption processes on these types of biochars and to obtain information on the rate of sorption. As it was mentioned above, three kinetics models (pseudo-first order, pseudo-second order, and intra-particle diffusion models) were used for this, and the overlapping of the experimental data with the kinetic curves obtained by modeling are presented in Figure 6. Also, the kinetic parameters calculated from mathematical equations of each kinetic model are summarized in Table 3.

As can be seen from Figure 6 and Table 3, the pseudo-second order model better represents the sorption kinetics of Co(II) ions on all types of biochars (ABC, MBC, and SBC, respectively), because the correlation coefficients have the highest values ( $R^2 > 0.999$ ), and the sorption capacities at equilibrium calculated from this model ( $q_e$ , mg/g) are very close to those obtained experimentally ( $q_{e,exp}$ , mg/g).

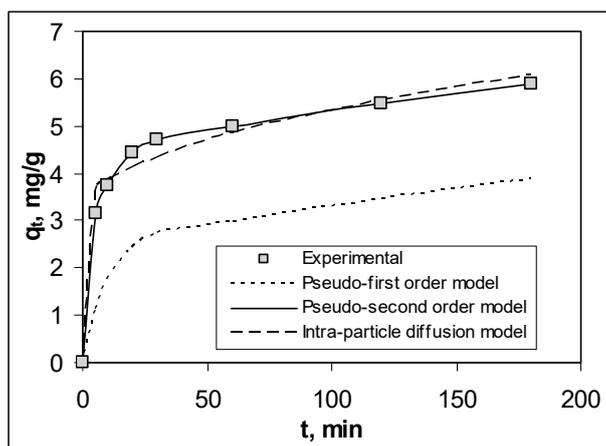
This indicates that the Co(II) sorption process involves chemical interactions [32] between metal ions from aqueous media and superficial functional groups of biochars, and the retention of Co(II) ions required two binding sites, which must have a proper geometric orientation. In addition, the rate constant of pseudo-second order kinetic model ( $k_2$ , g/mg min) increases in the order: MBC > SBC > ABC, suggesting that MBC has the most functional groups available for metal ion interactions, and therefore the retention of Co(II) ions is made the easiest. This observation is supported by the FTIR spectra (Figure 2) which have indicated since the beginning, that MBC has more superficial functional groups than SBC and ABC.



(a)



(b)



(c)

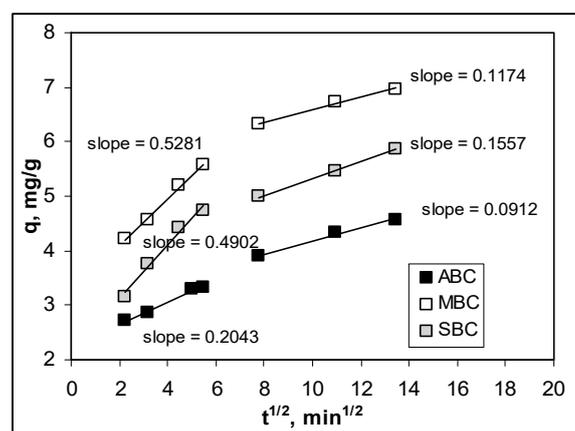
**Figure 6.** Kinetics modeling of Co(II) ions sorption on (a): ABC, (b): MBC, and (c) SBC (Experimental conditions: Initial pH = 5.0; 8.0 g biochar/L;  $c_0 = 48$  mg Co(II)/L; 25 °C).

**Table 3.** Kinetics parameters for the sorption of Co(II) ions on the three types of biochars.

Biochar		ABC	MBC	SBC
	$q_{e,exp}$ , mg/g	4.5705	6.9742	5.8794
Pseudo-first order model	$R^2$	0.8244	0.8976	0.8927
	$q_e$ , mg/g	0.7037	2.7931	2.2182
	$k_1$ , 1/min	0.0054	0.0092	0.0074
Pseudo-second order model	$R^2$	0.9997	0.9992	0.9997
	$q_e$ , mg/g	4.7281	7.1684	5.9880
	$k_2$ , g/mg min	0.0235	0.0211	0.0223
Intra-particle diffusion model	$R^2$	0.9695	0.9279	0.8972
	$c$ , mg/L	2.3902	3.9756	3.1604
	$k_{diff}$ , mg/g min <sup>1/2</sup>	0.1729	0.2475	0.2165

On the other hand, the relative high values of regression coefficients ( $R^2$ ) obtained in the case of modeling the experimental data using the intra-particle diffusion model suggest that the elementary diffusion processes have also a certain contribution to the sorption of Co(II) ions. However, the deviation from origin indicates that these elementary diffusion processes are not the rate controlling step [38,39]. The Co(II) ions diffusion into biochars particles is done quickly, since the rate constants of the diffusion process ( $k_{diff}$ , mg/g min<sup>1/2</sup>) are at least with an order of magnitude larger than the rate constants of the pseudo-second order kinetic model ( $k_2$ , mg/g min), and follows the order: MBC > SBC > ABC (see Table 3).

Nevertheless, this order is in contradiction with the data presented in Table 1, which shows that MBC has the largest surface area and therefore, in this case, the diffusion processes should be slower. This contradiction can be explained if the modeling of the experimental kinetic results using the intra-particle diffusion model is analyzed more closely. The linear representations of the intra-particle diffusion model (Figure 7) indicate that for all types of biochar, retention of Co(II) ions involves several elementary diffusion processes, because they can be divided into two distinct regions.

**Figure 7.** Linear representations of intra-particle diffusion model for retention of Co(II) ions on ABC, MBC, and SBC.

According to the study of Cheung et al., 2007 [38], the first region represents the film diffusion, while the second region describes the diffusion of metal ions into the pores of the biochars. The higher values of slopes (which represent the rate constants) of the first region compared with those of the second regions shows that the binding sites of biochars are located at the surface and are available to interact with Co(II) ions from aqueous solution [39].

Under these conditions, it can be said that even if MBC has the highest surface area (which means a rough surface with many pores), the presence of numerous superficial functional groups (Figure 2)

makes the interactions of these with Co(II) ions to be done quickly and easily. Once the superficial functional groups are occupied, the penetration of Co(II) ions into the biochar granule is prevented, and the importance of elemental diffusion processes decreases considerably. Consequently, the rate constant of the elementary diffusion process is high.

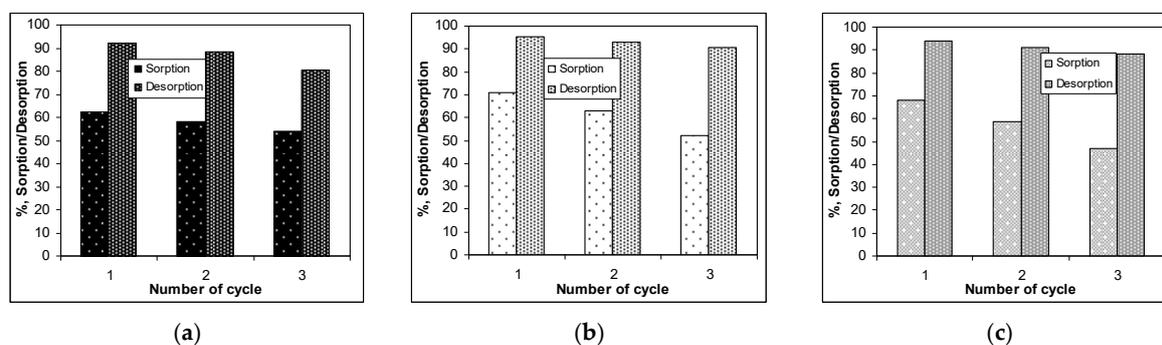
Unlike MBC, in the case of ABC, which has on its surface only few superficial functional groups (Figure 2), the binding of Co(II) ions on the surface of the particles does not create geometric obstructions. Consequently, Co(II) ions are forced to penetrate inside the ABC particles in search of new free functional groups to interact with. This makes the elemental diffusion processes to be more important, which takes time, and thus the obtained rate constant has a lower value (Table 3).

Regardless to the weight of elemental diffusion processes, the retention of Co(II) ions on the three types of biochars (ABC, MBC, and SBC) takes place until the formation of a monolayer coverage, according to the Langmuir model assumptions.

### 3.4. Recovery of Co(II) Ions and Biochars Regeneration

The recovery of retained Co(II) ions and biochars regeneration should be also discussed to highlight the practical applicability of these adsorbent materials in wastewater treatment at large scale [40]. In this study, three sorption/desorption cycles have been done for each type of biochar, using the same sample. The desorption agent used every time was HNO<sub>3</sub> solution (0.1 mol/L), while the sorption of Co(II) ions was done in considered optimal conditions (pH = 5.0; biochar dose = 8 g/L;  $c_0 = 150$  mg Co(II)/L; temperature = 25 °C). The experimental results obtained after each cycle of sorption/desorption are illustrated in Figure 8.

It can be seen from Figure 8 that in all the three cycles the recovery of retained Co(II) ions by desorption is a quantitative one for all types of biochars, and after desorption, the biochars can be successfully used in another sorption cycle, without that the efficiency of the sorption process to be significantly affected. These observations highlight the potential applicability of these adsorbent materials in multiple sorption/desorption cycles, which is an important advantage for industrial wastewater treatment systems, both for technological and economical reasons.



**Figure 8.** Sorption/desorption percentages obtained at retention of Co(II) ions on (a) ABC, (b) MBC, and (c) SBC.

On the other hand, from careful analysis of the experimental data presented in Figure 8, two important observations can be made, namely: (i) The sorption efficiency slightly decreases from cycle 1 to cycle 3, and this decrease follows the order: SBC (up to 20%) > MBC (up to 18%) > ABC (up to 8%), and (ii) the desorption efficiency also shows a tendency to decrease from cycle 1 to cycle 3, but in this case the order is: ABC (up to 12%) > SBC (up to 8%) > MBC (up to 5%). The different variation of the sorption and desorption efficiency as the number of cycles of use increases is mainly determined by the structure of biochars. Thus, the low number of functional groups on the surface of ABC (Figure 2) determines that the sorption efficiency of Co(II) ions to remains almost constant, while the desorption efficiency decreases from cycle 1 to cycle 3. This is probably because not all Co(II) ions retained on ABC can be desorbed by the treatment with 0.1 mol/L HNO<sub>3</sub> solution. In case of MBC and

SBC, where the number of superficial functional groups is higher (Figure 2), the more evident decrease of the sorption efficiency from cycle 1 to cycle 3 is an indication that some functional groups from their surface are destroyed or degraded during desorption. However, almost all retained Co(II) ions are readily recovered by treatment with 0.1 mol/L HNO<sub>3</sub> solution.

Starting from these observations, it can be said that the efficiency of certain biochar in the sorption processes of metal ions from aqueous media depends on the nature of the biomass used as raw material and preparation conditions. The choice of preparation conditions must be made in such a way as to obtain a material with a porous structure and a larger number of superficial functional groups. In this way the obtained biochar will have high efficiency in removal and recovery of metal ions from aqueous media.

#### 4. Conclusions

This study analyzed the removal of Co(II) ions from aqueous media using three types of biochars obtained from algae waste biomass (ABC), mustard waste biomass (MBC), and soy waste biomass (SBC). The biochar samples were obtained by pyrolysis of waste biomass resulted from biofuels production, at relative low temperature (600–650 °C), when a mass decrease of up to 50% of biomass raw materials was achieved. In addition, SEM and FTIR analysis indicated that the biochar samples have a porous and permeable structure and have various types of functional groups on their surface, which can represent the binding sites for Co(II) ions from aqueous media.

The batch sorption experiments were performed as a function of initial Co(II) ions concentration and contact time, at constant initial solution pH (5.0), and room temperature (25 ± 1 °C). The obtained experimental results show that the sorption capacity of all types of biochars increases with the increase of the initial Co(II) ions concentration, and that the contact time required to reach the equilibrium is minimum 60 min. The isotherm and kinetic modeling of the experimental data indicate that all the sorption processes are well described by the Langmuir isotherm model and pseudo-second order kinetic model. The amount of Co(II) ions required to obtain the monolayer coverage depends on the type of biochar, and follow the order: MBC > SBC > ABC, similar with the variation of the rate constant of the pseudo-second order kinetic model. These observations suggest that the MBC has the most functional groups on its surface, and these are available for metal ion interactions.

The desorption experiments show that all types of biochars can be successfully used in at least three sorption/desorption cycles, without that, the process efficiency would be significantly affected. All these aspects highlight the potential applicability of these adsorbent materials in industrial wastewater treatment systems, and their advantages both from technological and economical point of views.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4441/11/8/1565/s1>, Figure S1: Derivatograms recorded for algae waste biomass (a), mustard waste biomass (b) and soy waste biomass (c).

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